# **18.** CHEMICAL KINETICS

### **1. INTRODUCTION**

Chemical kinetics deals with the study of rate of chemical reactions. Rate of reaction is defined as change in concentration of reactants or products per unit time. It is influenced by various factors such as nature of substance, physical state of substance, temperature, concentration, presence of catalyst, etc.

### 2. RATE OF REACTIONS

The rate of reaction is expressed in mol  $L^{-1} s^{-1}$ .

Rate of reaction =  $\frac{\text{Change in the concentration of reactants or(Products)}}{\text{Time}}$ 

#### Time

### 2.1 Average Rate of Reaction

Average rate of reaction is defined as change in the concentration of reactants (or products) during large interval of time. If  $\Delta C$  is the change in the concentration of reactants and products in  $\Delta t$  time, then

Average rate = 
$$\frac{\text{Change in the concentration of reactants or(Products)}}{\text{Time}} = \pm \frac{\Delta C}{\Delta t} = \pm \frac{C_2 - C_1}{t_2 - t_1}$$

The graph shows the progress of reaction with respect to time.



Figure 18.1: Concentration vs Time

Unit of average rate of reaction = 
$$\frac{\text{Unit of concentration}}{\text{Unit of time}} = \frac{\text{gram mole / Litre}}{\text{second}} = \text{g mol } L^{-1} \text{ sec}^{-1}$$

#### **MASTERJEE CONCEPTS**

For gases, pressure is replaced by concentration. Thus, unit will be atm sec<sup>-1</sup>

 $PV = nRT \text{ or } P = \left[\frac{n}{V}\right]RT \text{ or } P = CRT$  $\frac{\Delta[P]}{\Delta t} = \frac{\Delta[C]}{\Delta t} \cdot RT \text{ or } Rate \text{ in } [atm/sec] = Rate \text{ in } [molarity/sec] \times RT$ 

Vaibhav Krishnan (JEE 2009, AIR 22)

### 2.2 Expression of Rate of Reaction

For the following reaction

$$\begin{split} n_1 A + n_2 B &\rightarrow m_1 C + m_2 D \\ \text{rate of reaction} = & -\frac{1}{n_1} \frac{\Delta[A]}{\Delta t} = -\frac{1}{n_2} \frac{\Delta[B]}{\Delta t} = +\frac{1}{m_1} \frac{\Delta[C]}{\Delta t} = +\frac{1}{m_2} \frac{\Delta[D]}{\Delta t} \end{split}$$

For the reaction  $2H_2O_2 \rightarrow 2H_2O + O_2$ 

The rate of reaction =  $\frac{\Delta[O_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[H_2O_2]}{\Delta t}$ 

### 2.3 Instantaneous Rate of Reaction

Instantaneous rate of reaction is defined as the average reaction rate during a very short interval of time or rate of reaction at a particular time.

Instantaneous rate =  $\pm \lim_{\Delta t \to 0} \frac{\Delta c}{\Delta t} = \frac{dc}{dt}$ 

**Note:** For the reaction  $n_1A + n_2B \rightarrow m_1C + m_2D$ 

Instantaneous rate of reaction =  $-\frac{1}{n_1}\frac{d[A]}{dT} = -\frac{1}{n_2}\frac{d[B]}{dT} = +\frac{1}{m_1}\frac{d[C]}{dT} = +\frac{1}{m_2}\frac{d[D]}{dT}$ 



Figure 18.2: Instantaneous Plot

#### **MASTERJEE CONCEPTS**

Rate of reaction and rate of change of concentration of a reactant (or product) are two different terms, except when stoichiometric coefficient involved is unity. On the other, rate of reaction is equal to the rate of change of concentration of a reactant (or a product) divided by the corresponding stoichiometric coefficient.

Nikhil Khandelwal (JEE 2009, AIR 94)

### 2.4 Reaction Life Time

It is defined as the time taken to complete 98% of the reaction. The shorter the life time, the faster the reaction. Halflife period is defined as either the time taken to complete half of the reaction or during which the concentration of the reactant is reduced to one half of its initial value. It is denoted by  $t_{1/2}$ . **Illustration 1:** For the reaction  $R \rightarrow P$ , the concentration of a reactant changes from 0.03 M to 0.02 M in 25 min. Calculate the average rate of reaction using units of time both in minutes and seconds. (JEE MAIN)

Sol: Average rate = 
$$-\frac{\Delta[R]}{\Delta t} = -\frac{[R]_2 - [R]_1}{t_2 - t_1} = -\frac{0.02M - 0.030M}{25 \text{ minutes}} = -\frac{-0.01M}{25 \text{ minutes}}$$
  
=  $4 \times 10^{-4} \text{ mol } L^{-1} \text{ min}^{-1} = \frac{0.01M}{25 \times 60\text{s}} = 6.66 \times 10^{-6} \text{ mol } L^{-1} \text{ sec}^{-1}.$ 

**Illustration 2:** Decomposition of N<sub>2</sub>O<sub>5</sub> is expressed by the equation, N<sub>2</sub>O<sub>5</sub>  $\longrightarrow$  2NO<sub>2</sub> +  $\frac{1}{2}$ O<sub>2</sub>

If, during a certain time interval, the rate of decomposition of  $N_2O_5$  is  $1.8 \times 10^{-3}$  mol L<sup>-1</sup> min<sup>-1</sup>. Calculate the rates of formation of NO<sub>2</sub> and O<sub>2</sub> during the same interval. (JEE MAIN)

**Sol:** Decomposition of N<sub>2</sub>O<sub>5</sub> has the following rate expression:

 $-\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2} \frac{\Delta[NO_2]}{\Delta t} = 2 \frac{\Delta[O_2]}{\Delta t}$ So,  $\frac{\Delta[NO_2]}{\Delta t} = 2 \frac{\Delta[N_2O_5]}{\Delta t} = 2 \times 1.8 \times 10^{-3} = 3.6 \times 10^{-3} \text{ mol } L^{-1} \text{ min}^{-1}$ and  $\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2} \times 1.8 \times 10^{-3} = 9 \times 10^{-4} \text{ mol } L^{-1} \text{ min}^{-1}$ 

(Rate is always positive and hence  $-\frac{\Delta[N_2O_5]}{\Delta t}$  is taken positive.)

**Illustration 3:** During the analysis of the products, even when a portion of the mixture is removed, the rate of reaction in the remaining mixture is not affected. Explain. (JEE ADVANCED)

**Sol:** The rate of reaction depends on concentration, which remains constant even if a portion of the mixture is removed, i.e. amount of substance is independent of the concentration and hence remains unaffected.

**Illustration 4:** For the reaction  $A + B \rightarrow C + D$ , the rate law equation  $= K_1 [A] + K_2 [A] [B]$ , where  $K_1$  and  $K_2$  represent two different constants and the products are formed by two different mechanisms. Explain the relative magnitudes of the rates of two individual mechanisms? **(JEE ADVANCED)** 

**Sol:** The rate of formation of products for both the reaction mechanisms must be of the same order of magnitude. Different magnitude reflects only the rate of reaction of the one which is faster among the two mechanisms. Also, it involves rate of formation of product from A as well as product from A and B.

### **3. RATE CONSTANT**

Consider a simple reaction  $A \rightarrow B$ 

At a particular instant, if  $C_A$  is the molar concentration or acitve mass of A, then  $\frac{dx}{dt} \propto C_A$  or  $\frac{dx}{dt} = kC_A$ 

where k is a proportionality constant, called velocity constant or rate constant or specific reaction rate.

At a fixed temperature, if 
$$C_A = 1$$
, then rate  $= \frac{dx}{dt} = k$  ...(i)

Thus, rate constant can be defined as rate of reaction at unit concentration of the reactants. Let us consider a general reaction  $aA + bB \rightarrow Product$ 

Rate = 
$$\left(\frac{dx}{dt}\right) \propto [A]^a [B]^b = k [A]^a [B]^b$$
 when  $[A] = [B] = 1$  mol/L, then rate = k

### **MASTERJEE CONCEPTS**

For a particular reaction, rate constant is independent of the concentration of the reactants and dependent only on temperature.

Neeraj Toshniwal (JEE 2009, AIR 21)

### 3.1 Units of Rate Constant

For reactions of different order, unit for rate constant is as follows:



#### **MASTERJEE CONCEPTS**

When order of reaction is not mentioned explicitly, then it can be determined using the unit of rate constant. For example, if the unit of rate constant is  $M^{-1}sec^{-1}$ , then order = 1-(-1)=2.

#### Aman Gour (JEE 2012, AIR 230)

### 3.2 Rate of Reaction and Reaction Rate Constant

**Table 18.1:** Difference between rate of reaction and reaction rate constant

S.No.	Rate of reaction	Reaction rate constant
1.	Speed at which reactants converts into products.	Proportionality constant.
2.	Measured as the rate of decrease in concentration of reactants or the rate of increase in concentration of products with time.	Equal to the rate of reaction when the concentration of each of the reactants is unity.
3.	Depends upon the initial concentration of reactants.	Independent of the initial concentration of the reactants and has a constant value at fixed temperature.

### **3.3 Factors Affecting Rate of Reaction**

- (a) **Concentration:** According to the law of mass action the greater the concentration of the reactants, the more rapidly the reaction proceeds.
- (b) **Pressure (Gaseous reaction):** Increasing the pressure, decreases the volume and simultaneously increases the concentration. Therefore the rate of reaction increases.
- (c) **Temperature:** Increase in temperature increases the reaction rate. It has been observed that rate either doubles or triples for every 10°C rise in temperature. Temperature coefficient of reaction rate,  $\frac{k_{T+10}}{k_T} \approx 2 \text{ or } 3$ , where  $k_{T+10}$  and  $k_{\tau}$  are rate constants at two temperature, differing by 10°C.
- (d) Nature of the reactants: The rate depends upon specific bonds of the reactants involved in the reaction and hence on the nature of reactants.

- (e) Surface area of the reactants: In heterogeneous reactions, if the reactants are in more powdered form, then velocity is greater [as more active centres are available].
- (f) **Catalyst:** It has an immense effect on the rate of reaction. Positive catalyst increases the rate of reaction by decreasing the activation energy, while negative catalyst decreases the rate of reaction by increasing the activation energy. Catalyst mainly affects the activation energy of reaction and hence the rate constant and rate of reaction changes.
- (g) Intensity of radiation: The rate of photochemical reactions generally increases with increase in intensity of radiation.

**Illustration 5:** The rate law of a chemical reaction  $2NO + O_2 \rightarrow 2NO_2$  is  $K[NO]^2 [O_2]$ . If the volume of reaction vessel is reduced to 1/4th of its original value, then what will be the change in rate of reaction? (JEE MAIN)

**Sol:** For, 
$$2NO + O_2 \rightarrow 2NO_2$$
 Rate = K[NO]<sup>2</sup> [O<sub>2</sub>]

Let us take a moles of NO and b moles of O<sub>2</sub> to start a reaction at any time in a vessel with a capacity of V L.

$$\mathbf{r}_{1} = \mathbf{K} \left[ \frac{\mathbf{a}}{\mathbf{V}} \right]^{2} \left[ \frac{\mathbf{b}}{\mathbf{V}} \right] \qquad \dots (\mathbf{i})$$

if volume of vessel is reduced to  $\frac{V}{4}$ , then the rate for same number of NO and O<sub>2</sub> moles.

$$r_{2} = K \left[ \frac{a}{V/4} \right]^{2} \left[ \frac{b}{V/4} \right] = 64 K \left[ \frac{a}{V} \right]^{2} \left[ \frac{b}{V} \right] \qquad \dots (ii)$$

Dividing equation (ii) by (i),  $\frac{r_2}{r_1} = 64$  i.e.  $r_2$  is 64 times of  $r_1$ 

Ilustration 6: Dinitrogen pentoxide decomposes as follows:

(JEE ADVANCED)

 $N_{2}O_{5} \rightarrow 2NO_{2} + \frac{1}{2}O_{2} \text{ If } \frac{-d[N_{2}O_{5}]}{dt} = K_{1}[N_{2}O_{5}], \ \frac{d[NO_{2}]}{dt} = K_{2} [N_{2}O_{5}] \text{ and } = 2 \frac{d[O_{2}]}{dt} = K_{3} [N_{2}O_{5}]$ 

Derive a relation between  $K_1$ ,  $K_2$  and  $K_3$ .

Sol: For the given reaction

$$\frac{d[N_2O_5]}{d[N_2O_5]} = \frac{1}{2} \frac{d[NO_2]}{d[NO_2]} = 2 \frac{d[O_2]}{d[O_2]}$$

$$\frac{v_2 v_3}{dt} = \frac{1}{2} \frac{u_1 v_2 v_3}{dt} = 2 \frac{u_1 v_2 v_3}{dt}$$
 Putting given values  
$$K_1 [N_2 O_5] = \frac{1}{2} K_2 [N_2 O_5] = 2 K_3 [N_2 O_5] \text{ or } 2 K_1 = K_2 = 4 K_3$$

#### 3.4 Rate Law

(a) It may not depend upon the concentration of each reactant or product of the reaction.

Suppose, mA + nB  $\rightarrow$  Product  $\mathbb{R} \propto [A]^m [B]^n$ .

- (b) Rate of chemical reaction is directly proportional to the concentration of reactants.
- (c) The rate law represents the experimentally observed rate of reaction, which depends upon the slowest step of the reaction.
- (d) Rate law cannot be deduced from the equation for a given reaction. It can be found out by experiments only.
- (e) The rate law may not bear a simple relationship for the stoichiometric equation.
- (f) It may not depend upon the concentration of species, which do not appear in the equation for the overall reaction.

### 4. ORDER OF REACTION

The order of any reaction may be defined as the sum of the powers to which the concentration terms are raised in order to determine the rate of reaction.

For the reaction:  $mA+nB \rightarrow product$ 

The experimental data suggests that

Rate  $=k[A]^{p}[B]^{q}$ ; then the order with respect to A = p and the order with respect to B = q and the total order of the reaction = p + q.

Reactions having order equal to 0 are zero-order reactions.

Reactions having order equal to 1, are 1st order reactions.

Reactions having order equal to 2 are IInd order reactions.

Reactions having order equal to 3 are IIIrd order reactions

#### **MASTERJEE CONCEPTS**

- Order can be zero, fractional or integer.
- Stoichiometric coefficients m and n of the reactants are always not equal to orders p and q.

B Rajiv Reddy (JEE 2012, AIR 11)

### **5. MOLECULARITY OF A REACTION**

It is defined as the number of molecules, atom or radicals that participate in the reaction. Depending on the number of participating molecules, the reaction can be unimolecular, bimocelular, trimolecular, etc.

Participating molecules	Molecularity
One molecule	unimolecular, 1
Two molecule	bimolecular, 2
Three molecule	trimolecular, 3

### MASTERJEE CONCEPTS

- Molecularity of a reaction is moslty between 1 to 3, but never zero. It is rare that molecularity exceeds 3.
- Misconception: Order and molecularity are one and the same. But order may or may not be equal to
  molecularity of the reaction.

#### Rohit Kumar (JEE 2012, AIR 79)

S. No.	Molecularity	Order of reaction
1.	It is the total number of reacting molecules (atoms or ions) leading to chemical change.	It is the sum of powers of molar concentrations of the reacting molecules in the rate equation of the reaction.
2.	It is always a whole number.	It may be a whole number, zero, fractional, positive or negative.

#### Table 18.2: Differences between order and molecularity

3.	It is a theoretical concept.	It is experimentally determined.
4.	It is meaningful only for simple reactions or individual steps of a complex reaction. It is meaningless for overall complex reaction.	It is meant for the reaction and not for its individual steps.

Illustration 7: Write the order of the following reactions?

Reaction	Exp. rate equ.
$H_2 + Cl_2 \rightarrow 2HCl$	$r = k[H_2]^0[CI_2]^0$
$H_2 + Br_2 \rightarrow 2HBr$	$r = k[H_2][Br_2]^{1/2}$
$H_2 + I_2 \rightarrow 2HI$	$r = k[H_2][I_2]$

**Sol:** Order is the number to which the concentration of the reactants/products are raised corresponding mostly to the coefficients.

Reaction	Exp. rate equ.	Order
$H_2 + CI_2 \rightarrow 2HCI$	$r = k[H_2]0[Cl_2]0$	0
$H_2 + Br_2 \rightarrow 2HBr$	$r = k[H_2][Br_2]1/2$	3/2
$H_2 + I_2 \rightarrow 2HI$	$r = k[H_2][I_2]$	2

Illustration 8: For the reaction 2NO + C	$_2 \rightarrow$ 2NOCI At 300 K, following data are obtained:	(JEE ADVANCED)
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Front Nie	Initial Con	Initial Data	
Εχρτ. Νο.	[NO]	[Cl <sub>2</sub> ]	initial kate
1.	0.010	0.010	1.2 × 10 <sup>-4</sup>
2.	0.010	0.020	2.4 × 10 <sup>-4</sup>
3.	0.020	0.020	9.6 × 10 <sup>-4</sup>

What is the rate law for the reaction and the order of the reaction? Also calculate the specific rate constant.

#### **Sol:** Let the rate law for the reaction be

Rate = k $[NO]^{\times} [Cl_2]^{y}$			
From expt. (1), $1.2 \times 10^{-4} = k [0.010]^{x} [0.010]^{y}$			
From expt. (2), $2.4 \times 10^{-4} = k [0.010]^{\times} [0.020]^{y}$			
Dividing Equation (ii) by Equation (i),			
$\frac{2.4 \times 10^{-4}}{1.2 \times 10^{-4}} = \frac{[0.020]^{y}}{[0.010]^{y}} \text{ or } 2 = (2)^{y} \text{ y} = 1$			
From expt. (2), $2.4 \times 10^{-4} = k [0.010]^{x} [0.020]^{y}$			
From expt. (3), 9.6 × $10^{-4} = k [0.020]^{x} [0.020]^{y}$			
Dividing Equation (iii) by Equation (ii), $\frac{9.6 \times 10^{-4}}{2.4 \times 10^{-4}} = \frac{[0.020]^x}{[0.010]^x}$ or $4 = 2^x$ , $x = 2$			
Order of reaction = $x + y = 2 + 1 = 3$			
Rate law for the reaction is			
Rate = $k[NO]^2 [CI_2]$			

#### (JEE MAIN)

....(i) ....(ii) Considering Equation (i) again,  $1.2 \times 10^{-4} = k[0.010]^2[0.010]$ 

$$k = \frac{1.2 \times 10^{-4}}{[0.010]^3} = 1.2 \times 10^2 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$$

### 6. REACTION OF VARIOUS ORDERS

### 6.1 Zero-Order Reactions

Rate of the reaction proportional to zero power of the concentration of reactants is known as zero-order reaction. Consider the reaction

$$R \rightarrow P Rate = \frac{d[R]}{dt} = k[R]^0$$

As any quantity raised to power zero is unity

Rate = 
$$\frac{d[R]}{dt}$$
 = k × 1 ; d[R] = - k dt

Integrating on both sides [R] = -kt + I

where I is the constant of integration.

At t = 0, the concentration of the reactant  $R = [R]_{0}$ , where  $[R]_{0}$  is initial concentration of the reactant.

Substituting in equation (i)

$$[R]_0 = -k \times 0 + I [RI_0] = I$$

Substituting the value of I in the equation (i)

$$[R] = -kt + [R]_{0}$$

Equation of a straight line, y = mx + c. We get a straight line with slope = -k and intercept equal to  $[R]_{0'}$  when [R] is plotted against t.

Simplifying equation (ii), we get the rate constant  $k = k = \frac{[R_0] - [R]}{t}$  ...(iii)

Zero-order reactions occur only under special conditions and hence they are uncommon. Some enzyme catalyzed reactions and reactions which occur on metal surfaces are a few examples of zero-order reactions. Another example of zero-order reaction is decomposition of gaseous ammonia on a hot platinum surface at high pressure.

$$2NH_{3}(g) \xrightarrow{1130K} N_{2}(g) + 3H_{2}(g) ; Rate = k[NH_{3}]^{0} = k$$

Here, platinum acts as a catalyst. The metal surface reacting with gas molecules under high pressure gets saturated. So, a further change in reaction conditions does not alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration. The thermal decomposition of HI on gold surface is another example of zero-order reaction.

# (A) Unit of rate constant: $k = \frac{[R]_0[R]}{t}$ k mol L<sup>-1</sup> sec<sup>-1</sup>

Unit of rate of reaction and unit of rate constant are the same.

(B) Half-life period  $(t_{1/2})$ : It is the time taken to complete half of the reaction.

At t = t<sub>1/2</sub>; R = 
$$\frac{R_0}{2}$$
  $t_{1/2} = \frac{R_0}{2K}$  or  $t_{1/2} \propto R_0$ 

It is directly proportional to the initial concentration of the reactant.



....(i)

### **6.2 First-Order Reactions**

Rate of the reaction is proportional to the first power of the concentration of the reactant. For example,  $R \rightarrow P$ 

$$\begin{aligned} &\text{Rate} = -\frac{d[\textbf{R}]}{dt} = k \ [\textbf{R}] \quad \text{or} \quad -\frac{d[\textbf{R}]}{[\textbf{R}]} = -kdt \\ &\text{Integrating the above equation, we get } \ln [\textbf{R}] = -kt + 1 \quad \dots(iv) \\ &\text{I is the integration constant ; hence its value can be determined easily.} \\ &\text{When } t = 0, \ \textbf{R} = [\textbf{R}]_{o'} \text{ where } [\textbf{R}]_{o} \text{ is the initial concentration of the reactant.} \\ &\text{Therefore, equation (iv) can be written as } \ln [\textbf{R}]_{o} = -k \times 0 + I = I \\ &\text{Substituting I in equation (iv)} \\ &\ln [\textbf{R}] = -kt + \ln[\textbf{R}]_{o} \qquad \dots(v) \\ &\text{Rearranging this equation } \ln \frac{[\textbf{R}]}{[\textbf{R}]_{o}} = -kt \text{ or } k = \frac{1}{t} \ln \frac{[\textbf{R}]_{0}}{[\textbf{R}]} \qquad \dots(vi) \\ &\text{At time } t_{1'} \text{ from equation (iv)} \ln[\textbf{R}]_{1} = -kt_{1} + \ln[\textbf{R}]0 \qquad \dots(vii) \\ &\text{At time } t_{2'} \ln[\textbf{R}]_{2} = -kt_{2} + \ln[\textbf{R}]_{0} \qquad \dots(viii) \\ &\text{where } [\textbf{R}]_{1} \text{ and } [\textbf{R}]_{2} \text{ are the concentrations of the reactants at time } t_{1} \text{ and } t_{2} \text{ respectively. Subtracting (viii) from (vii)} \\ &\ln[\textbf{R}]_{1} - \ln[\textbf{R}]_{2} = -kt_{1} - (-kt_{2}) \qquad \ln \frac{[\textbf{R}]_{1}}{[\textbf{R}]_{2}} = k(t_{2} - t_{1}) \\ &k = \frac{1}{(t_{2} - t_{1})} \qquad \ln \frac{[\textbf{R}]_{1}}{[\textbf{R}]_{2}} = -kt \\ &\text{This partition and lose be written as } \ln \frac{[\textbf{R}]_{1}}{[\textbf{R}]_{2}} = -kt \\ &\text{This partition are hard to iden } (\textbf{P}) = (\textbf{P}) \quad \textbf{P}) \quad \textbf{P} \\ &\text{This partition are hard to iden } (\textbf{P}) = (\textbf{P}) \quad \textbf{P}) \\ &\text{This partition are hard to iden } (\textbf{P}) = (\textbf{P}) \quad \textbf{P}) \\ &\text{This partition are hard to iden } (\textbf{P}) = (\textbf{P}) \quad \textbf{P}) \\ &\text{This partition are hard to iden } (\textbf{P}) = (\textbf{P}) \quad \textbf{P}) \\ &\text{This partition are hard to iden } (\textbf{P}) = (\textbf{P}) \quad \textbf{P}) \\ &\text{This partition are hard to iden } (\textbf{P}) = (\textbf{P}) \quad \textbf{P}) \\ &\text{The partition are hard to iden } (\textbf{P}) = (\textbf{P}) \quad \textbf{P}) \\ &\text{This partition are hard to iden } (\textbf{P}) = (\textbf{P}) \quad \textbf{P}) \\ &\text{This partition are hard to iden } (\textbf{P}) = (\textbf{P}) \quad \textbf{P}) \\ &\text{This partition are hard to iden } (\textbf{P}) = (\textbf{P}) \quad \textbf{P}) \\ &\text{This partition are hard to iden } (\textbf{P}) = (\textbf{P}) \quad \textbf{P}) \\ &\text{This partition are hard to iden } (\textbf{P}) = (\textbf{P}) \quad \textbf{P}) \\ &\text{This partition are hard to iden }$$

Taking antilog on both sides  $[R] = [R]_0 e^{-kt}$ 

When  $\ln [R]$  is plotted against t, we obtain a straight line with slope = -k and intercept equal to  $\ln [R]_{0}$ 

The first-order rate equation (vi) can also be written in the form

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} ...(x)$$

$$\log \frac{[R]_0}{[R]} = \frac{R}{2.303}$$

If we plot a graph between log  $[R]_{0}/[R]$  and t, the slope = k/2.303

Hydrogenation of ethene is an example of first-order reaction.

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$
  
Rate = k [C\_2H\_4]

All natural and artificial radioactive decay of unstable nuclei takes place by first-order kinetics.



Figure 18.4: First order plot

#### **Examples:**

- (a)  $^{226}_{88}$ Ra  $\rightarrow^{4}_{2}$ He  $+^{222}_{86}$ Rn ; Rate = k[Ra]
- (b) Decomposition of  $N_2O_5$  and  $N_2O$  are few more examples of first-order reactions.
  - (i) Unit of rate constant:  $K = \frac{2.303}{t} \log \frac{[R]_0}{[R]} = \sec^{-1}$
  - (ii) Half-life period  $(t_{1/2})$ :

At t = 
$$t_{1/2'} R = \frac{R_0}{2}$$
, K= $\frac{2.303}{t_{1/2}} \log \frac{R_0}{R_0/2} = \frac{2.303}{t_{1/2}} \times \log 2 = \frac{0.693}{t_{1/2}}$   
 $t_{1/2} = \frac{0.693}{K}$ 

### 6.3 Pseudo-Order Reactions

Reactions whose actual order is different from that expected using rate law expression are called pseudo-order reactions, e.g

 $RCI + H_2O \rightarrow ROH + HCI$ 

Expected rate law:

Rate = k [RCl][H<sub>2</sub>O]; expected order = 1+1 = 2

Actual rate law: Rate = k' [RCI] Actual order = 1

Water is taken in excess; therefore, its concentration may be taken constant. The reaction is, therefore, pseudo first order. Similarly, the acid catalyzed hydrolysis of ester, viz.,

 $RCOOR' + H_2O \rightarrow RCOOH + R'OH$ 

follows first order kinetics: Rate = k [RCOOR']

It is also a pseudo first-order reaction.

### 6.4 Some Examples of First-Order Reactions and Their Rate Constants

#### (a) For Gas Phase Reaction

Let us consider a typical first-order gas phase reaction

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

Let p<sub>i</sub> be the initial pressure of A and p<sub>t</sub> the total pressure at time 't'. Integrated rate equation is as follows:

Total pressure  $p_t = p_A + p_B + p_C$  (pressure units)

 $p_A$ ,  $p_B$  and  $p_C$  are the partial pressures of A, B and C, respectively

Decreasing x atm pressure of A at time t to form one mole of B and C each. The increase in pressure of B and C will also be x atm each.

	A(g) –	$\rightarrow$	B(g)	+	C(g)
At time, t = 0	p <sub>i</sub> atm		0 atm		0 atm
At time t	(p <sub>i</sub> – x) atm		x atm		x atm

Where  $p_i$  is the initial pressure at time t = 0.

 $P_{t} = (p_{i} - x) + x + x = p_{i} + x$ 

 $x = (p_t - p_i)$ , where  $p_A = p_i - x = p_i - (p_t - p_i) = 2p_i - p_t$ 

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

#### (b) Pseudo-Unimolecular Reaction:

Inversion of cane sugar

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$
  
Sucrose Glucose Fructose

The progress of the reaction can be studied using a polarimeter. Cane sugar and glucose are dextrorotatory while fructose is laevorotatory. Let  $\theta_0$  is polarimetric reading at t = 0;  $\theta_t$  is polarimetric reading after time t and  $\theta_{\infty}$  is polarimetric reading after infinite time.

$$k = \frac{2.303}{t} \log \frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty}$$

#### (c) (i) Decomposition of $H_2O_2$

$$H_2O_2 \xrightarrow{Pt} H_2O + \frac{1}{2}O_2$$

The progress of the reaction can be studied by two methods. (1)Volume of oxygen gas at different intervals of times is measured and or (2) definite amount of reaction mixture is titrated with standard KMnO<sub>4</sub> at different intervals of time. If V<sub>0</sub> represent the initial volume of KMnO<sub>4</sub> and V<sub>t</sub> final volume of KMnO<sub>4</sub> at any time t Then,  $R_0 \propto V_0, R \propto V_t$ 

Therefore

re, 
$$K = -\frac{2.303}{t} \log \frac{V_0}{V_t}$$

#### (ii) Decomposition of Ammonium Nitrite

 $NH_4NO_2 \rightarrow N_2 + 2H_2O$ 

If  $V_t$  is the volume of  $N_2$  evolved at any time t and  $V_{\infty}$  is the volume of  $N_2$  evolved when the decomposition is complete. Then,

$$K = \frac{2.303}{t} \log \frac{V_{\infty}}{V_{\infty} - V_{t}}$$

#### (d) Hydrolysis of Ethyl Acetate (Ester)

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

Kinetics of this reaction is studied by titrating a definite volume of the reaction mixture with standard alkali solution.

If  $V_0$ ,  $V_t$  and  $V_\infty$  are volumes of standard alkali needed to neutralize a definite amount of x, will be proportional to  $V_t - V_0$  and a, will be proportional to  $V_\infty - V_0$ 

Hence,  $K = \frac{2.303}{t} \log \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$ 

#### (e) Oxide Layer Formation

 $K = \frac{1}{t} \ln \frac{\tau_{max}}{\tau_{max} - \tau}$  where  $\tau_{max}$  is the thickness of oxide layer after  $\infty$  times and  $\tau$  is the thickness of oxide layer at

time 't'.

(f) Bacterial Growth:  $K = \frac{1}{t} ln \frac{a+x}{a}$ 

...(xi)

### 6.5 Second-Order Reaction

A reaction is said to be of second order if its reaction rate involves two different concentrations.

The kinetics of second-order reactions are given as follows:

(a) When concentrations of both reactants are same or two molecules of the same reactant are involved in the change, i.e.

$$\begin{array}{l} \mathsf{A} + \mathsf{B} \rightarrow \mathsf{Products} \; \mathsf{or} \qquad 2\mathsf{A} \rightarrow \mathsf{Products}; \; \frac{\mathsf{d}x}{\mathsf{d}t} = \mathsf{k}(\mathsf{a}-\mathsf{x})^2, \\ \mathsf{k} = \; \frac{1}{\mathsf{t}} \cdot \frac{\mathsf{x}}{\mathsf{a}(\mathsf{a}-\mathsf{x})} \end{array}$$

Where a is the initial concentration of the reactant or reactants and x is the concentration of the reactant changed in time t.

(b) When the initial concentrations of the two reactants are different, i.e.,

 $A + B \rightarrow Products$ 

Initial conc. a b

 $\frac{dx}{dt} = k(a - x)(b - x) \ ; \ \frac{2.303}{t(a - b)} log_{10} \frac{b(a - x)}{a(b - x)}$ 

(a - x)and (b - x) are the concentrations of A and B, respectively, after time interval, t.

#### Characteristics of the second-order reactions

- (a) The value of k (velocity constant) depends on the unit of concentration. The unit of k is expressed as (mol/litre)<sup>-1</sup> time<sup>-1</sup> or litre mol<sup>-1</sup> time<sup>-1</sup>. When 't' is plotted against  $\frac{1}{(a-x)}$  the resultant slope is a straight line. Rearranging equation for k. t =  $\frac{1}{k(a-x)} - \frac{1}{ka}$ . The slope of the line is  $\frac{1}{k}$ , where 'k' can be evaluated.
- **(b)** Half-life period  $(t_{1/2}) = \frac{1}{k} \cdot \frac{0.5a}{a \times 0.5a} = \frac{1}{ka}$



Figure 18.5 Second order plot

Thus, half-life period is inversely proportional to initial concentration.

(c) Second-order reaction confirms to the first order when one of the reactants is present in large excess.

Consider, 
$$k = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$$
. If  $a >>> b$ , then  $(a - x) \approx a$  and  $(a - b) \approx a$   
Hence,  $k = \frac{2.303}{ta} \log_{10} \frac{ba}{a(b-x)}$  or  $ka = k' = \frac{2.303}{t} \log_{10} \frac{b}{(b-x)}$ 

here since 'a' being very large is a constant after the change. Thus, the reaction follows first-order kinetics with respect to the reactant taken relatively in small amount.

#### **Examples of second-order reactions**

(a) Hydrolysis of ester by an alkali (saponification).

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

- **(b)** The decomposition of NO<sub>2</sub> into NO and O<sub>2</sub>.  $2NO_2 \rightarrow 2NO + O_2$
- (c) Conversion of ozone into oxygen at 100°C.  $2O_3 \rightarrow 3O_2$
- (d) Thermal decomposition of chlorine monoxide.  $2Cl_2O \rightarrow 2Cl_2 + O_2$

### 6.6 Third-Order Reaction

Reaction is said to be of third order if its reaction rate involves three different concentrations. When the concentration of all the three reactants is same or three molecules of the same reactant are involved, the rate expression is given as:

$$3A \rightarrow \text{Products}; A + B + C \rightarrow \text{Products}; \frac{dx}{dt} = k(a - x)^3$$
$$k = \frac{1}{t} \cdot \frac{x(2a - x)}{2a^2(a - x)^2}$$

Therefore

#### **Characteristics of third-order reactions**

• Half-life period =  $\frac{1}{k} \cdot \frac{0.5a(2a - 0.5a)}{2a^2(0.5a)^2} = \frac{1}{k} \frac{0.5a \times 1.5a}{2a^2 \times 0.5a \times 0.5a} = \frac{3}{2a^2k}$ 

Thus, half-life is inversely proportional to the square of initial concentration.

- The change in the unit of concentration changes the numerical value of k.
- The unit of k is expressed in (mol/litre)<sup>-2</sup> time<sup>-1</sup> or L<sup>2</sup> mol<sup>-2</sup> sec<sup>-1</sup>.

#### **Examples of third-order reactions**

- Reaction between nitric oxide and oxygen. 2NO +  $O_2 \rightarrow 2NO_2$
- Reaction between nitric oxide and chlorine. 2NO +  $Cl_2 \rightarrow 2NOCl$

#### **Examples**

**For a zero-order reaction,** as shown in the following figure, the plot of [A] versus time is a straight line with k = -ve slope. Other graphs are curved for a zero-order reaction.



Figure 18.6: Plot of [A] versus time





Figure 18.7: Plot of the logarithm of [A] versus time



**For a second-order reaction**, as shown in the following figure, the plot of 1/[A] versus time is a straight line with k =-ve slope of the line. Other graphs are curved for a second-order reaction.

Figure 18.8: Plot of 1/[A] versus time

### 6.7 Parallel Reactions

$$A_{k_{2}} = \begin{bmatrix} A_{0} \end{bmatrix} e^{-kt} \quad \begin{bmatrix} B \end{bmatrix} = \frac{k_{1}[A]_{0}}{k_{1} + k_{2}} (1 - e^{-kt}) \quad \begin{bmatrix} C \end{bmatrix} = \frac{k_{2}[A]_{0}}{k_{1} + k_{2}} (1 - e^{-kt})$$

Variation of concentration A, B and C with time may be graphically represented as,

#### **Examples:**





Figure 18.9: Parallel reactions

### **6.8 Consecutive Reactions**

$$A \xrightarrow{k_{1}} B \xrightarrow{k_{2}} C$$

$$[A]_{t} = [A_{0}] e^{-k_{1}t} ; \qquad [B]_{t} = \frac{k_{1}[A]_{0}}{[k_{2} - k_{1}]} \left[ e^{-k_{1}t} - e^{-k_{2}t} \right]$$

$$[C]_{t} = [A_{0}] - ([A]_{t} + [B]_{t}) ; \qquad [B]_{max} = [A_{0}] \cdot \left(\frac{k_{1}}{k_{2}}\right)^{\frac{k_{2}}{k_{2} - k_{1}}} t_{max} = \frac{1}{K_{1} - K_{2}} ln \frac{K_{1}}{K_{2}}$$



Figure 18.10: Consecutive reactions

Examples: (i) Decomposition of ethylene oxide:

 $(CH_2)_2O \xrightarrow{k_1} CH_3CHO$  $CH_3CHO \xrightarrow{k_2} CO + CH_4$ 

#### 6.9 Reversible Reactions

 $A \xleftarrow{k_{1}}{k_{2}} B$ Initial state (t = 0) a 0 Conc. at time (t) a - x x Equilibrium conc. (a - x<sub>e</sub>) x<sub>e</sub>; k<sub>1</sub> + k<sub>2</sub> =  $\frac{2.303}{t} \log_{10} \left\{ \frac{x_{e}}{x_{e} - x} \right\} \frac{x_{eq}}{a - x_{eq}} = \frac{K_{f}}{K_{b}}$ 

**Illustration 9:** If the time required to decompose  $SO_2Cl_2$  to half of its initial amount is 60 minutes and the decomposition is a first-order reaction, then calculate the rate constant of the reaction. (JEE MAIN)

Sol: For a first-order reaction. k =  $\frac{0.693}{t_{1/2}}$  $\frac{0.693}{t_{1/2}} = \frac{0.693}{60 \text{ minutes}} = \frac{0.693}{60 \times 60 \text{ seconds}} = 1.925 \times 10^{-4} \text{ s}^{-1}$ 

**Illustration 10:** Consider a first-order reactions, if it takes 5 minutes for the initial concentration of 0.6 mol  $L^{-1}$  to become 0.4 mol  $L^{-1}$  Then how long will it take for the initial concentration to become 0.3 mol  $L^{-1}$ ? (JEE MAIN)

**Sol:** For a first-order reaction  $k = \frac{2.303}{k} log \frac{[A]_0}{[A]_t}$ 

We have,  $[A]_0 = 0.6 \text{ mol } L^{-1}$   $[A]_t = 0.4 \text{ mol } L^{-1}$  t = 5 min

So, k =  $\frac{2.303}{5 \text{ min}} \times \log \frac{0.6}{0.4} = \frac{2.303}{5} \log 1.5 \text{ min}^{-1} = \frac{2.303 \times 0.1761}{5} \text{ min}^{-1} = 8.1 \times 10^{-2} \text{ min}^{-1}$ 

For, 
$$[A]_{t} = 0.3 \text{ mol } L^{-1}$$
;  $t = \frac{2.303}{k} \log \frac{[A]_{0}}{[A]_{t}} = \frac{2.303}{8.1 \times 10^{-2}} \log \frac{0.6}{0.3} = \frac{2.303}{8.1 \times 10^{-2}} \log 2 = 8.5 \text{ min.}$ 

**Illustration 11:** The following were obtained during the first order thermal decomposition of  $N_2O_5$  (g) at constant volume:

$$2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$$

S.No.	Time (sec)	Total Pressure (atm)
1.	0	0.5
2.	100	0.512

Calculate the rate constant.

**Sol:** Let the pressure of  $N_2O_5(g)$  decrease by 2x atm when two moles of  $N_2O_5$  decompose to give two moles of  $N_2O_4$  (g) and one mole of  $O_2(g)$ . Therefore pressure of  $N_2O_4(g)$  increases by 2x atm and that of  $O_2(g)$  increases by x atm.

**Illustration 12:** In a second-order reaction, in which both the reactants have same concentration, consider 20% of the reaction is completed in 500 sec. What is the time required for 60% completion? (JEE ADVANCED)

Sol: The equation for second order with both the reactants having same concentration is

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)} \text{ If } a = 100 \text{ , } x = 20 \text{ , } t = 500 \text{ sec.}$$
  
So, 
$$k = \frac{1}{500} \times \frac{20}{100 \times (100 - 20)} \text{ When } a = 100 \text{ , } x = 60 \text{ , } t = ?$$
$$t = \frac{1}{k} \cdot \frac{60}{100 \times 40}$$

Substituting the value of k,

 $t = \frac{500 \times 100 \times 80}{20} \times \frac{60}{100 \times 40}$  or t = 3000 sec

### 7. THE REACTION MECHANISM

#### 7.1 Elementary Reactions

Elementary reaction are single step reactions in which order and molecularity are always the same. In another words, rate law and the law of mass action have the same expression.

### 7.2 Complex Reactions

These are multi-step reactions in which order and molecularity may or may not be same.

- (a) In these types of reactions, intermediates are formed during the reaction which is different from the reactants and the products formed.
- (b) Each step involved in this reaction is an elementary reaction.

#### (JEE ADVANCED)

- (c) The overall rate of reaction will be equal to the rate of slowest step. Hence the slowest step is called the rate determining step (RDS) of reaction. A reaction can have more than one RDS.
- (d) The overall molecularity of reaction and the molecularity of the RDS are the same . However, it has no significance.
- (e) The order of reaction and the overall order of reaction may not be the same. It depends on the concentrations involved in the rate law expression of RDS. If it is not overall order, it may be determined by equilibrium approach or by steady state approximation.

For a complex reaction, order is not equal to molecularity.

### 7.3 Reaction Mechanism

The steps involved in a reaction and determining which step is the slowest or rate determining is called mechanism.

A series of steps (known as elementary processes) leading to the formation of products or by which the overall chemical reaction occurs is called the reaction mechanism.

For e.g.

The reaction between H<sub>2</sub> and I<sub>2</sub> to form hydrogen iodide was originally postulated as a simple one-step reaction.

 $H_{2} + I_{2} = 2HI$ 

Rate =  $k[H_2][I_2]$ 

But, the formation of HI has been explained on the basis of the following mechanism:

$I_2 \rightarrow 2I$	(fast)	(i)
$H_2 + I \rightarrow H_2 I$	(fast)	(ii)
$H_2 I + I \rightarrow 2HI$	(slow)	(iii)

Overall reaction:  $H_2 + I_2 \rightarrow 2HI$ 

### 8. DETERMINATION OF RATE LAW FOR A COMPLEX REACTION

### 8.1 Equilibrium Approach

The concentration of intermediate can be determined from equilibrium constant of the reaction involved.

For example, let the mechanism of reaction A + 2B  $\rightarrow$  C + D is

**Step I:** A + B 
$$\xleftarrow{k_1}{k_2}$$
 |

**Step II:**  $I + B \xrightarrow{k_2} C + D$ 

Overall rate of reaction,  $r = rate of step II = k_2[I][B]$ 

But this cannot be considerd as correct because the overall rate of reaction should be in terms of concentrations of A and B (reactants). The concentration of I can be related with the concentrations of A and B with the help of first equilibrium.

For step I, equilibrium constant,  $K_{eq} = \frac{k_1}{k_{-1}} = \frac{[I]}{[A][B]}$   $\therefore$   $[I] = \frac{k_1}{k_{-1}} [A][B]$ 

Putting this value in equation (i),  $r = k_2 \frac{k_1}{k_{-1}}$  [A][B].[B] = k[A][B]<sup>2</sup>, where,  $k = \frac{k_1}{k_{-1}}$ 

Hence, the overall rate of reaction is 1 + 2 = 3

....(i)

### 8.2 Steady State Approach

In this method, we assume that the intermediates formed are so reactive that after some time from initiation of reaction (called induction period), the net rate of their formation becomes zero. They react with the same rate of their formation. For example, let the mechanism of reaction

 $A + 2B \rightarrow C + D$  is

**Step I:** A + B  $\xleftarrow{k_1}{k_2}$  I **Step II:** I + B  $\xrightarrow{k_2}$  C + D

The rate of reaction may be given as  $r = + \frac{d[C]}{dt} = k_2 [I] [B]$ 

Now, from steady state approximation on the intermediate,  $I - \frac{d[I]}{dt} = 0$ 

or 
$$k_1[A][B] - k_1[I] - k_2[I][B] = 0$$
 or,  $[I] = \frac{k_1[A][B]}{k_1 + k_2[B]}$ 

Substituting this value in equation (ii),  $r = k_2 \cdot \frac{k_1[A][B]}{k_{-1} + k_2[B]} \cdot [B] = \frac{k_1k_2[A][B]^2}{k_{-1} + k_2[B]}$ 

#### **MASTERJEE CONCEPTS**

- When the intermediate is less stable, better results are obtained by steady state approximation, when the
  intermediate is more stable, better results are obtained by eqilibrium approach. More stable intermediate
  reacts very less and hence, the concentration of intermediate at any time remains nearly equal to its
  equilibrium concentration.
- When conditions of equilibrium approach are applied on the result obtained from steady state approximation, the same rate law expression is obtained. For the above reaction, step I is faster than step II. As step I is at equilibrium,

$$r_1 = r_{-1} >> r_2 \text{ or, } k_{-1}[1] >> k_2[1][B] \text{ or, } k_{-1} >> k_2[B]$$

therefore,  $k_{-1} + k_2[B] \approx k_{-1}$ 

Now, the rate expression obtained from steady state is

$$r = \frac{k_2 k_1 [A] [B]^2}{k_{-1} + k_2 [B]} \approx [A] [B]^2$$

Which is exactly same expression obtained from equilibrium approach.

Aishwarya Karnawat (JEE 2012, AIR 839)

**Illustration 13:** The reaction 2NO +  $Br_2 \rightarrow 2NOBr$  obeys the following mechanism:

**Step I:** NO + Br<sub>2</sub>  $\xleftarrow{\text{fast}}$  NOBr<sub>2</sub>

**Step II:** NOBr<sub>2</sub>  $\xrightarrow{\text{Slow}}$  2NOBr

Suggest the rate expression.

**Sol:** The slowest step is the Rate determining step.

(JEE MAIN)

...(ii)

Step II is the step that determines the rate of the reaction and hence, 
$$r = k[NOBr_2][NO]$$
 ...(i)

However, NOBr<sub>2</sub> is an intermediate and thus its concentration is determined step I.

For step I, equilibrium constant 
$$k_{eq} = \frac{[NOBr_2]}{[NO][Br_2]}$$
 ...  $[NOBr_2] = k_{eq}[NO] [Br_2]$  ...(ii)  
Thus, by equations (i) and (ii),  $r = k. k_{eq}[NO]^2[Br_2]$  or,  $r = k'[NO]^2 [Br_2]$  where  $k' = k. k_{eq}$ 

#### Illustration 14: The following mechanisms are proposed for the reaction

 $CO + NO_2 \rightarrow CO_2 + NO$  at low temperature:

- (a)  $2NO_2 \rightarrow N_2O_4$  (fast)  $N_2O_4 + 2CO \rightarrow 2CO_2 + 3NO$  (slow)
- (b)  $2NO_2 \rightarrow NO_3 + NO$  (slow)  $NO_3 + CO \rightarrow NO_2 + CO_2$  (fast)

Which of the above mechanism are consistent with the observed rate law: +  $\frac{d[CO_2]}{dt} = k[NO_2]^2$  (JEE ADVANCED)

**Sol:** For mechanism (a),  $r = rate of step II = k[N_2O_4][CO]^2$ 

Now, from step I: 
$$k_{eq} = \frac{[N_2O_4]}{[NO_2]^2}$$
 or,  $[N_2O_4] = k_{eq}[NO_2]^2$ 

Hence from (i).  $r = k.k_{eq} [NO_2]^2 [CO]^2$ , but it is not the given rate law

Hence, the mechanism is not consistent with the rate law.

For mechanism (b), r = rate of step,  $I = k[NO_2]^2$ , which is the given rate law.

### 9. COLLISION THEORY OF REACTION RATE/ARRHENIUS THEORY

#### **Postulates:**

- Collision of reactant molecules leads to chemical reaction. The number of collisions taking place per unit time
  per unit volume of the reaction mixture is known as collision frequency (Z). The value of collision frequency is
  very high (of the order of 10<sup>25</sup> to 10<sup>28</sup>) in case of binary collisions.
- Not every collision brings a chemical change. Only effective collisions bring about a chemical change to form
  products. The effective collisions are less when compared to the total number of collisions. Collisions that
  do not form a product are ineffective elastic collisions, i.e. molecules just collide and disperse in different
  directions with different velocities. For effective collision, the following two barriers are to be cleared.

### 9.1 Energy Barrier

The minimum energy required by colliding molecules for the chemical reaction to take place is known as threshold energy.



Figure 18.11: Threshold Plot

....(i)

#### 18.20 | Chemical Kinetics -

The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy.

Activation energy = threshold energy – average kinetic energy of reacting molecules.

Threshold energy = initial potential energy of reactant molecules + activation energy.

Collision of high energy molecules that overcomes the forces of repulsion and forms an unstable molecule cluster is called an activated complex. Its life span is very less. Thus, the activated complex breaks to either form reactants again or form new substances, i.e. products. The activation energy (E<sub>a</sub>) depends upon the nature of chemical bonds undergoing rupture and is independent of enthalpies of reactants and products.

The following graphs show the energy changes during exothermic and endothermic reactions versus the progress of the reaction.



Figure 18.12: Energy profile diagram for exothermic and endothermic reaction

- (a) Every reaction, whether exothermic or endothermic, needs to overcome an energy barrier for reactants to get converted to products.
- (b) Lower the activation energy, higher will be the fraction of effective collisions leading to faster reaction and vice versa.
- (c) Activation energy  $E_a = E_{(activated complex)} E_{(ground state)}$

 $\Delta H$  = activation energy of forward reaction – activation energy of backward reaction.

(i) When  $E_{af} < E_{ab}$ ;  $\Delta E = -v$  and,  $\Delta H = -ve$ 

Thus, when the activation energy for the forward reaction is less than that for the backward reaction, energy is released.

(ii) When  $E_{af} > E_{ab}$ ;  $\Delta E = + ve$  and,  $\Delta H = + ve$ 

Thus, when the activation energy for the forward reaction is more than that for the backward reaction, energy is absorbed.

### 9.2 Orientation Factor

- To form products reactants should have a proper orientation in addition to sufficient energy.
- Rate of reaction is directly proportional to the number of effective collisions.

Rate =  $-\frac{dx}{dt}$  = collision frequency × fraction of effective collisions = Z × f



Figure 18.13: Collision theory

### 9.3 Temperature Dependance of Rate Constant

The temperature dependence of the rate of a chemical reaction can be accuratly explained by Arrhenius Equation  $k = Ae^{\frac{-E}{a}/RT}$  ...(i)

where, k=Arrhenius factor, E<sub>a</sub>=activation energy, R=gas constant, T=temperature

According to the Arrhenius equation, for most reactions, the rate constant increases with increase in temperature. : The parameters A and  $E_a$  for a given reaction are collectively called Arrhenius parameters. Value of  $E_a$  is determined from the graph for  $\frac{1}{T}$  and ln k is determined experimentally. Value of A inturn is calculated once  $E_a$  is known. In the Arrhenius equation (i), the factor  $e^{-Ea/RT}$  corresponds to the fraction of molecules with kinetic energy greater than  $E_a$ .

Taking natural logarithm of both sides of equation (i), we get  $\ln k = \ln A - \frac{E_a}{RT}$  ....(ii)

The plot of ln k versus 1/T gives a straight line according to the equation (ii) as shown in the below figure.



Figure 18.14: Plot of In k versus 1/T

Thus, it has been found from Arrhenius equation (i) that increase in temperature or decrease in activation energy results in an increase in the rate of the reaction and an exponential increase in the rate constant.

In the plot, slope =  $-\frac{E_a}{R}$  and intercept = In A. So we can calculate  $E_a$  and A using these values.

At temperature 
$$T_1$$
, equation (ii) becomes  $\ln k_1 = -\frac{E_a}{RT_1} + \ln A$  ....(iii)

At temperature 
$$T_{2'}$$
 equation (ii) becomes  $\ln k_2 = -\frac{E_a}{RT_2} + \ln A$  ....(iv)

(since A is constant for a given reaction)

 $k_1$  and  $k_2$  are the values of rate constants at temperatures  $T_1$  and  $T_2$  respectively. Subtracting equation (iii) from (iv), we obtain

$$\ln k_{2} - \ln k_{1} = \frac{E_{a}}{RT_{1}} - \frac{E_{a}}{RT_{2}} ; \ln \frac{k_{2}}{k_{1}} = \frac{E_{a}}{R} \left[ \frac{1}{T_{1}} - \frac{1}{T_{2}} \right] ; \log \frac{k_{2}}{k_{1}} = \frac{E_{a}}{2.303R} \left[ \frac{1}{T_{1}} - \frac{1}{T_{2}} \right]$$

#### Maxwell's-Boltzmann Distribution Curve:

The peak of the curve corresponds to the most probable kinetic energy, i.e. kinetic energy of maximum fraction of molecules. Number of molecules decreases with energies higher or lower than this value. When the temperature is raised, the maximum of the molecules moves to the higher energy value (figure) and the curve broadens out, i.e. spreads to the right such that there is a greater proportion of molecules with much higher energies. The area under the curve must be constant since total probability should always be unity at any given time. We can mark the position of E<sub>a</sub> on Maxwell Boltzmann distribution curve.



Figure 18.15: Distribution curve showing temperature dependence of rate of a reaction

Increase in the temperature of the substance increases the fraction of molecules, which collide with molecules with energies greater than  $E_a$ . It is clear from the diagram that in the curve at (T +10), the area showing the fraction of molecules having energy equal to or greater than activation energy gets doubled leading to doubling the rate of a reaction.

### 9.4 Effect of Catalyst

A catalyst is a substance which alters the rate of a reaction without undergoing any permanent chemical change. For example, MnO<sub>2</sub> catalyses the following reaction so as to increase its rate considerably

$$2\text{KCIO}_3 \xrightarrow{\text{MnO}_2} 2\text{KCI} + 3\text{O}_2$$



Figure 18.16: Effect of catalyst on activation energy

**Catalytic Mechanism:** The mechanism of the catalyst can be explained by intermediate complex theory. According to this theory a catalyst reacts with the reactant to form temporary bonds resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.

It is believed that the catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier.

According to Arrhenius equation,  $k = Ae^{-E_a/RT}$ , the lower the value of activation energy, the faster will be the rate of a reaction.

#### **MASTERJEE CONCEPTS**

#### **For catalysts**

- Even a small amount of the catalyst has the ability to catalyze a large amount of reactants.
- Gibbs energy,  $\Delta G$ , of a reaction is independent of the catalyst.
- It has an effect on spontaneous reactions but does not catalyse non-spontaneous reactions.
- Catalyst does not change the equilibrium constant of a reaction, rather it helps to attain equilibrium faster, i.e. it catalyses the forward as well as the backward reaction to the same extent so that the equilibrium state remains same and is reached earlier.

#### For collision theory

- Activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.
- It considers atoms/molecules to be hard spheres and ignores their structural aspect.
- Comparing the equation (vi) with Arrhenius equation, we can say that A is related to collision frequency.

#### Saurabh Chaterjee (JEE Advanced 2013, AIR)

**Note:** In the following reaction formation of methanol from bromo-ethane depends upon the orientation of reactant molecules. Only proper orientation of reactant molecules lead to bond formation, else it simply bounce back and no products are formed.

 $CH_3 + OH^- \rightarrow CH_3OH + Br^-$ 



**Steric Factor:** For effective collisions, the probability or steric factor (P) is introduced. It helps the molecules for a proper oriented i.e., Rate =  $PZ_{AB} e^{-E_{A}/RT}$ 

**Illustration 15:** What will be the effect of temperature on rate constant?

#### (JEE MAIN)

**Sol:** Rate constant of a reaction is nearly doubled with rise in temperature by 10°C. The dependence of the rate constant on temperature is given by Arrhenius equation,  $k = Ae^{-E_a/RT}$ , where A is called frequency factor and  $E_a$  is the activation energy of the reaction.

**Illustration 16:** How is the value of activation energy calculated from the rate constants at two different temperatures. If the value of activation energy is 50 kJ/mol then show that by increasing the temperature from 300 K to 310 K, rate constant becomes nearly double. (JEE MAIN)

**Sol:** We know that Arrhenius equation can be written as  $\log k = \log A - \frac{E_a}{2.303RT}$ 

If  $k_1$  and  $k_2$  are the rate constants at two different temperature  $T_1$  and  $T_2$  then Arrhenius equation at both the temperatures can written as

$$\log k_1 = \log A - \frac{E_a}{2.303R} \frac{1}{T_1} ; \log k_2 = \log A - \frac{E_a}{2.303R} \frac{1}{T_2}$$

Subtracting equation (i) from (ii), we get  $\log k_2 - \log k_1 = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$  or  $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$ 

From the values of  $k_1$  and  $k_2$  at temperature  $T_1$  and  $T_{2'} E_a$  can be calculated.

Given  $T_1 = 300K, T_2 = 310 K, E_a = 50 kJ \text{ or } 50,000 J$ 

Put these values in eq. (iii),  $\log \frac{k_2}{k_1} = \frac{50000}{2.303 \times 8.314} \left[ \frac{1}{300} - \frac{1}{310} \right] = \frac{50000}{2.303 \times 8.314} \left[ \frac{310 - 300}{310 \times 300} \right]$ 

or 
$$\log \frac{k_2}{k_1} = 0.2808 = \text{Antilog } 0.2808 = 1.91 \approx 2$$

It is clear that by increasing the temperature from 300 K to 310 K doubles the rate constant.

#### **Illustration 17:** Even an exothermic reaction has activation energy. Why?

#### (JEE ADVANCED)

**Sol:** A reaction can either be endothermic or exothermic, but it possesses a minimum energy level for the molecules to cross the energy barrier for the reaction to take place. Also

Threshold energy =  $\Sigma E_{R} + E_{a}$  and  $\Delta H = \Sigma E_{P} - \Sigma E_{R}$  ( $\Delta H$  may be + ve or - ve)

For example, burning of carbon is highly exothermic process, yet it does not start of its own. The activation energy of combustion of carbon is quite high and thus, in spite of exothermic nature, the reaction starts only when flame is applied to the heap of carbon contents.

**Illustration 18:** A first-order reaction is 50% complete in 30 min at 27°C and in 10 min at 47°C. Calculate the rate constants, and the energy of activation of the reaction in kJ/mol. (JEE ADVANCED)

**Sol:** Time for the completion of 50% reaction means  $t_{1/2}$ .

It means  $t_{1/2}$  of the reaction at 27°C is 30 min and at 47°C is 10 min.

We know that 
$$k = \frac{0.693}{t_{1/2}}$$
 or  $k = \frac{0.693}{30} = 0.0231 \text{ min}^{-1}(\text{at } 27^{\circ}\text{C}) \text{ and } k = \frac{0.693}{10} = 0.0693 \text{ min}^{-1}(\text{at } 47^{\circ}\text{C})$   
We know that  $\log \frac{k_2}{k_1} = \frac{E_a}{2.303\text{R}} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$   
 $k_2 = 0.0693 \text{ min}^{-1}, k_1 = 0.0231 \text{ min}^{-1}, T_1 = 27 + 273 = 300 \text{ K}, T_2 = 47 + 273 = 320 \text{ K},$   
 $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}, E_a = ?$   
 $\log \frac{0.0693}{0.0231} = \frac{E_a}{2.303 \times 8.314} \left[ \frac{1}{300} - \frac{1}{320} \right]$   
or  $\log 3 = \frac{E_a}{2.303 \times 8.314} \left[ \frac{320 - 300}{300 \times 320} \right]$   
 $0.4771 = \frac{E_a}{2.303 \times 8.314} \left[ \frac{20}{300 \times 320} \right]$   
or  $E_a = \left[ \frac{0.4771 \times 2.303 \times 8.314 \times 300 \times 320}{20} \right] = 43848.49 \text{ J mol}^{-1} = 43.85 \text{ kJ mol}^{-1}$ 

### **10. METHODS OF DETERMINATION OF ORDER OF REACTION**

### 10.1 Method of Integration (Hit and Trial Method)

The most simple method is the one in which the quantities a, x and t are determined and substituted in the kinetic equations of various orders. The equation which gives the most constant value for the specific rate constant (k) for a series of time intervals is the one corresponding to the order of reaction. If all the reactants are at the same molar concentrations, the kinetic equations are:

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}, \text{ for first-order reactions;}$$
$$k = \frac{1}{t} \left[ \frac{1}{(a-x)} - \frac{1}{a} \right], \text{ for second-order reactions;}$$

$$k = \frac{1}{2t} \left[ \frac{1}{(a-x)^2} - \frac{1}{a^2} \right], \text{ for third-order reactions;}$$

### **10.2 Graphical Method**

A graphical method based on the respective rate laws can also be used to determine the order of reaction.

If the plot of log (a - x) versus 't' is a straight line, the reaction follows first order.

If the plot of  $\frac{1}{(a-x)}$  versus 't' is a straight line, the reaction follows second order. If the plot of  $\frac{1}{(a-x)^2}$  versus 't' is a straight line, the reaction follows third order. In general, for a reaction of nth order, a graph of  $\frac{1}{(a-x)^{n-1}}$  versus 't ' must be a straight line.

### 10.3 Half-Life Method

A general expression for the half-life, (t\_{\_{1/2}} ), is given by t\_{\_{1/2}} \propto \frac{1}{a^{n-1}}



Figure 18.17: Plots of half-lives versus concentration ( $t_{_{1/2}} \propto a^{1-n}$ )

This relation can be used to determine order of reaction 'n'.

### 10.4 Van't Hoff Differential Method

Relationship between velocity V of n<sup>th</sup> order reaction and concentration of reactants C is given by

Van't Hoff, n =  $\frac{\log(V_1 / V_2)}{\log(C_1 / C_2)}$ 

Where,  $C_1$  and  $C_2$  are two different concentrations, while  $V_1$  and  $V_2$  are their velocities.

### 10.5 Ostwald Isolation Method

This method is used to find out the order of complex reactions. If  $n_{A'}$ ,  $n_{B}$  and  $n_{C}$  molecules of substance A, B and C, respectively are present in a reaction, then  $n_{A}$  +  $n_{B}$  +  $n_{C}$  will be the order of reaction:

When B and C are in excess, the order of reaction will be  $n_A$ .

When A and B are in excess, the order of reaction will be n<sub>c</sub>.

When A and C are in excess, the order of reaction will be  $n_{B}$ .

## PROBLEM-SOLVING TACTICS

(a) To determine the average rate for change in concentration over a time period.

Average rate of reaction is the change in concentration of reactants (or products) during large interval of time.

Rate = 
$$-\frac{[\text{reactant at } t_2] - [\text{reactant at } t_1]}{t_2 - t_1}$$

Square brackets denote concentration.

Negative sign in the above equation is used to make the rate of reaction positive. Minus sign can be ignored when calculating average rates from products.

Rate = 
$$-\frac{\Delta [reactant]}{\Delta t}$$
 or  $rate = \frac{\Delta [product]}{\Delta t}$ 

**(b)** To determine instantaneous rate from a plot of concentration versus time: Instantaneous rate at time t is determined as follows:

(i) Calculate the negative slope of the curve between concentration of a reactant and time at t.

(ii) Calculate the slope of the curve between concentration of a product and time at t.

(c) Problem-solving tactics to determine the initial rate from a plot of concentration versus time: The initial rate of a reaction is the instantaneous rate at the start of the reaction (i.e., when t = 0).

Initial rate is equal to the negative slope of the curve between reactant concentration and time at t = 0.

(d) To determining the order of a reaction from its rate law

Rate law of a reaction is used to determine:

- The order of the reaction with respect to one or more reactants.
- The overall order of the reaction.

rate =  $k[A]^n[B]^m[c]^p$ 

For the rate law: Order with respect to A = n; order with respect to B = m, order with respect to C = p

Reaction or overall order = n + m + p

Note: The stoichiometric coefficient in the balanced equation for a chemical reaction is usually different from the order.



Figure 18.18: Plot of concentration versus time

Reaction	Experimental Rate Law	Order
$NO_2 + CO \rightarrow NO + CO_2$	rate = $k[NO_2]^2$	2nd order reaction 2nd order in $NO_2$ 0 order in CO
$CH_{3}CHO \rightarrow CH_{4} + CO$	rate = $k[CH_3CHO]^2$	2nd order reaction 2nd order in CH <sub>3</sub> CHO

(e) To determining rate laws from graphs of concentration versus time (integrated rate laws).

To determine the rate law for a reaction for different concentration (or the values of some function of concentration) versus time, make three graphs.

[A] versus t (linear for a zero-order reaction)

In [A] versus t (linear for a 1<sup>st</sup> order reaction)

1 / [A] versus t (linear for a 2<sup>nd</sup> order reaction)

The graph that is linear indicates the order of the reaction with respect to A. Then, you can choose the correct rate equation:

For a zero-order reaction,	Rate = k	(k = -ve slope of line)
For a first order reaction,	rate = $k[A]$	(k = -ve slope of line)
For a second order reaction,	rate = $k[A]^2$	(k = slope of line)

(f) Regarding questions of half lives:

For a zero-order reaction  $A \rightarrow \text{products}$ , rate = k,  $t_{\frac{1}{2}} = [A_0] / 2k$ 

For a first-order reaction A  $\rightarrow$  products, rate = k[A], t<sub>1/2</sub> = 0.693 / k

For a second-order reaction  $2A \rightarrow \text{products or } A + B \rightarrow \text{products (when } [A] = [B])$ , rate =  $k[A]^2$ ,  $t_{\mu} = 1 / k[A_0]$ 

Graphical Relations and half-lives: Differences in half-lives for reactions of different orders (0, 1st, or 2nd) are determined by plotting graphs between reactant [A] and time (t). Change in time changes the concentration of a reactant to half.

(i) For a zero-order reaction, half-life decreases with decreasing concentration.

(ii) For a 1st order reaction, half-life is constant.

(iii) For a second-order reaction, half-life increases with decreasing concentration.





For a first-order reaction:

 $A \rightarrow products$ , rate = k  $A \rightarrow products$ , rate = k[A]

For a second-order reaction:  $2A \rightarrow \text{products/A} + B \rightarrow \text{products}$ (when [A] = [B], rate = k[A]<sup>2</sup>

### 18.28 | Chemical Kinetics —

# POINTS TO REMEMBER

Торіс	Formula				
Average rate of reaction	Average rate = $\frac{\text{Change in the concentration of reactants or(Products)}}{\text{Time}} = \pm \frac{\Delta C}{\Delta t} = \pm \frac{C_2 - C_1}{t_2 - t_1}$				
Instantaneous rate of reaction	Instantaneous rate = $\lim_{\Delta t \to 0} \frac{\Delta C}{\Delta t} = \frac{dC}{dt}$				
	For the reaction $n_1A + n_2B \rightarrow m_1C + m_2D$				
	Instantaneous Rate of reaction = $-\frac{1}{n_1}\frac{d[A]}{dT} = -\frac{1}{n_2}\frac{d[B]}{dT} = +\frac{1}{m_1}\frac{d[C]}{dT} = +\frac{1}{m_2}\frac{d[D]}{dT}$				
Factors affecting	Nature of reactants and products				
	Concentration	perature n of Reactants			
	Concentration of Reactants     Presence of catalyst				
	Effect of Sunlight				
Law of mass action and rate constant	The rate at which a substance is directly proportional to its active mass and the rate at which a reaction proceeds is proportional to the product of the active masses of the reacting substances $ \begin{pmatrix} dx \end{pmatrix} \begin{pmatrix} dx \end{pmatrix} $				
	For a reaction, $aA + bB \rightarrow product rate = \left(\frac{dt}{dt}\right) \propto [A]^a[B]^b; \left(\frac{dt}{dt}\right) = k[A]^a[B]^b$				
	where k is rate constant or velocity constant.				
	When [A] = [B] = 1 mol/L, then $\frac{dx}{dt} = k$				
Unit of rate constant	Unit of rate constant = $\left[\frac{\text{litre}}{\text{mol}}\right]^{n-1} \times \text{sec}^{-1}$				
	When n = order of reaction.				
Various types of reactions	Type of reaction	Integrated rate equation	Unite of rate constant	t <sub>1/2</sub> Half-life period	t <sub>3/4</sub> period
	Zero-order reaction	$-\frac{d[A]}{dt} = k_0[A]^0$ Differential form $\frac{dx}{dt} = k$	Concentration time <sup>-1</sup>	$\frac{A_0}{2k}$	

	First-order reaction	$k_{1} = \frac{2.303}{t} \log_{10} \frac{a}{(a - x)}$ Differential form $\frac{dx}{dt}$ = k(a - x)	Time <sup>-1</sup>	$\frac{0.693}{K_1}$	$2 \times \frac{0.693}{K_1} = \frac{1.382}{k_1}$
	Second-order reaction	$k_{2} = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$ Differential form $\frac{dx}{dt}$ $= k(a-x)^{2}$	Mole <sup>-1</sup> litre time <sup>-1</sup>	$\frac{1}{K_2a}$	$\frac{3}{K_2a}$
	Third-order reaction	$k_{3} = \frac{1(2a - x)}{t2a^{2}(a - x)^{2}}$ Differential form $\frac{dx}{dt}$ $= k(a - x)^{3}$	Litre <sup>2</sup> mole <sup>-2</sup> time <sup>-1</sup>	$\frac{1}{2}\frac{3}{K_2a}$	
Relationship between Rate of reaction and rate constant	Zero Order r (conc) <sup>0</sup>	First Order Seco	r (conc) <sup>2</sup>	hird Order	
	(Juoj) t	(A) t t t t t t t t t t t t t t t t t t t	t	t	
	t <sub>1/2</sub> (conc) <sup>0</sup>	t <sub>1/2</sub> t <sub>1/2</sub> t <sub>1/2</sub>	t <sub>1/2</sub>	1/a	
Half-Life	$t_{_{1/2}} \propto \frac{1}{a^{n-1}}$ whe	re n = order of reaction			
Arrhenius theory	$\log \frac{k_2}{k_1} = \frac{E_a}{2.303}$	$\overline{R\left[\frac{1}{T_1} - \frac{1}{T_2}\right]}$			
	$k = Ae^{-La/12}$ where $k_1$ and $k_2$ are rate constant at temperatures $T_1$ and $T_2$ , respectively ( $T_2 > T_1$ ).				