

## 20

## Chemical Kinetics

## CHAPTER

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So far we have studied equilibrium reactions. In these reactions, the rates of the two opposing reactions are equal and the concentrations of reactants or products do not change with lapse of time. But most chemical reactions are **spontaneous reactions**. These reactions occur from left to right till all the reactants are converted to products. A spontaneous reaction may be slow or it may be fast. For example, the reactions between aqueous sodium chloride and silver nitrate is a fast reaction. The precipitate of  $\text{AgCl}$  is formed as fast as  $\text{AgNO}_3$  solution is added to  $\text{NaCl}$  solution. On the contrary, the rusting of iron is a slow reaction that occurs over the years.

The branch of Physical chemistry which deals with the rate of reactions is called Chemical Kinetics. The study of Chemical Kinetics includes :

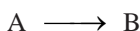
- (1) The rate of the reactions and rate laws.
- (2) The factors as temperature, pressure, concentration and catalyst, that influence the rate of a reaction.
- (3) The mechanism or the sequence of steps by which a reaction occurs.

The knowledge of the rate of reactions is very valuable to

understand the chemical of reactions. It is also of great importance in selecting optimum conditions for an industrial process so that it proceeds at a rate to give maximum yield.

### REACTION RATE

The rate of a reaction tells us to what speed the reaction occurs. Let us consider a simple reaction



The concentration of the reactant A decreases and that of B increases as time passes. The **rate of reactions is defined as the change in concentration of any of reactant or products per unit time**. For the given reaction the rate of reaction may be equal to the rate of disappearance of A which is equal to the rate of appearance of B.

Thus

$$\begin{aligned} \text{rate of reaction} &= \text{rate of disappearance of } A \\ &= \text{rate of appearance of } B \end{aligned}$$

$$\begin{aligned} \text{or} \quad \text{rate} &= - \frac{d[A]}{dt} \\ &= + \frac{d[B]}{dt} \end{aligned}$$

where [ ] represents the concentration in moles per litre whereas 'd' represents infinitesimally small change in concentration. Negative sign shows the concentration of the reactant A decreases whereas the positive sign indicates the increase in concentration of the product B.

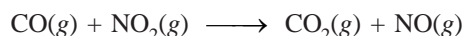
### UNITS OF RATE

Reactions rate has the units of concentration divided by time. We express concentrations in moles per litre (mol/litre or mol/l or mol l<sup>-1</sup>) but time may be given in any convenient unit second (s), minutes (min), hours (h), days (d) or possible years. Therefore, the units of reaction rates may be

$$\begin{array}{ll} \text{mole/litre sec} & \text{or} \quad \text{mol l}^{-1} \text{ s} \\ \text{mole/litre min} & \text{or} \quad \text{mol l}^{-1} \text{ min}^{-1} \\ \text{mole/litre hour} & \text{or} \quad \text{mol l}^{-1} \text{ h}^{-1} \text{ and, so on} \end{array}$$

### Average Rate of Reaction is a Function of Time

Let us consider the reaction between carbon monoxide (CO) and nitrogen dioxide.



The average rate of reaction may be expressed as

$$\text{rate} = \frac{-\Delta[\text{CO}]}{\Delta t} = - \frac{d[\text{CO}]}{dt}$$

The concentration of CO was found experimentally every 10 seconds. The results of such an experiment are listed below.

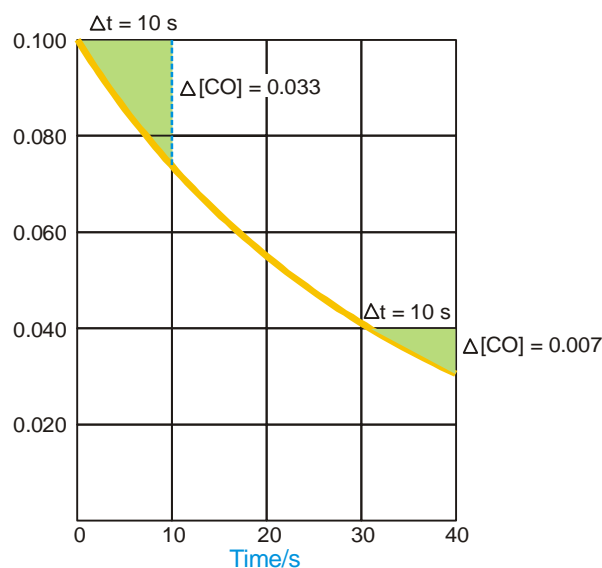
Conc. of CO	0.100	0.067	0.050	0.040	0.033
Time (sec)	0	10	20	30	40

The results are also shown graphically in Fig. 20.1.

As the reaction proceeds the concentration of CO decreases rapidly in the initial stages of the reaction. Then the concentration of CO decreases more and more slowly. Obviously the rate of reaction is a function of time.

Over the first 10 seconds, the average rate is

$$\frac{-d[\text{CO}]}{dt} = \frac{-(0.067 - 0.100)}{(10 - 0)} = \frac{0.033}{10} = 0.0033 \text{ mol l}^{-1} \text{ s}^{-1}$$



■ **Figure 20.1**  
Graph of CO concentrations versus time. The average rate is equal to the slope of the curve. The average rates for the first 10 and the last 10 seconds are shown.

In the time interval between 30 and 40 seconds, the average rate is much smaller.

$$\frac{-d[\text{CO}]}{dt} = \frac{-(0.033 - 0.040)}{(40 - 30)} = \frac{0.007}{10} = 0.0007 \text{ mol l}^{-1} \text{ s}^{-1}$$

The reaction is indeed slowing down with time.

We shall see that average rates are not always useful. They cover a large time interval during which the rate of reaction changes significantly. So, a better way to estimate the rate of reaction, we need to make the time interval as small as possible.

### Instantaneous Rate of Reaction

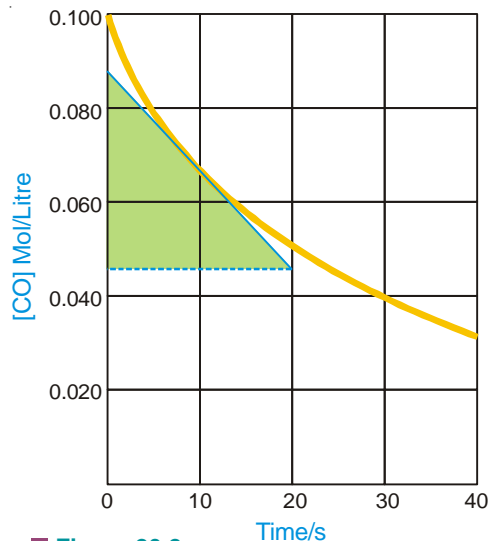
The average rates obtained by finding the slope of the curve are not always useful. They cover a large time interval during which the rate of reaction changes significantly. So, a better way to estimate the rate of reaction is to make the time interval as small as possible. If the interval be infinitesimally small (that is as  $\Delta t$  approaches zero), the rate is referred to as the **instantaneous rate** and is written in calculus as

$$\text{rate} = \frac{d[\ ]_t}{dt}$$

where  $[ ]_t$  is the concentration at time  $t$ . In the present case,

$$\text{the instantaneous rate} = \frac{-d[\text{CO}]_t}{dt}$$

Thus at any time the instantaneous rate is equal



■ **Figure 20.2**  
The slope of tangent at 10 seconds is equal to the instantaneous rate.

to the slope of a straight line drawn tangent to the curve at that time. For example, in Fig. 20.2 the instantaneous rate at 10 seconds is found to be  $0.0022 \text{ mol l}^{-1} \text{ s}^{-1}$ .

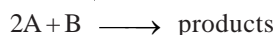
### RATE LAWS

At a fixed temperature the rate of a given reaction depends on concentration of reactants. The exact relation between concentration and rate is determined by measuring the reaction rate with different initial reactant concentrations. By a study of numerous reactions it is shown that : **the rate of a reaction is directly proportional to the reactant concentrations, each concentration being raised to some power.**

Thus for a substance A undergoing reaction,

$$\begin{aligned} \text{rate} & \propto [\text{A}]^n \\ \text{or} & \text{rate} = k [\text{A}]^n \end{aligned} \quad \dots(1)$$

For a reaction



the reaction rate with respect to A or B is determined by varying the concentration of one reactant, keeping that of the other constant. Thus the rate of reaction may be expressed as

$$\text{rate} = k [\text{A}]^m [\text{B}]^n \quad \dots(2)$$

Expressions such as (1) and (2) tell the relation between the rate of a reaction and reactant concentrations.

**An expression which shows how the reaction rate is related to concentrations is called the rate law or rate equation.**

The power (exponent) of concentration  $n$  or  $m$  in the rate law is usually a small whole number integer (1, 2, 3) or fractional. The proportionality constant  $k$  is called the **rate constant** for the reaction.

**Examples of rate law :**

	REACTIONS	RATE LAW
(1)	$2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$	$\text{rate} = k [\text{N}_2\text{O}_5]$
(2)	$\text{H}_2 + \text{I}_2 \longrightarrow 2\text{HI}$	$\text{rate} = k [\text{H}_2] [\text{I}_2]$
(3)	$2\text{NO}_2 \longrightarrow 2\text{NO} + \text{O}_2$	$\text{rate} = k [\text{NO}_2]^2$
(4)	$2\text{NO} + 2\text{H}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$	$\text{rate} = k [\text{H}_2] [\text{NO}]^2$

In these rate laws where the quotient or concentration is not shown, it is understood to be 1. That is  $[\text{H}_2]^1 = [\text{H}_2]$ .

It is apparent that the rate law for a reaction must be determined by experiment. It cannot be written by merely looking at the equation with a background of our knowledge of Law of Mass Action. However, for some elementary reactions the powers in the rate law may correspond to coefficients in the chemical equation. **But usually the powers of concentration in the rate law are different from coefficients.** Thus for the reaction (4) above, the rate is found to be proportional to  $[\text{H}_2]$  although the quotient of  $\text{H}_2$  in the equation is 2. For NO the rate is proportional to  $[\text{NO}]^2$  and power '2' corresponds to the coefficient.

### ORDER OF A REACTION

**The order of a reaction is defined as the sum of the powers of concentrations in the rate law.**

Let us consider the example of a reaction which has the rate law

$$\text{rate} = k [\text{A}]^m [\text{B}]^n \quad \dots(1)$$

The order of such a reaction is  $(m + n)$ .

The order of a reaction can also be defined with respect to a single reactant. Thus the reaction order with respect to A is  $m$  and with respect to B it is  $n$ . The **overall order of reaction** ( $m + n$ ) may range from 1 to 3 and can be fractional.

**Examples of reaction order :**

RATE LAW	REACTION ORDER
rate = $k [\text{N}_2\text{O}_5]$	1
rate = $k [\text{H}_2] [\text{I}_2]$	$1 + 1 = 2$
rate = $k [\text{NO}_2]^2$	2
rate = $k [[\text{H}_2] [\text{NO}]^2]$	$1 + 2 = 3$
rate = $k [\text{CHCl}_3] [\text{Cl}_2]^{1/2}$	$1 + \frac{1}{2} = 1\frac{1}{2}$

Reactions may be classified according to the order. If in the rate law (1) above

$m + n = 1$ , it is **first order reaction**

$m + n = 2$ , it is **second order reaction**

$m + n = 3$ , it is **third order reaction**

### ZERO ORDER REACTION

A reactant whose concentration does not affect the reaction rate is not included in the rate law. In effect, the concentration of such a reactant has the power 0. Thus  $[\text{A}]^0 = 1$ .

A **zero order reaction is one whose rate is independent of concentration**. For example, the rate law for the reaction



at  $200^\circ \text{C}$  is

$$\text{rate} = k [\text{NO}_2]^2$$

Here the rate does not depend on  $[\text{CO}]$ , so this is not included in the rate law and the power of  $[\text{CO}]$  is understood to be zero. The reaction is **zeroth order** with respect to  $\text{CO}$ . The reaction is second order with respect to  $[\text{NO}_2]$ . The overall reaction order is  $2 + 0 = 2$ .

### MOLECULARITY OF A REACTION

Chemical reactions may be classed into two types :

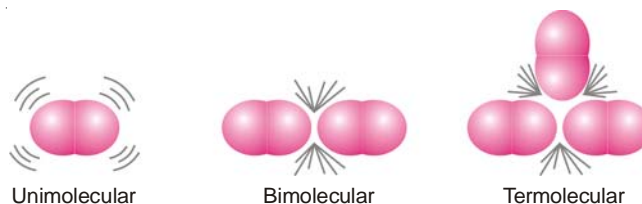
- Elementary reactions
- Complex reactions

An **elementary reaction** is a simple reaction which occurs in a single step.

A **complex reaction** is that which occurs in two or more steps.

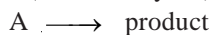
### Molecularity of an Elementary Reaction

The molecularity of an elementary reaction is defined as : **the number of reactant molecules involved in a reaction**.

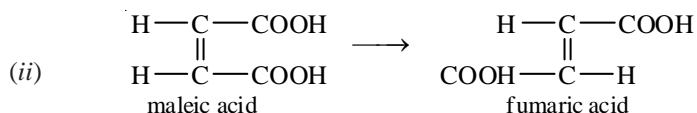


Thus the molecularity of an elementary reaction is 1, 2, 3, etc., according as one, two or three reactant molecules are participating in the reaction. The elementary reactions having molecularity 1, 2 and 3 are called **unimolecular, bimolecular and termolecular** respectively. Thus we have :

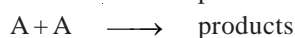
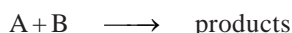
(a) **Unimolecular reactions** : (molecularity = 1)



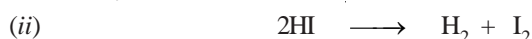
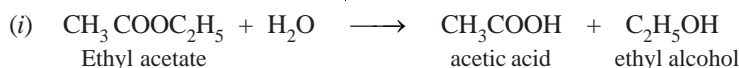
Examples are : (i)  $\text{Br}_2 \longrightarrow 2\text{Br}$



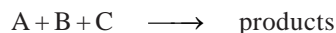
(b) **Bimolecular reactions** : (molecularity = 2)



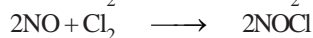
Examples are :



(c) **Termolecular reactions** : (molecularity = 3)

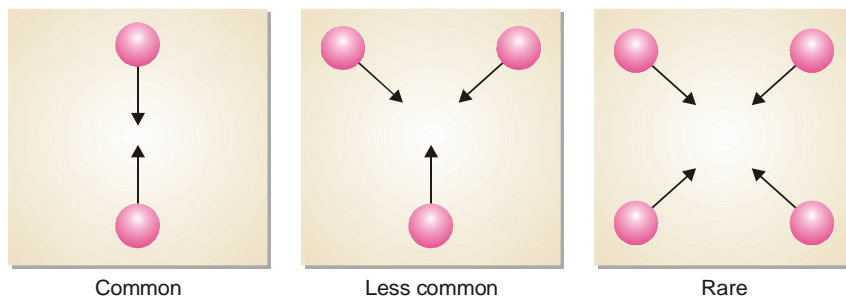


Examples are :



### Why High Molecularity Reactions are Rare ?

Most of the reactions involve one, two or at the most three molecules. The reactions involving four or more molecules are very rare. The rarity of reactions with high molecularity can be explained on the basis of the kinetic molecular theory. According to this theory, the rate of a chemical reaction is proportional to the number of collisions taking place between the reacting molecules. The chances of simultaneous collision of reacting molecules will go on decreasing with increase in number of molecules. Thus the possibility of three molecules colliding together is much less than in case of bimolecular collision. For a reaction of molecularity 4, the four molecules must come closed and collide with one another at the same time. The possibility of their doing so is much less than even in the case of termolecular reaction. Hence the reactions involving many molecules proceed through a series of steps, each involving two or three or less number of molecules. Such a reaction is called a complex reaction and the slowest step determines the overall rate of the reactions.

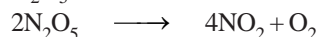


■ **Figure 20.3**  
Chances of simultaneous collision between reacting molecules decrease as the molecularity increases.

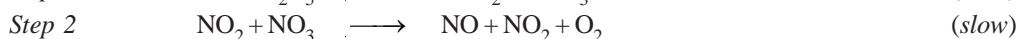
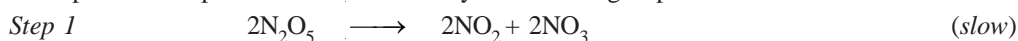
### Molecularity of a Complex Reaction

Most chemical reactions are complex reactions. These occur in a series of steps. Each step is an elementary reaction. The stepwise sequence of elementary reactions that convert reactions to products is called the **mechanism of the reaction**. In any mechanism, some of the steps will be fast, others will be slow. A reaction can proceed no faster than its slowest step. Thus the slowest step is the **rate-determining step** of the reaction.

The decomposition of  $N_2O_5$ ,



is an example of a complex reaction. It occurs by the following steps :



Each elementary reaction has its own molecularity equal to the number of molecules or atoms participating in it. It is meaningless to give the molecularity of the overall reaction because it is made of several elementary reactions, each, perhaps with a different molecularity. At best could be thought of as : **the number of molecules or atoms taking part in the rate-determining step**.

Thus step 2 in the above mechanism is rate-determining and has molecularity '2' which could be considered as the molecularity of the decomposition reaction of  $N_2O_5$ .

### MOLECULARITY VERSUS ORDER OF REACTION

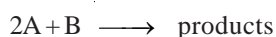
The term molecularity is often confused with order of a reaction.

The total number of molecules or atoms which take part in a reaction as represented by the chemical equation, is known as the **molecularity of reaction**.

The sum of the powers to which the concentrations are raised in the rate law is known as the **order of reaction**.

### Molecularity and Order are Identical for Elementary Reactions or Steps

The rate of an elementary reaction is proportional to the number of collisions between molecules (or atoms) of reactions. The number of collisions in turn is proportional to the concentration of each reactant molecule (or atom). Thus for a reaction.



$$\text{rate} \propto [A][A][B]$$

or 
$$\text{rate} = k[A]^2[B] \quad (\text{rate law})$$

Two molecules of A and one molecule of B are participating in the reaction and, therefore, molecularity of the reaction is  $2 + 1 = 3$ . The sum of powers in the rate law is  $2 + 1$  and hence the reaction order is also 3. Thus **the molecularity and order for an elementary reaction are equal**.

**TABLE 20.1. MOLECULARITY AND ORDER FOR ELEMENTARY REACTIONS.**

Reactions	Molecularity	Rate law	Order
$A \longrightarrow \text{products}$	1	$\text{rate} = k[A]$	1
$A + A \longrightarrow \text{products}$	2	$\text{rate} = k[A]^2$	2
$A + B \longrightarrow \text{products}$	2	$\text{rate} = k[A][B]$	2
$A + 2B \longrightarrow \text{products}$	3	$\text{rate} = k[A][B]^2$	3
$A + B + C \longrightarrow \text{products}$	3	$\text{rate} = k[A][B][C]$	3

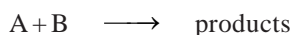
## Differences Between Order and Molecularity

Order of a Reaction	Molecularity of a Reaction
<ol style="list-style-type: none"> <li>1. It is the <b>sum of powers</b> of the concentration terms in the rate law expression.</li> <li>2. It is an <b>experimentally</b> determined value.</li> <li>3. It can have <b>fractional</b> value.</li> <li>4. It can assume <b>zero value</b>.</li> <li>5. Order of a reaction <b>can change</b> with the conditions such as pressure, temperature, concentration.</li> </ol>	<ol style="list-style-type: none"> <li>1. It is number of <b>reacting species</b> undergoing simultaneous collision in the elementary or simple reaction.</li> <li>2. It is a <b>theoretical</b> concept.</li> <li>3. It is always a <b>whole number</b>.</li> <li>4. It <b>can not have zero value</b>.</li> <li>5. Molecularity is <b>invariant</b> for a chemical equation.</li> </ol>

## PSEUDO-ORDER REACTIONS

A reaction in which one of the reactants is present in a large excess shows an order different from the actual order. **The experimental order which is not the actual one is referred to as the pseudo order.** Since for elementary reactions molecularity and order are identical, pseudo-order reactions may also be called **pseudo molecular reactions**.

Let us consider a reaction



in which the reactant B is present in a large excess. Since it is an elementary reaction, its rate law can be written as

$$\text{rate} = k [A] [B]$$

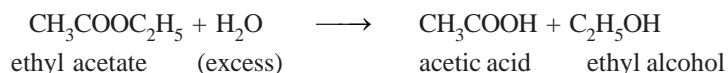
As B is present in large excess, its concentration remains practically constant in the course of reaction. Thus the rate law can be written as

$$\text{rate} = k' [A]$$

where the new rate constant  $k' = k [B]$ . Thus the actual order of the reaction is second-order but in practice it will be first-order. Therefore, the reaction is said to have a **pseudo-first order**.

## Examples of Pseudo-order Reactions

- (1) **Hydrolysis of an ester.** For example, ethyl acetate upon hydrolysis in aqueous solution using a mineral acid as catalyst forms acetic acid and ethyl alcohol.

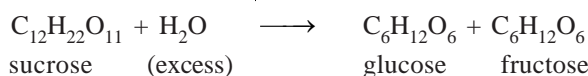


Here a large excess of water is used and the rate law can be written as

$$\begin{aligned} \text{rate} &= k [\text{CH}_3\text{COOH}] [\text{H}_2\text{O}] \\ &= k' [\text{CH}_3\text{COOH}] \end{aligned}$$

The reaction is actually second-order but in practice it is found to be first-order. Thus it is a pseudo-first order reaction.

- (2) **Hydrolysis of sucrose.** Sucrose upon hydrolysis in the presence of a dilute mineral acid gives glucose and fructose.



If a large excess of water is present,  $[\text{H}_2\text{O}]$  is practically constant and the rate law may be written as

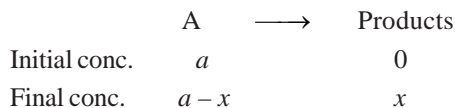


$$\begin{aligned}\text{rate} &= k [\text{C}_{12}\text{H}_{22}\text{O}_{11}] [\text{H}_2\text{O}] \\ &= k [\text{C}_{12}\text{H}_{22}\text{O}_{11}]\end{aligned}$$

The reaction though of second-order is experimentally found to be first-order. Thus it is a pseudo-first-order reaction.

### ZERO ORDER REACTIONS

In a zero order reaction, rate is independent of the concentration of the reactions. Let us consider a zero-order reaction of the type



$$\text{Rate of reaction} = \frac{-d[A]}{dt} = k_0[A]^0$$

$$\text{or} \quad \frac{dx}{dt} = \frac{-d(a-x)}{dt} = k_0(a-x)^0 = k_0$$

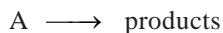
On integrating we get

$$k_0 = \frac{x}{t} \quad \text{or} \quad x = k_0 t$$

where  $k_0$  is the rate constant of a zero-order reaction, the unit of which is concentration per unit time. In zero order reaction, the **rate constant is equal to the rate of reaction at all concentrations.**

### FIRST ORDER REACTIONS

Let us consider a first order reaction



Suppose that at the beginning of the reaction ( $t = 0$ ), the concentration of A is  $a$  moles litre<sup>-1</sup>. If after time  $t$ ,  $x$  moles of A have changed, the concentration of A is  $a - x$ . We know that for a first order reaction, the rate of reaction,  $dx/dt$ , is directly proportional to the concentration of the reactant. Thus,

$$\frac{dx}{dt} = k(a-x)$$

$$\text{or} \quad \frac{dx}{a-x} = k dt \quad \dots(1)$$

Integration of the expression (1) gives

$$\int \frac{dx}{a-x} = \int k dt$$

$$\text{or} \quad -\ln(a-x) = kt + I \quad \dots(2)$$

where  $I$  is the constant of integration. The constant  $k$  may be evaluated by putting  $t = 0$  and  $x = 0$ .

Thus,

$$I = -\ln a$$

Substituting for  $I$  in equation (2)

$$\ln \frac{a}{a-x} = kt \quad \dots(3)$$

$$\text{or} \quad k = \frac{1}{t} \ln \frac{a}{a-x}$$

Changing into common logarithms

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \dots(4)$$

The value of  $k$  can be found by substituting the values of  $a$  and  $(a-x)$  determined experimentally at time interval  $t$  during the course of the reaction.

Sometimes the integrated rate law in the following form is also used :

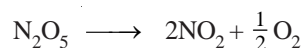
$$k = \frac{2.303}{t_2 - t_1} \log \frac{(a - x_1)}{(a - x_2)}$$

where  $x_1$  and  $x_2$  are the amounts decomposed at time intervals  $t_1$  and  $t_2$  respectively from the start.

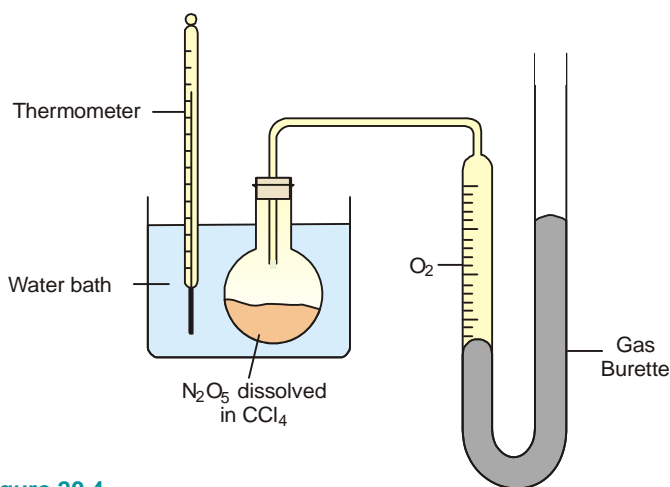
### Examples of First order Reactions

Some common reactions which follow first order kinetics are listed below :

(1) **Decomposition of  $N_2O_5$  in  $CCl_4$  solution.** Nitrogen pentoxide in carbon tetrachloride solution decomposes to form oxygen gas,



The reaction is carried in an apparatus shown in Fig. 20.4. The progress of the reaction is monitored by measuring the volume of oxygen evolved from time to time.



■ **Figure 20.4**  
An apparatus for monitoring the volume of  $O_2$  evolved in the decomposition of  $N_2O_5$  dissolved in carbon tetrachloride.

If  $V_t$  be the volume of  $O_2$  at any time  $t$  and  $V_\infty$  the final volume of oxygen when the reaction is completed, the  $V_\infty$  is a measure of the initial concentration of  $N_2O_5$  and  $(V_\infty - V_t)$  is a measure of undecomposed  $N_2O_5$  ( $a-x$ ) remaining at time  $t$ . Thus,

$$k = \frac{2.303}{t} \log_{10} \frac{V_\infty}{V_\infty - V_t}$$

On substituting values of  $V_\infty$ ,  $(V_\infty - V_t)$  at different time intervals,  $t$ , the value of  $k$  is found to be constant. Thus it is a reaction of the first order.

**SOLVED PROBLEM.** From the following data for the decomposition of  $\text{N}_2\text{O}_5$  in  $\text{CCl}_4$  solution at  $48^\circ\text{C}$ , show that the reaction is of the first order

$t$ (mts)	10	15	20	$\infty$
Vol of $\text{O}_2$ evolved	6.30	8.95	11.40	34.75

**SOLUTION**

For a first order reaction the integrated rate equation is

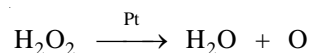
$$\frac{1}{t} \log \frac{V_\infty}{V_\infty - V_t} = k$$

In this example,  $V_\infty = 34.75$

$t$	$V_\infty - V_t$	$\frac{1}{t} \log \frac{V_\infty}{V_\infty - V_t}$	$= k$
10	28.45	$\frac{1}{10} \log \frac{34.75}{28.45}$	$= 0.00868$
15	25.80	$\frac{1}{15} \log \frac{34.75}{25.80}$	$= 0.00862$
20	23.35	$\frac{1}{20} \log \frac{34.75}{23.35}$	$= 0.00863$

Since the value of  $k$  is fairly constant, it is a **first order reaction**.

(2) **Decomposition of  $\text{H}_2\text{O}_2$  in aqueous solution.** The decomposition of  $\text{H}_2\text{O}_2$  in the presence of Pt as catalyst is a first order reaction.



The progress of the reaction is followed by titrating equal volumes of the reaction mixture against standard  $\text{KMnO}_4$  solution at different time intervals.

**SOLVED PROBLEM.** A solution of  $\text{H}_2\text{O}_2$  when titrated against  $\text{KMnO}_4$  solution at different time intervals gave the following results :

$t$ (minutes)	0	10	20
Vol $\text{KMnO}_4$ used for 10 ml $\text{H}_2\text{SO}_4$	23.8 ml	14.7 ml	9.1 ml

Show that the decomposition of  $\text{H}_2\text{O}_2$  is a first order reaction.

**SOLUTION**

The integrated rate equation for first order reaction is

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

Since volume of  $\text{KMnO}_4$  used in the titration is measure of concentration of  $\text{H}_2\text{O}_2$  in solution,

$$\begin{aligned} a &= 23.8 \text{ ml} \\ (a-x) &= 14.7 \quad \text{when } t = 10 \text{ mts} \\ (a-x) &= 9.1 \quad \text{when } t = 20 \text{ mts} \end{aligned}$$

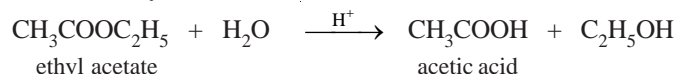
Substituting these values in the rate equation above, we have

$$\begin{aligned} k &= \frac{2.303}{10} \log \frac{23.8}{14.7} \\ &= 0.2303 (\log 23.8 - \log 14.7) \end{aligned}$$

$$\begin{aligned}
 &= 0.2303(1.3766 - 1.1673) \\
 &= 0.04820 \\
 \text{and} \quad k &= \frac{2.303}{20} \log \frac{23.8}{9.1} \\
 &= 0.10165(\log 23.8 - \log 9.1) \\
 &= 0.10165(1.3766 - 0.9595) = 0.04810
 \end{aligned}$$

Since the value of  $k$  is almost constant, the decomposition of  $\text{H}_2\text{O}_2$  is a **first order reaction**.

(3) **Hydrolysis of an Ester.** The hydrolysis of ethyl acetate or methyl acetate in the presence of a mineral acid as catalyst, is a first order reaction.



For studying the kinetics of the reaction, a known volume of ethyl acetate is mixed with a relatively large quantity of acid solution, say  $N/2$  HCl. At various intervals of time, a known volume of the reaction mixture is titrated against a standard alkali solution. Hydrolysis of the ester produces acetic acid. Therefore as the reaction proceeds, the volume of alkali required for titration goes on increasing.

**SOLVED PROBLEM.** The following data was obtained on hydrolysis of methyl acetate at  $25^\circ\text{C}$  in  $0.35\text{N}$  hydrochloric acid. Establish that it is a first order reaction.

$t$ (secs)	0	4500	7140	$\infty$
ml alkali used	24.36	29.32	31.72	47.15

#### SOLUTION

For a first order reaction,

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

At any time, the volume of alkali used is needed for the acid present as catalyst and the acid produced by hydrolysis.

The volume of alkali used for total change from  $t_0$  to  $t_\infty$  gives the initial concentration of ester.

Thus,

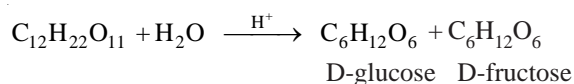
$$\begin{aligned}
 a &= 47.15 - 24.36 = 22.79 \text{ ml} \\
 (a-x) \text{ after } 4500 \text{ sec} &= 47.15 - 29.32 = 17.83 \text{ ml} \\
 (a-x) \text{ after } 7140 \text{ sec} &= 47.15 - 31.72 = 15.43 \text{ ml}
 \end{aligned}$$

Substituting values in the rate equation above, we have

$$\begin{aligned}
 k &= \frac{2.303}{4500} \log \frac{22.79}{17.83} = 0.00005455 \\
 k &= \frac{2.303}{7140} \log \frac{22.79}{15.43} = 0.0000546
 \end{aligned}$$

Since the values of  $k$  in the two experiments are fairly constant, the reaction is of the first order.

(4) **Inversion of Cane sugar (sucrose).** The inversion of cane sugar or sucrose catalyzed with dil HCl,



follows the first order kinetics. The progress of the reaction is followed by noting the optical rotation of the reaction mixture with the help of a polarimeter at different time intervals. The optical rotation

goes on changing since D-glucose rotates the plane of polarised light to the right and D-fructose to the left. **The change in rotation is proportional to the amount of sugar decomposed.**

Let the final rotation be  $r_\infty$ , the initial rotation  $r_0$  while the rotation at any time  $t$  is  $r_t$

The initial concentration,  $a$  is  $\propto (r_0 - r_\infty)$ .

The concentration at time  $t$ ,  $(a - x)$  is  $\propto (r_t - r_\infty)$

Substituting in the first order rate equation,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a - x}$$

we have

$$k = \frac{2.303}{t} \log_{10} \frac{(r_0 - r_\infty)}{(r_t - r_\infty)}$$

If the experimental values of  $t$ ,  $(r_0 - r_\infty)$  and  $(r_t - r_\infty)$  are substituted in the above equation, a constant value of  $k$  is obtained.

**SOLVED PROBLEM.** The optical rotation of sucrose in 0.9N HCl at various time intervals is given in the table below.

time (min)	0	7.18	18	27.1	$\infty$
rotation (degree)	+24.09	+21.4	+17.7	+15	-10.74

Show that inversion of sucrose is a first order reaction.

#### SOLUTION

The available data is substituted in the first order rate equation for different time intervals.

$$k = \frac{2.303}{t} \log_{10} \frac{r_0 - r_\infty}{r_t - r_\infty}$$

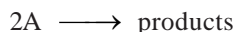
$r_0 - r_\infty = 24.09 - (-10.74) = 34.83$  for all time intervals. Thus, the value of rate constant can be found.

time ( $t$ )	$r_t = r_\infty$	$k = \frac{1}{t} \log \frac{(r_0 - r_\infty)}{(r_t - r_\infty)}$
7.18	32.14	$k = \frac{1}{7.18} \log \frac{34.83}{32.14} = 0.0047$
18	28.44	$k = \frac{1}{18} \log \frac{34.83}{28.44} = 0.0048$
27.1	25.74	$k = \frac{1}{27.1} \log \frac{34.83}{25.74} = 0.0048$

Since the value of  $k$  comes out to be constant, the inversion of sucrose is a **first order reaction**.

## SECOND ORDER REACTIONS

Let us take a second order reaction of the type



Suppose the initial concentration of A is  $a$  moles litre<sup>-1</sup>. If after time  $t$ ,  $x$  moles of A have reacted, the concentration of A is  $(a - x)$ . We know that for such a second order reaction, rate of reaction is proportional to the square of the concentration of the reactant. Thus,

$$\frac{dx}{dt} = k(a - x)^2 \quad \dots(1)$$

where  $k$  is the rate constant, Rearranging equation (1), we have

$$\frac{dx}{(a-x)^2} = k dt \quad \dots(2)$$

On integration, it gives

$$\frac{1}{a-x} = kt + I \quad \dots(3)$$

where  $I$  is integration constant.  $I$  can be evaluated by putting  $x = 0$  and  $t = 0$ . Thus,

$$I = \frac{1}{a} \quad \dots(4)$$

Substituting for  $I$  in equation (3)

$$\frac{1}{a-x} = kt + \frac{1}{a}$$

$$kt = \frac{1}{a-x} - \frac{1}{a}$$

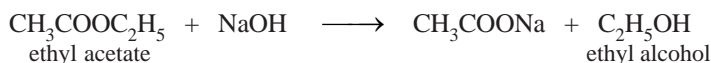
Thus

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

This is the integrated rate equation for a second order reaction.

#### Examples of Second order Reaction

**Hydrolysis of an Ester by NaOH.** This is typical second order reaction.



The reaction is carried in a vessel at a constant temperature by taking equimolar amounts of ethyl acetate and NaOH. Measured volumes of the reaction mixture (say, 25 ml) are withdrawn at various times and titrated against a standard acid. The volume of the acid used is a measure of the concentration of NaOH or ester. Thus the volume of the acid used when  $t = 0$ , gives the initial concentration ( $a$ ) of the reactants. The volume of acid consumed at any other time  $t$  gives  $(a - x)$ . The value of  $x$  can be calculated. The rate constant  $k$  can be determined by substituting values in the second order integrated rate equation.

**SOLVED PROBLEM.** Hydrolysis of ethyl acetate by NaOH using equal concentration of the reactants, was studied by titrating 25ml of the reaction mixture at different time intervals against standard acid. From the data given below, establish that this is a second order reaction.

$t$ (mts)	0	5	15	25
ml acid used	16.00	10.24	6.13	4.32

#### SOLUTION

The second order integrated rate equation is

$$k = \frac{1}{at} \cdot \frac{x}{a(a-x)} \quad \dots(1)$$

The volume of acid used at any time is a measure of concentration of the unreacted substances at that time.

Therefore,

$$a, \text{ initial concentration} = 16.00$$

$$\text{after 5 mts } (a-x) = 10.24 \quad \text{and} \quad x = 5.76$$

after 15 mts  $(a - x) = 6.13$  and  $x = 9.85$   
 after 25 mts  $(a - x) = 4.32$  and  $x = 11.68$

Substituting values in the rate equation (1), we have

$$k = \frac{1}{16 \times 5} \cdot \frac{5.76}{10.24} = 0.0070$$

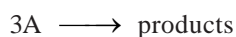
$$k = \frac{1}{16 \times 15} \cdot \frac{9.85}{6.13} = 0.0067$$

$$k = \frac{1}{16 \times 25} \cdot \frac{11.68}{4.32} = 0.00675$$

The values of  $k$  being fairly constant, this reaction is of the second order.

### THIRD ORDER REACTIONS

Let us consider a simple third order reaction of the type



Let the initial concentration of A be  $a$  moles litre<sup>-1</sup> and after time  $t$ ,  $x$ , moles have reacted. Therefore, the concentration of A becomes  $(a - x)$ . The rate law may be written as :

$$\frac{dx}{dt} = k(a - x)^3 \quad \dots(1)$$

Rearranging equation (1), we have

$$\frac{dx}{(a - x)^3} = k dt \quad \dots(2)$$

On integration, it gives

$$\frac{1}{2(a - x)^2} = kt + I \quad \dots(3)$$

where  $I$  is the integration constant.  $I$  can be evaluated by putting  $x = 0$  and  $t = 0$ . Thus,

$$I = \frac{1}{2a^2}$$

By substituting the value of  $I$  in (3), we can write

$$kt = \frac{1}{2(a - x)^2} - \frac{1}{2a^2}$$

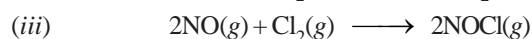
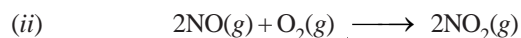
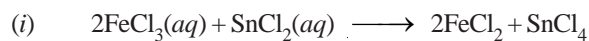
Therefore,

$$k = \frac{1}{t} \cdot \frac{x(2a - x)}{2a^2(a - x)^2}$$

This is the integrated rate equation for a third order reaction.

### Examples of Third order Reactions

There are not many reactions showing third order kinetics. A few of the known examples are :



### UNITS OF RATE CONSTANT

The units of rate constant for different orders of reactions are different.

**Units of Zero order Rate constant**

For a zero order reaction, the rate constant  $k$  is given by the expression

$$k = \frac{d[A]}{dt} = \frac{\text{mol}}{\text{litre}} \times \frac{1}{\text{time}}$$

Thus the units of  $k$  are

$$\text{mol l}^{-1} \text{time}^{-1}$$

Time may be given in seconds, minutes, days or years.

**Units of First order Rate constant**

The rate constant of a first order reaction is given by

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$$

Thus the rate constant for the first order reaction is independent of the concentration. It has the unit

$$\text{time}^{-1}$$

**Units of Second order Rate constant**

The rate constant for a second order reaction is expressed as

$$\begin{aligned} k &= \frac{1}{t} \times \frac{x}{[A]_0([A]_0 - x)} \\ \text{or} \quad &= \frac{\text{concentration}}{\text{concentration} \times \text{concentration}} \times \frac{1}{\text{time}} \\ &= \frac{1}{\text{concentration}} \times \frac{1}{\text{time}} \\ &= \frac{1}{\text{mole/litre}} \times \frac{1}{\text{time}} \\ &= \text{mol}^{-1} \text{l time}^{-1} \end{aligned}$$

Thus the units for  $k$  for a second order reactions are

$$\text{mol}^{-1} \text{l time}^{-1}$$

**Units of Third order Rate constant**

The rate constant for a third order reaction is

$$\begin{aligned} k &= \frac{1}{t} \cdot \frac{x(2a - x)}{2a^2(a - x)^2} \\ \text{or} \quad &= \frac{\text{concentration} \times \text{concentration}}{(\text{concentration})^2 \times (\text{concentration})^2} \times \frac{1}{\text{time}} \\ &= \frac{1}{(\text{concentration})^2} \times \frac{1}{\text{time}} \\ &= \frac{1}{(\text{mol/litre})^2} \times \frac{1}{\text{time}} \end{aligned}$$

Thus the units of  $k$  for third order reaction are

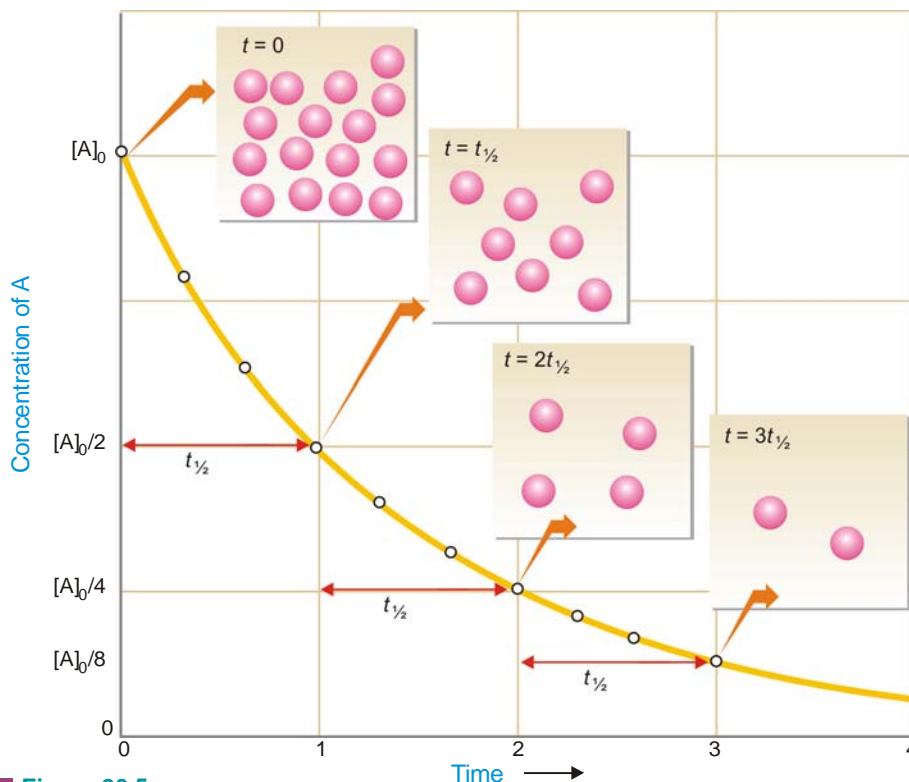
$$\text{mol}^{-2} \text{l}^2 \text{time}^{-1}$$

**HALF-LIFE OF A REACTION**

Reaction rates can also be expressed in terms of **half-life** or **half-life period**. It is defined as : **the time required for the concentration of a reactant to decrease to half its initial value.**



In other words, half-life is the time required for one-half of the reaction to be completed. It is represented by the symbol  $t_{1/2}$  or  $t_{0.5}$ .



■ **Figure 20.5** First-order half-life. Concentration of a reactant A as a function of time for a first-order reaction. The concentration falls from its initial value,  $[A]_0$ , to  $[A]_0/2$  after one half-life, to  $[A]_0/4$  after a second half-life, to  $[A]_0/8$  after a third half-life, and so on. For a first-order reaction, each half-life represents an equal amount of time.

#### Calculation of Half-life of a First order Reaction

The integrated rate equation (4) for a first order reaction can be stated as :

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

where  $[A]_0$  is initial concentration and  $[A]$  is concentration at any time  $t$ . Half-life,  $t_{1/2}$ , is time when initial concentration reduces to  $\frac{1}{2}$  i.e.,

$$[A] = \frac{1}{2}[A]_0$$

Substituting values in the integrated rate equation, we have

$$k = \frac{2.303}{t_{1/2}} \log \frac{[A]_0}{1/2[A]_0} = \frac{2.303}{t_{1/2}} \log 2$$

$$\text{or } t_{1/2} = \frac{2.303}{k} \log 2 = \frac{2.303}{k} \times 0.3010$$

$$\text{or } t_{1/2} = \frac{0.693}{k}$$

It is clear from this relation that :

- (1) half-life for a first order reaction is **independent of the initial concentration**.
- (2) it is **inversely proportional to  $k$** , the rate-constant.

### Calculation of Time for Completing any Fraction of the Reaction

As for half-change, we can calculate the time required for completion of any fraction of the reaction. For illustration, let us calculate the time in which two-third of the reaction is completed. First order integrated rate equation is

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

Here, the initial concentration has  $\frac{2}{3}$  reacted reducing it to  $\frac{1}{3}$ . Thus,

$$[A] = \frac{1}{3}[A]_0$$

Substituting values in the rate equation

$$\begin{aligned} t_{3/4} &= \frac{2.303}{k} \log \frac{[A]_0}{1/3[A]_0} = \frac{2.303}{k} \log 3 \\ &= \frac{2.303}{k} \times 0.4771 \end{aligned}$$

**SOLVED PROBLEM 1.** Compound A decomposes to form B and C the reaction is first order. At 25°C the rate constant for the reaction is 0.450 s<sup>-1</sup>. What is the half-life of A at 25°C ?

#### SOLUTION

We know that for a first order reaction, half-life  $t_{1/2}$ , is given by the expression

$$t_{1/2} = \frac{0.693}{k}$$

where  $k$  = rate constant

Substituting the value of  $k = 0.450 \text{ s}^{-1}$ , we have

$$t_{1/2} = \frac{0.693}{0.450 \text{ s}^{-1}} = \mathbf{1.54 \text{ s}}$$

Thus half-life of the reaction  $A \rightarrow B + C$  is 1.54 seconds.

**SOLVED PROBLEM 2.** The half-life of a substance in a first order reaction is 15 minutes. Calculate the rate constant.

#### SOLUTION

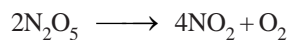
For a first order reaction

$$t_{1/2} = \frac{0.693}{k}$$

Putting  $t_{1/2} = 15 \text{ min}$  in the expression and solving for  $k$ , we have

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{15 \text{ min}} = \mathbf{4.62 \times 10^{-2} \text{ min}^{-1}}$$

**SOLVED PROBLEM 3.** For the reaction



the rate is directly proportional to  $[\text{N}_2\text{O}_5]$ . At  $45^\circ\text{C}$ , 90% of the  $\text{N}_2\text{O}_5$  reacts in 3600 seconds. Find the value of the rate constant  $k$ .

**SOLUTION**

Since rate is  $\propto [\text{N}_2\text{O}_5]$  it is first order reaction. The integrated rate equation is

$$k = \frac{2.303}{t} \log \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]}$$

When 90% of  $\text{N}_2\text{O}_5$  has reacted, the initial concentration is reduced to  $\frac{1}{10}$ . That is,

$$[\text{N}_2\text{O}_5] = \frac{1}{10}[\text{N}_2\text{O}_5]_0$$

Substituting values in the rate equation,

$$\begin{aligned} k &= \frac{2.303}{3600} \log \frac{[\text{N}_2\text{O}_5]_0}{\frac{1}{10}[\text{N}_2\text{O}_5]_0} \\ &= \frac{2.303}{3600} \log 10 = \frac{2.303}{3600} \times 1 \end{aligned}$$

Thus

$$k = \frac{2.303}{3600} = 6.40 \times 10^{-4} \text{ s}^{-1}$$

**SOLVED PROBLEM 4.** The rate law for the decomposition of  $\text{N}_2\text{O}_5 (l)$  is : rate =  $k [\text{N}_2\text{O}_5]$  where  $k = 6.22 \times 10^{-4} \text{ sec}^{-1}$ . Calculate half-life of  $\text{N}_2\text{O}_5 (l)$  and the number of seconds it will take for an initial concentration of  $\text{N}_2\text{O}_5 (l)$  of 0.100 M to drop to 0.0100 M.

**SOLUTION**

**Calculation of half-life**

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.22 \times 10^{-4} \text{ sec}^{-1}} = 1.11 \times 10^3 \text{ sec}$$

**Calculation of time in seconds for drop of  $[\text{N}_2\text{O}_5]$  from 0.100 M to 0.0100 M**

From first order integrated rate equation,

$$t = \frac{2.303}{k} \log \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t}$$

or

$$t = \frac{2.303}{k} \log \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t}$$

Substituting values

$$\begin{aligned} t &= \frac{2.303}{6.22 \times 10^{-4}} \log \frac{0.100}{0.0100} \\ &= \frac{2.303}{6.22 \times 10^{-4}} \times 1 \\ &= 3.70 \times 10^3 \text{ sec} \end{aligned}$$

**SOLVED PROBLEM 5.** For a certain first order reaction  $t_{0.5}$  is 100 sec. How long will it take for the reaction to be completed 75% ?

**SOLUTION**

**Calculation of  $k$**

For a first order reaction

$$t_{1/2} = \frac{0.693}{k}$$

or 
$$100 = \frac{0.693}{k}$$

$\therefore k = \frac{0.693}{100} = 0.00693 \text{ sec}^{-1}$

**Calculation of time for 75% completion of reaction**

The integrated rate equation for a first order reaction is

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

or 
$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

When  $\frac{3}{4}$  initial concentration has reacted, it is reduced to  $\frac{1}{4}$

Substituting values in the rate equation

$$\begin{aligned} t_{3/4} &= \frac{2.303}{0.00693} \log \frac{[A]_0}{\frac{1}{4}[A]_0} \\ &= \frac{2.303}{0.00693} \log 4 = \mathbf{200 \text{ sec}} \end{aligned}$$

**SOLVED PROBLEM 6.** A first order reaction is one-fifth completed in 40 minutes. Calculate the time required for its 100% completion.

**SOLUTION**

**Calculation of  $k$**

For a first order reaction

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

After 40 mts, the initial concentration is reduced to  $\frac{4}{5}$  That is,

$$[A] = \frac{4}{5} [A]_0$$

Substituting values in the equation above

$$k = \frac{2.303}{40} \log \frac{[A]_0}{\frac{4}{5}[A]_0}$$

or 
$$k = \frac{2.303}{40} \log 5 - \log 4 = 0.00558 \text{ mt}^{-1}$$

**Calculation of time required for 100% completion**

We know that for first order reaction

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

If reaction is 100% complete in, say,  $t_1$  time, we have,  $[A] = 0$ . Thus,

$$t_1 = \frac{2.303}{0.00558} \log \frac{[A]_0}{0} = \infty$$

**SOLVED PROBLEM 7.** 50% of a first order reaction is complete in 23 minutes. Calculate the time required to complete 90% of the reaction.

**SOLUTION****Calculation of  $k$** 

$$t_{0.5} = \frac{0.693}{k}$$

or

$$k = \frac{0.693}{t_{0.5}} = \frac{0.693}{23} = 0.0301304 \text{ min}^{-1}$$

**Calculation of time for 90% completion of the reaction**

For first order reaction, integrated rate equation is

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \quad \dots(1)$$

or

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]} \quad \dots(2)$$

When 90% of the initial concentration has reacted, 10% of it is left. That is,

$$[A] = \frac{1}{10} [A]_0$$

Substituting values in equation (2)

$$\begin{aligned} t &= \frac{2.303}{0.0301304} \log \frac{[A]_0}{\frac{1}{10}[A]_0} = \frac{2.303}{0.0301304} \log 10 \\ &= \frac{2.303}{0.0301304} = \mathbf{76.4 \text{ min}} \end{aligned}$$

**Half-life for a Second order Reaction**

For the simple second order reaction  $2A \rightarrow \text{Products}$ , the integrated rate equation is

$$kt = \frac{1}{[A]} - \frac{1}{[A]_0}$$

where  $[A]_0$  is the initial concentration and  $[A]$  is the concentration when time  $t$  has elapsed.

When one-half life has elapsed,

$$[A] = \frac{1}{2}[A]_0$$

and we have

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

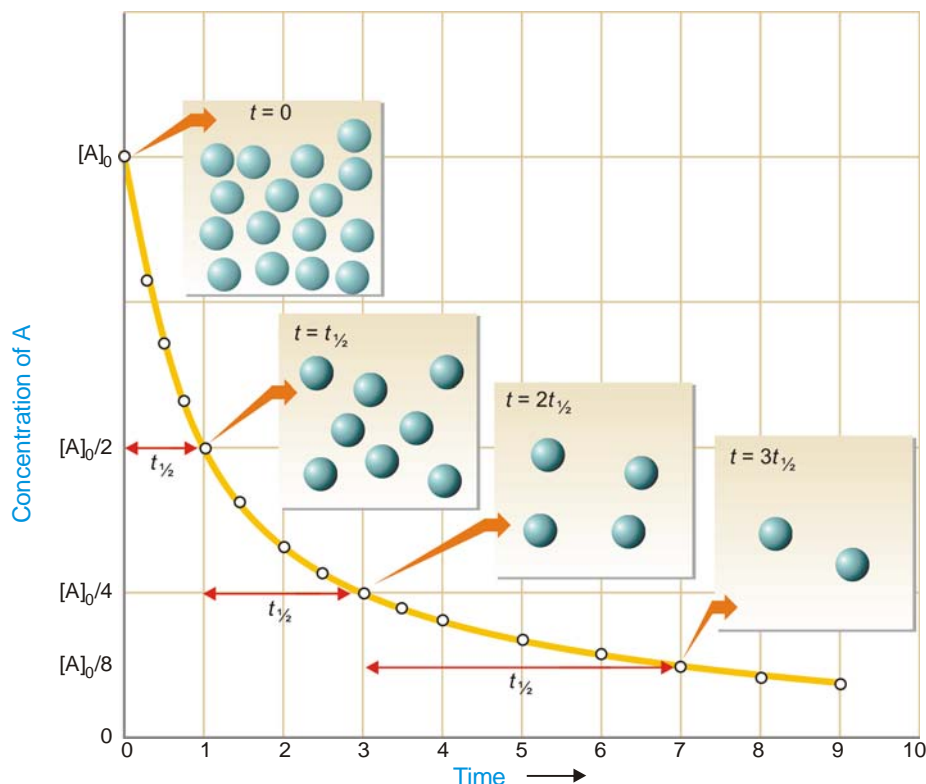
or

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

Solving for  $t_{1/2}$  we find that

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

As in case of a first order reaction, half-life for a second order reaction is inversely proportional to rate constant  $k$ . While half-life of a first order reaction is independent of initial concentration, **half-life of a second order reaction depends on initial concentration**. This fact can be used to distinguish between a first order and a second order reaction.



■ Figure 20.6

**Second-order half-life.** Concentration of a reactant A as a function of time for a second-order reaction. Note that each half-life is twice as long as the preceding one because  $t_{1/2} = 1/k[A]_0$  and the concentration of A at the beginning of each successive half-life is smaller by a factor of 2.

### HOW TO DETERMINE THE ORDER OF A REACTION

There are at least four different methods to determine the order of a reaction.

#### (1) Using integrated rate equations

The reaction under study is performed by taking different initial concentrations of the reactant ( $a$ ) and noting the concentration ( $a - x$ ) after regular time intervals ( $t$ ). The experimental values of  $a$ ,

$(a - x)$  and  $t$  are then substituted into the integrated rate equations for the first, second and third order reactions. **The rate equation which yields a constant value of  $k$  corresponds to the correct order of the reaction.** This method of ascertaining the order of a reaction is essentially a method of hit-and-trial but was the first to be employed. It is still used extensively to find the order of simple reactions.

## (2) Graphical method

For reactions of the type  $A \rightarrow$  products, we can determine the reaction order by seeing whether a graph of the data fits one of the integrated rate equations.

### In case of First order

We have already derived the integrated rate equation for first order as

$$\ln \frac{a}{a-x} = kt$$

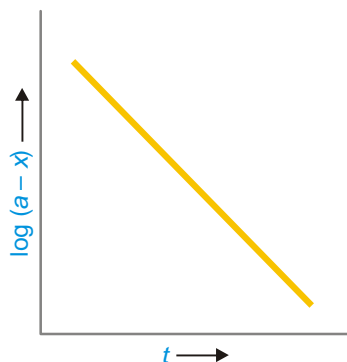
Simplifying, it becomes

$$\begin{array}{ccccccc} \ln(a-x) & = & -kt & + & \ln a \\ \uparrow & & \uparrow & & \uparrow \\ y & = & mx & + & b \end{array}$$

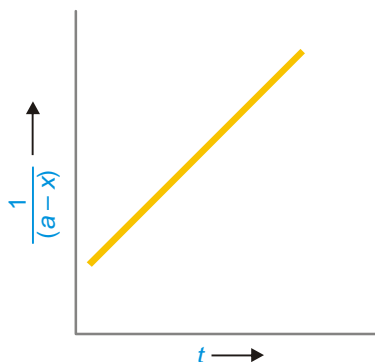
Thus the two variables in the first order rate equation are :

$$\ln \frac{a}{a-x} \text{ and } t$$

Hence, if  $\ln \frac{a}{a-x}$  is plotted against  $t$  and straight line results (Fig. 20.7), the corresponding reaction is of the first order. However, if a curve is obtained, the reaction is not first order.



■ **Figure 20.7**  
Plot of  $\log(a-x)$  against  $t$  for a first order reaction.



■ **Figure 20.8**  
Plot of  $1/(a-x)$  against  $t$  for a second order reaction.

### In case of Second order

We have already shown that second order rate equation can be written as

$$\begin{array}{ccccccc} \frac{1}{a-x} & = & kt & + & \frac{1}{a} \\ \uparrow & & \uparrow & & \uparrow \\ y & = & mx & + & b \end{array}$$

This is the equation of a straight line,  $y = mx + b$ . Here the two variables are

$$\frac{1}{a-x} \text{ and } t$$

Thus when  $\frac{1}{a-x}$  is plotted against  $t$  and we get a straight line (Fig. 20.8), the reaction is second order. In case a curve is obtained, the reaction is not second order.

### (3) Using half-life period

Two separate experiments are performed by taking different initial concentrations of a reactant. The progress of the reaction in each case is recorded by analysis. When the initial concentration is reduced to one-half, the time is noted. Let the initial concentrations in the two experiments be  $[A_1]$  and  $[A_2]$ , while times for completion of half change are  $t_1$  and  $t_2$  respectively.

**Calculation of order of reaction.** We know that half-life period for a first order reaction is independent of the initial concentration,  $[A]$ . We also know :

$$\text{half-life} \propto \frac{1}{[A]} \quad \text{for 2nd order reaction}$$

$$\text{half-life} \propto \frac{1}{[A]^2} \quad \text{for 3rd order reaction}$$

$$\text{half-life} \propto \frac{1}{[A]^{n-1}} \quad \text{for } n\text{th order reaction}$$

Substituting values of initial concentrations and half-life periods from the two experiments, we have

$$t_1 \propto \frac{1}{[A_1]^{n-1}} \quad t_2 \propto \frac{1}{[A_2]^{n-1}}$$

$$\text{and} \quad \frac{t_2}{t_1} = \left[ \frac{A_1}{A_2} \right]^{n-1}$$

$$(n-1) \log \left[ \frac{A_2}{A_1} \right] = \log \left[ \frac{t_1}{t_2} \right]$$

Solving for  $n$ , the order of reaction

$$n = 1 + \frac{\log [t_1/t_2]}{\log [A_2/A_1]}$$

**SOLVED PROBLEM.** In the reduction of nitric oxide, 50% of reaction was completed in 108 seconds when initial pressure was 336 mm Hg and in 147 seconds initial pressure was 288 mm Hg. Find the order of the reaction.

#### SOLUTION

We know that

$$\frac{t_2}{t_1} = \left[ \frac{A_1}{A_2} \right]^{n-1} \quad \dots(1)$$

where  $t_1$  and  $t_2$  are half-life periods and  $[A_1]$  and  $[A_2]$  are the corresponding initial concentrations, while  $n$  is the order of the reaction.

Taking logs of the expression (1), we have

$$n = 1 + \frac{\log [t_2/t_1]}{\log [A_1/A_2]} \quad \dots(2)$$

Substituting values in expression (2),

$$n = 1 + \frac{\log 108/147}{\log 288/336}$$



$$= 1 + \frac{0.1339}{0.0669} = 1 + 2 = 3$$

Therefore, the reaction is of the **third order**.

#### (4) The Differential method

This method was suggested by van't Hoff and, therefore, it is also called **van't Hoff's differential method**. According to it, the rate of a reaction of the  $n$ th order is proportional to the  $n$ th power of concentration.

$$-\frac{dC}{dt} = k C^n$$

where  $C$  = concentration at any instant. In two experiments performed with different initial concentrations, we can write

$$-\frac{dC_1}{dt} = k C_1^n \quad \dots(1)$$

$$-\frac{dC_2}{dt} = k C_2^n \quad \dots(2)$$

Taking logs of the expression (1) and (2)

$$\log\left(-\frac{dC_1}{dt}\right) = \log k + n \log C_1 \quad \dots(3)$$

$$\log\left(-\frac{dC_2}{dt}\right) = \log k + n \log C_2 \quad \dots(4)$$

On subtracting (4) from (3), we get

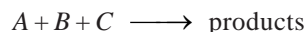
$$n = \frac{\log\left(-\frac{dC_1}{dt}\right) - \log\left(-\frac{dC_2}{dt}\right)}{\log C_1 - \log C_2} \quad \dots(5)$$

To find  $n$ ,  $\left(-\frac{dC}{dt}\right)$  in the two experiments is determined by plotting concentrations against time ( $t$ ).

The slope,  $\left(-\frac{dC}{dt}\right)$  at a given time interval is measured by drawing tangents. Using the values of slopes  $\left(-\frac{dC_1}{dt}\right)$  and  $\left(-\frac{dC_2}{dt}\right)$  in the equation (5),  $n$  can be calculated.

#### (5) 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 rate of reaction is concerned. Suppose the reaction under consideration is :



The order of the reaction with respect to  $A$ ,  $B$  and  $C$  is determined. For the determination of the order of reaction with respect to  $A$ ,  $B$  and  $C$  are taken in a large excess so that their concentrations are not affected during the reaction. The order of the reaction is then determined by using any of the methods described earlier. Likewise, the order of the reaction with respect to  $B$  and  $C$  is determined. If  $n_A$ ,  $n_B$  and  $n_C$  are the orders of the reaction with respect to  $A$ ,  $B$  and  $C$  respectively, the order of the reaction  $n$  is given by the expression.

$$n = n_A + n_B + n_C$$

### COLLISION THEORY OF REACTION RATES

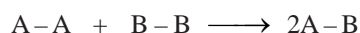
According to this theory, a **chemical reaction takes place only by collisions between the reacting molecules**. But not all collisions are effective. Only a small fraction of the collisions produce a reaction. The two main conditions for a collision between the reacting molecules to be productive are :

- (1) The colliding molecules must possess sufficient kinetic energy to cause a reaction.
- (2) The reacting molecules must collide with proper orientation.

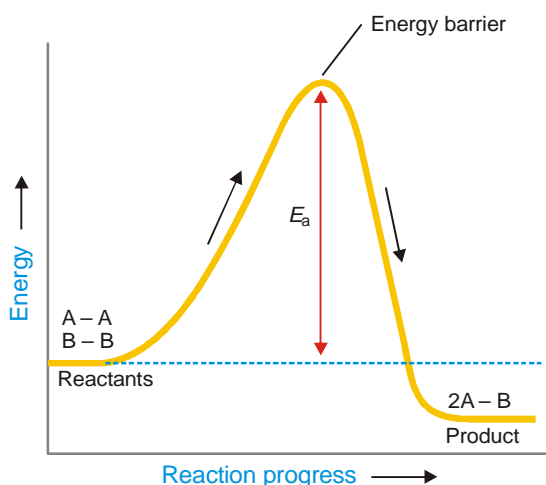
Now let us have a closer look at these two postulates of the collision theory.

#### (1) The molecules must collide with sufficient kinetic energy

Let us consider a reaction



A chemical reaction occurs by breaking bonds between the atoms of the reacting molecules and forming new bonds in the product molecules. The energy for the breaking of bonds comes from the kinetic energy possessed by the reacting molecules before the collision. Fig. 20.9 shows the energy of molecules  $\text{A}_2$  and  $\text{B}_2$  as the reaction  $\text{A}_2 + \text{B}_2 \rightarrow 2\text{AB}$  progresses.



■ **Figure 20.9**

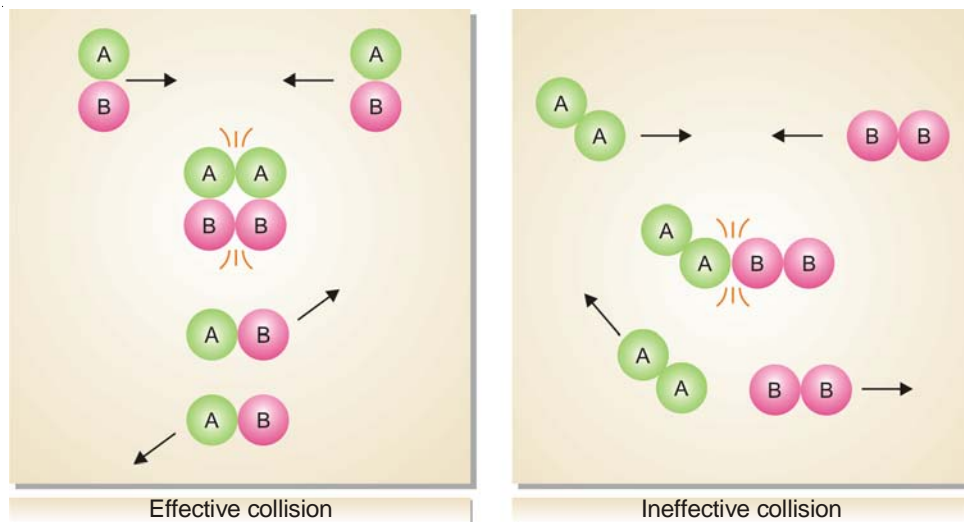
**The energy of the colliding molecules as the reaction  $\text{A}_2 + \text{B}_2 \rightarrow 2\text{AB}$  proceeds. The activation energy  $E_a$  provides the energy barrier.**

The Fig. 20.9 also shows the **activation energy,  $E_a$** , that is the minimum energy necessary to cause a reaction between the colliding molecules. Only the molecules that collide with a kinetic energy greater than  $E_a$ , are able to get over the barrier and react. The molecules colliding with kinetic energies less than  $E_a$  fail to surmount the *barrier*. The collisions between them are unproductive and the molecules simply bounce off one another.

#### (2) The molecules must collide with correct orientation

The reactant molecules must collide with favourable orientation (relative position). **The correct orientation is that which ensure direct contact between the atoms involved in the breaking and forming of bonds.** (Fig. 20.10)

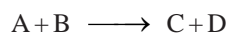
From the above discussion it is clear that : **Only the molecules colliding with kinetic energy greater than  $E_a$  and with correct orientation can cause reaction.**



■ **Figure 20.10**  
Orientations of reacting molecules  $A_2$  and  $B_2$  which lead to an effective and ineffective collision.

### Collision Theory and Reaction Rate Expression

Taking into account the two postulates of the collision theory, the reaction rate for the elementary process.



is given by the expression

$$\text{rate} = f \times p \times z$$

where  $f$  = fraction of molecules which possess sufficient energy to react;  $p$  = probable fraction of collisions with effective orientations, and  $z$  = collision frequency.

### EFFECT OF INCREASE OF TEMPERATURE ON REACTION RATE

It has been found that generally an increase of temperature increases the rate of reaction. As a rule, an increase of temperature by  $10^\circ\text{C}$  doubles the reaction rate. Thus the ratio of rate constants of a reaction at two different temperatures differing by 10 degree is known as **Temperature Coefficient**.

$$\begin{aligned} \text{i.e., Temperature Coefficient} &= \frac{k_{35^\circ}}{k_{25^\circ}} = \frac{k_{308}}{k_{298}} \\ &= 2 \text{ to } 3 \end{aligned}$$

It has been found that **generally an increase of temperature increases the rate of reaction**. As a rule, an increase of temperature by  $10^\circ\text{C}$  doubles the reaction rate.

### Temperature Dependence of Reaction Rate and Arrhenius Equation

We know that the kinetic energy of a gas is directly proportional to its temperature. Thus as the temperature of a system is increased, more and more molecules will acquire necessary energy greater than  $E_a$  to cause productive collisions. This increases the rate of the reaction.

In 1889, Arrhenius suggested a simple relationship between the rate constant,  $k$ , for a reaction and the temperature of the system.

$$k = A e^{-E_a/RT} \quad \dots(1)$$

This is called the **Arrhenius equation** in which  $A$  is an experimentally determined quantity,  $E_a$  is

the activation energy,  $R$  is the gas constant, and  $T$  is Kelvin temperature.

Taking natural logs of each side of the Arrhenius equation, it can be put in a more useful form :

$$\ln k = -\frac{E_a}{RT} + \ln A \quad \dots(2)$$

$$\log k = \frac{-E_a}{2.303 RT} + \log A \quad \dots(3)$$

If  $k_1$  and  $k_2$  are the values of rate constants at temperatures  $T_1$  and  $T_2$  respectively, we can derive

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right] \quad \dots(4)$$

Arrhenius equation is valuable because it can be used to calculate the activation energy,  $E_a$  if the experimental value of the rate constant,  $k$ , is known.

### Calculation of $E_a$ Using Arrhenius Equation

In slightly rearranged form Arrhenius equation (2) can be written as

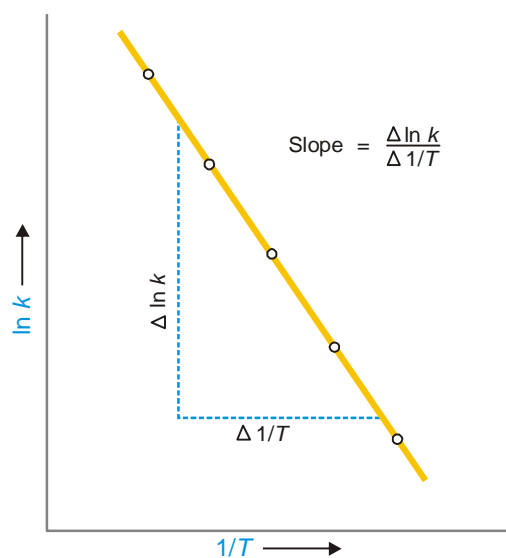
$$\ln k = -\frac{E_a}{R} \left( \frac{1}{T} \right) + \ln A \quad \dots(3)$$

$\uparrow \qquad \qquad \uparrow \qquad \qquad \uparrow$   
 $y = mx + b$

You can see that the equation (3) is that of a straight line,  $y = mx + b$ . The two variables in this equation are  $\ln k$  and  $1/T$ .

Thus if we plot the natural logarithm of  $k$  against  $1/T$ , we get a straight line (Fig. 20.11). From the slope of the line, we can calculate the value of  $E_a$ .

$$\text{Slope} = -\frac{E_a}{R}$$



■ **Figure 20.11**

The plot of  $\ln k$  versus  $1/T$  gives a straight line. The slope of line  $\Delta \ln k / \Delta 1/T$  gives  $E_a$  using the expression given above.

**SOLVED PROBLEM.** The values of the rate constant ( $k$ ) for the reaction  $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$  were determined at several temperatures. A plot of  $\ln k$  versus  $1/T$  gave a straight line of which the slope was found to be  $-1.2 \times 10^4 \text{ K}$ . What is the activation energy of the reaction ?

**SOLUTION**

We know that

$$\text{Slope} = -\frac{E_a}{R}$$

$$E_a = -R \times (\text{slope})$$

Substituting the values, we have

$$E_a = (-8.314 \text{ JK}^{-1} \text{ mol}^{-1})(-1.2 \times 10^4 \text{ K})$$

$$= 1.0 \times 10^5 \text{ J mol}^{-1}$$

Thus the activation energy for the reaction is  $1.0 \times 10^5 \text{ J mol}^{-1}$

**Calculation of  $E_a$  from the Values of  $k$  at Two Temperatures**

The rate constant,  $k$ , is measured at two temperatures.  $E_a$ , is then calculated using the formula that can be derived as follows from equation (3) above.

At temperature  $T_1$ , where the rate constant is  $k_1$ ,

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad \dots(1)$$

At temperature  $T_2$ , where the rate constant is  $k_2$ ,

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A \quad \dots(2)$$

Subtracting the equation (1) from the equation (2), we have

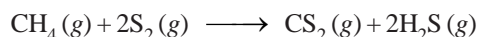
$$\ln k_2 - \ln k_1 = \left( -\frac{E_a}{RT_2} + \ln A \right) - \left( -\frac{E_a}{RT_1} + \ln A \right)$$

$$= -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

or 
$$\ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{or} \quad \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

Thus the values of  $k_1$  and  $k_2$  measured at  $T_1$  and  $T_2$  can be used to find  $E_a$ .

**SOLVED PROBLEM.** The gas-phase reaction between methane ( $\text{CH}_4$ ) and diatomic sulphur ( $\text{S}_2$ ) is given by the equation



At  $550^\circ\text{C}$  the rate constant for this reaction is  $1.1 \text{ l mol}^{-1} \text{ sec}$  and at  $625^\circ\text{C}$  the rate constant is  $6.4 \text{ l mol}^{-1} \text{ sec}$ . Calculate  $E_a$  for this reaction.

**SOLUTION**

Here  $k_1 = 1.1 \text{ litre mol}^{-1} \text{ sec}$      $T_1 = 550 + 273 = 823 \text{ K}$   
 $k_2 = 6.4 \text{ litre mol}^{-1} \text{ sec}$      $T_2 = 625 + 273 = 898 \text{ K}$

Substituting the values in the equation

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

$$\ln\left(\frac{6.4}{1.1}\right) = \frac{E_a}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{823 \text{ K}} - \frac{1}{898 \text{ K}} \right)$$

Solving for  $E_a$ , gives

$$E_a = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln\left(\frac{6.4}{1.1}\right)}{\left(\frac{1}{823 \text{ K}} - \frac{1}{898 \text{ K}}\right)}$$

$$= 1.4 \times 10^5 \text{ J/mol}$$

### SIMULTANEOUS REACTIONS

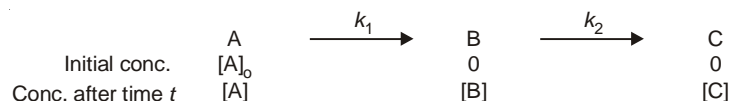
Sometimes there are some side reactions accompanying the main chemical reaction. Such reactions are known as **complex reactions** as these do not take place in a single step. In other words, such complex reactions proceed in a series of steps instead of a single step and the rate of overall reaction is in accordance with the stoichiometric equation for that reaction. Generally, following types of complications occur.

- (1) **Consecutive reactions**
- (2) **Parallel reactions**
- (3) **Reversible or opposing reactions**

These are discussed as follows :

#### (1) Consecutive Reactions

The reactions in which the final product is formed through one or more intermediate steps are called **consecutive reactions**. These are also known as **sequential** reactions. In such reactions the product formed in one of the elementary reactions acts as the reactant for some other elementary reaction. Various step reactions can be written for the overall reaction as shown below :



In the above reaction the product C is formed from the reactant A through intermediate B. In this reaction each stage has its own different rate constants  $k_1$  for the first step and  $k_2$  for the second step. The net or overall rate of reaction depends upon the magnitude of these two rate constants. The initial concentration and concentration after time  $t$  are shown below each species in above reaction under consideration.

It is clear that

$$[A]_0 = [A] + [B] + [C]$$

The differential rate expressions are

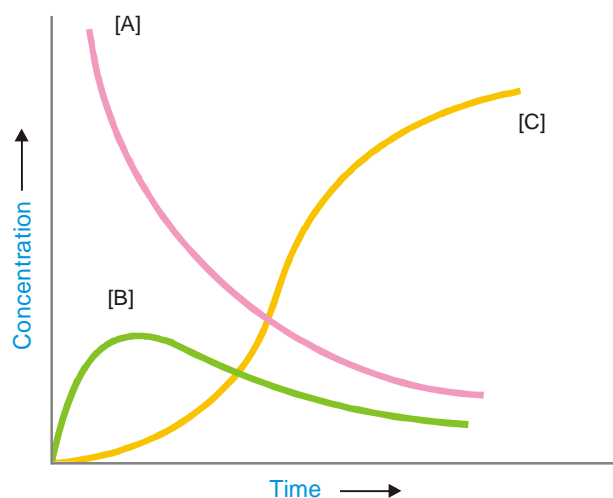
$$-\frac{d[A]}{dT} = k_1 [A]$$

$$\frac{d[B]}{dT} = k_1 [A] - k_2 [B]$$

and

$$\frac{d[C]}{dT} = k_2 [B]$$

During the course of the reaction the concentration of A, B and C vary as shown in the Fig. 20.12

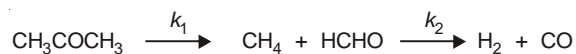


■ **Figure 20.12**  
Variation of concentration of reactants and products in a consecutive reaction.

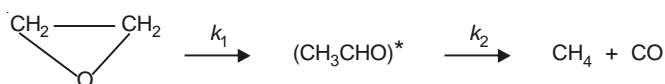
From the Fig 20.12 it is clear that the concentration of A decreases exponentially, the concentration of B first increases and then decreases and that of C increases (from zero) with time and finally attains the value equal to  $[A]_0$  (initial concentration A) when all A has changed into the final product C.

### Examples of First Order Consecutive Reactions

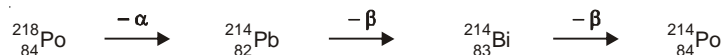
(a) Decomposition of dimethyl ether in gaseous phase



(b) Decomposition of Ethylene oxide

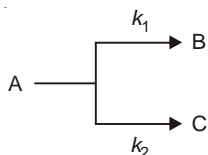


(c) Any radioactive decay of the type



### (2) Parallel or Side Reactions

In these reactions the reacting substance follows two or more paths to give two or more products. The preferential rate of such may be changed by varying the conditions like pressure, temperature or catalyst. The reaction in which the maximum yield of the products is obtained is called the main or major reaction while the other reaction (or reactions) are called side or parallel reactions. For example,



In the above reaction the reactant A gives two products B and C separately in two different reactions with rate constants  $k_1$  and  $k_2$  respectively. If  $k_1 > k_2$  the reaction  $\text{A} \rightarrow \text{B}$  will be the major reaction and  $\text{A} \rightarrow \text{C}$  will be the side or parallel reaction. Let us assume that both these reactions are of first order and concentration of A is  $[A]$  at the time  $t$ . The differential rate expressions are

$$r_1 = \frac{-d[A]}{dT} = k_1[A] \quad \dots(i)$$

and

$$r_2 = \frac{-d[A]}{dT} = k_2[A] \quad \dots(ii)$$

The total rate of disappearance of A is given by

$$\begin{aligned} \frac{-d[A]}{dT} &= r_1 + r_2 = k_1[A] + k_2[A] \\ &= (k_1 + k_2)[A] \\ &= k'[A] \end{aligned} \quad \dots(iii)$$

where  $k'$  is the first order rate constant. It is equal to the sum of the two constants  $k_1$  and  $k_2$  of two side reactions.

Integrating equation (iii), we get

$$\int \frac{-d[A]}{dT} = \int k'[A]$$

applying the limits  $[A]_0$  &  $[A]_t$  and 0 &  $t$ , we have

$$\begin{aligned} \int_{[A]_0}^{[A]_t} \frac{-d[A]}{dt} &= k' \int_0^t dt \\ \ln \frac{[A]_0}{[A]_t} &= k't + (k_1 + k_2)t \end{aligned} \quad \dots(iv)$$

where  $[A]_0$  is the initial concentration of the reactant A and  $[A]_t$  is concentration of A at time  $t$ .

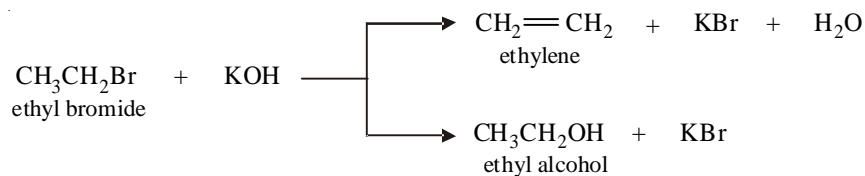
The ratio of the rates of two side reactions is obtained by dividing equations (i) by (ii), we have

$$\frac{r_1}{r_2} = \frac{k_1[A]}{k_2[A]} = \frac{k_1}{k_2} \quad \dots(v)$$

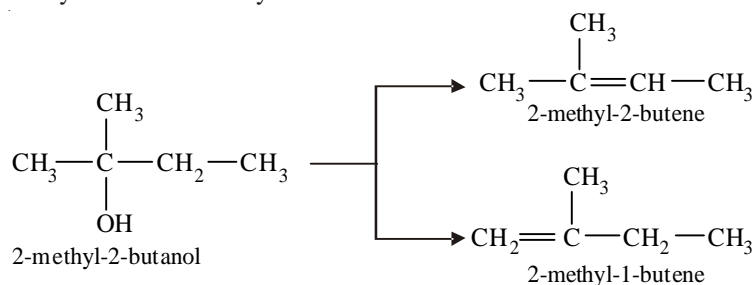
From equations (iv) and (v) we can calculate the individual rate constant  $k_1$  and  $k_2$ .

### Examples of Parallel or Side Reactions

(a) Reaction of ethyl bromide with potassium hydroxide

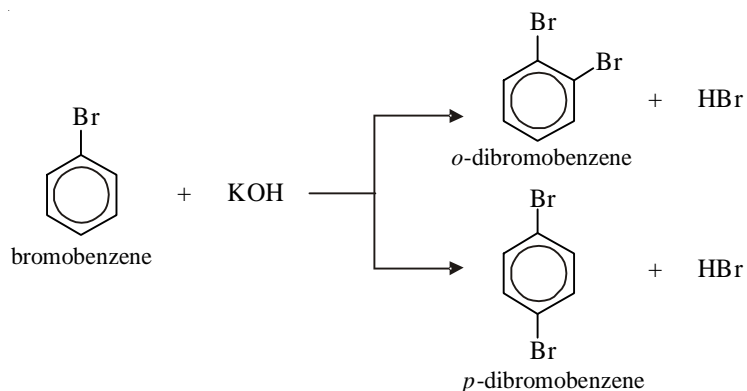


(b) Dehydration of 2-methyl-2-butanol





(c) Bromination of bromobenzene

**(3) Reversible or Opposing Reactions**

In reversible or opposing reactions the products formed also react to give back the reactants. Initially, the rate of forward reaction is very large which decreases with passage of time and the rate of backward or reverse reaction is zero which increases with passage of time. A stage is reached when two rates become equal. This situation is called the chemical equilibrium. It is dynamic in nature *i.e.*, all the species are reacting at the rate at which they are being formed. A reaction of this type may be represented as



where  $k_f$  and  $k_b$  are the rate constants of the forward and backward reactions respectively.

The overall rate of reaction is given by

Rate of Reaction = Rate of forward reaction – Rate of backward reaction

$$\text{i.e.,} \quad -\frac{d[\text{A}]}{dt} = \frac{d[\text{B}]}{dt} = k_f[\text{A}] - k_b[\text{B}] \quad \dots(i)$$

If  $[\text{A}]_0$  is the initial concentration of A and  $x$  moles of it have reacted in time  $t$

$$\text{then} \quad [\text{A}]_t = [\text{A}]_0 - x$$

$$\text{and} \quad [\text{B}] = x$$

Substituting these in equation (i), we get

$$\frac{dx}{dt} = k_f([\text{A}]_0 - x) - k_b x \quad \dots(ii)$$

$$\text{At equilibrium} \quad \frac{dx}{dt} = 0$$

$$\text{Hence} \quad k_f([\text{A}]_0 - x_{\text{eq}}) = k_b x_{\text{eq}} \quad \dots(iii)$$

where  $x_{\text{eq}}$  is the concentration of A that has reacted into B at equilibrium. From equation (iii) we have

$$k_b = k_f \left( \frac{[\text{A}]_0 - x_{\text{eq}}}{x_{\text{eq}}} \right)$$

Substituting the value of  $k_b$  in equation (ii), we get

$$\frac{dx}{dt} = k_f([A]_0 - x) - k_f \left( \frac{[A]_0 - x_{\text{eq}}}{x_{\text{eq}}} \right) x$$

Integrating this equation between the limits  $t = 0, x = 0$  and  $t = t, x = x_{\text{eq}}$ , we have

$$\int_0^x \frac{dx}{x_{\text{eq}} - x} = k_f \frac{[A]_0}{x_{\text{eq}}} \int_0^t dt$$

$$= -\ln(x_{\text{eq}} - x) + \ln x_{\text{eq}} = k_f \frac{[A]_0}{x_{\text{eq}}} t$$

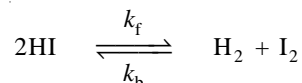
or 
$$\ln \frac{x_{\text{eq}}}{x_{\text{eq}} - x} = k_f \frac{[A]_0}{x_{\text{eq}}} t$$

From this equation we can find the value of  $k_f$  from the quantities  $[A]_0, x_{\text{eq}}$  and  $x$  at time  $t$ . All these quantities can be measured easily. From the value of  $k_f$  the value of  $k_b$  can be calculated by using the relation.

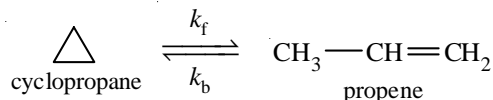
$$k_b = k_f \left( \frac{[A]_0 - x_{\text{eq}}}{x_{\text{eq}}} \right)$$

### Examples of Opposing Reactions

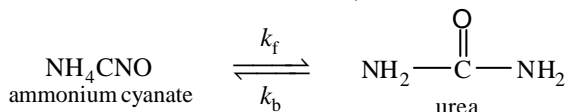
(a) Dissociation of hydrogen iodides



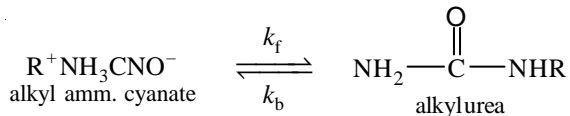
(b) Isomerisation of cyclopropane into propene



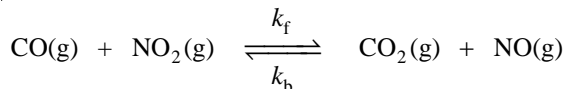
(c) Isomerisation of ammonium cyanate into urea in aqueous solution.



(d) Isomerisation of alkyl ammonium cyanate into substituted urea in aqueous solution



(e) Reaction between gaseous CO and NO<sub>2</sub>



### Limitations of the Collision Theory

The collision theory of reaction rates is logical and correct. However, it has been oversimplified and suffers from the following weaknesses.

- (1) **The theory applies to simple gaseous reactions only.** It is also valid for solutions in which the reacting species exist as simple molecules.

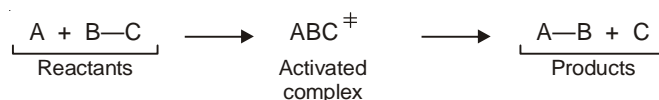
- (2) The values of rate constant calculated from the collision theory expression (Arrhenius equation) are in agreement with the experimental values only for simple bimolecular reactions. **For reactions involving complex molecules, the experimental rate constants are quite different from the calculated values.**
- (3) There is no method for determining the steric effect ( $p$ ) for a reaction whose rate constant has not been determined experimentally.
- (4) In the collision theory it is supposed that only the kinetic energy of the colliding molecules contributes to the energy required for surmounting the energy barrier. There is no reason why the rotational and vibrational energies of molecules should be ignored.
- (5) **The collision theory is silent on the cleavage and formation of bonds involved in the reaction.**

The various drawbacks in the simple collision theory do not appear in the modern transition-state theory.

### TRANSITION STATE THEORY

The **transition state** or **activated complex theory** was developed by Henry Eyring (1935). This theory is also called the **absolute rate theory** because with its help it is possible to get the absolute value of the rate constant. The transition state theory assumes that simply a collision between the reactant molecules does not really cause a reaction. During the collision, **the reactant molecules form a transition state or activated complex which decomposes to give the products.**

Thus,



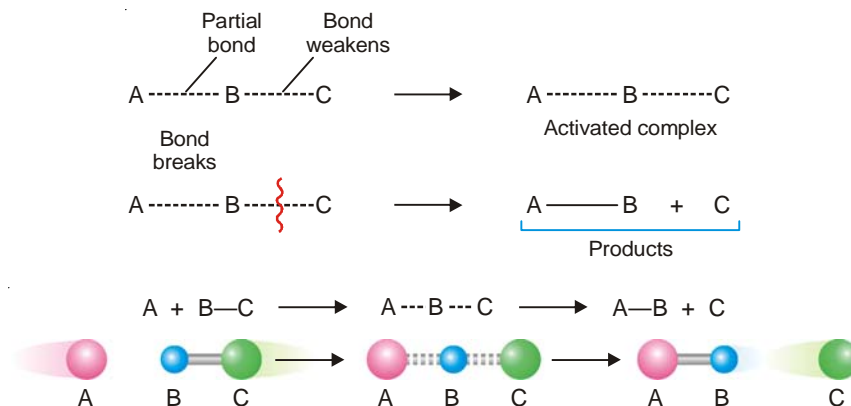
The double dagger superscript ( $\ddagger$ ) is used to identify the activated complex.

The transition state theory may be summarised as follows :

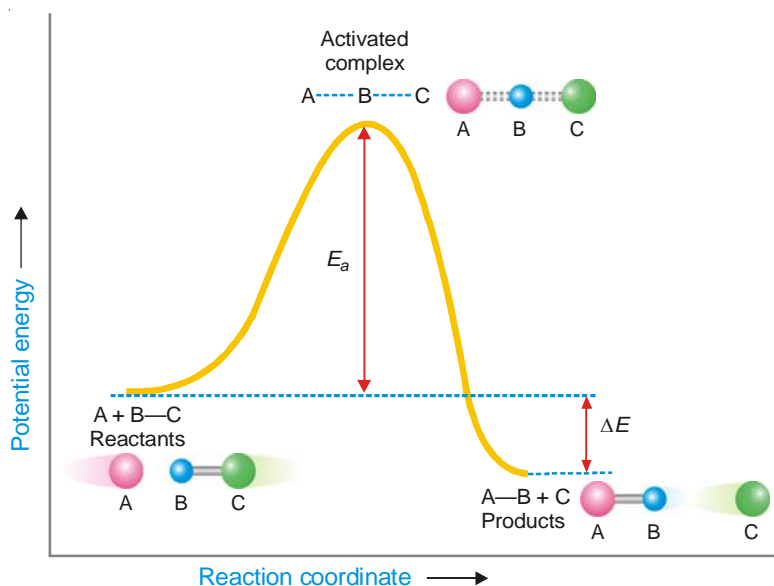
(1) In a collision, the fast approaching reactant molecules (A and BC) slow down due to gradual repulsion between their electron clouds. In the process **the kinetic energy of the two molecules is converted into potential energy.**

(2) As the molecules come close, **the interpenetration of their electron clouds occurs which allows the rearrangement of valence electrons.**

(3) A partial bond is formed between the atoms A and B with corresponding weakening of B – C bond. This leads to formation of an **activated complex** or **transition state**. The activated complex is momentary and decomposes to give the products (A–B + C)



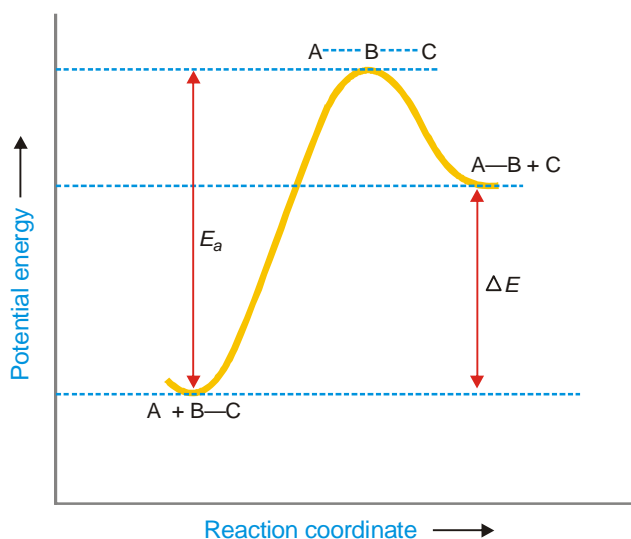
The activated complex theory may be illustrated by the **reaction energy diagram** (Fig. 20.13).



■ **Figure 20.13**  
Change of potential energy during a collision between the reactant molecules for an exothermic reaction.

Here the potential energy of the system undergoing reaction is plotted against the **reaction coordinate** (the progress of the reaction). The difference in the potential energy between the reactants and the activated complex is the **activation energy**,  $E_a$ . The reactants must have this minimum energy to undergo the reaction through the transition state.

As evident from the energy diagram, energy is required by the reactants to reach the transition state. Also, the energy is obtained in passing from the transition state to the products. If the potential energy of the products is less than that of the reactants (Fig. 20.14) the energy obtained in going from the activated complex to products will be more than the activation energy ( $E_a$ ). Thus such a reaction will be **exothermic**.

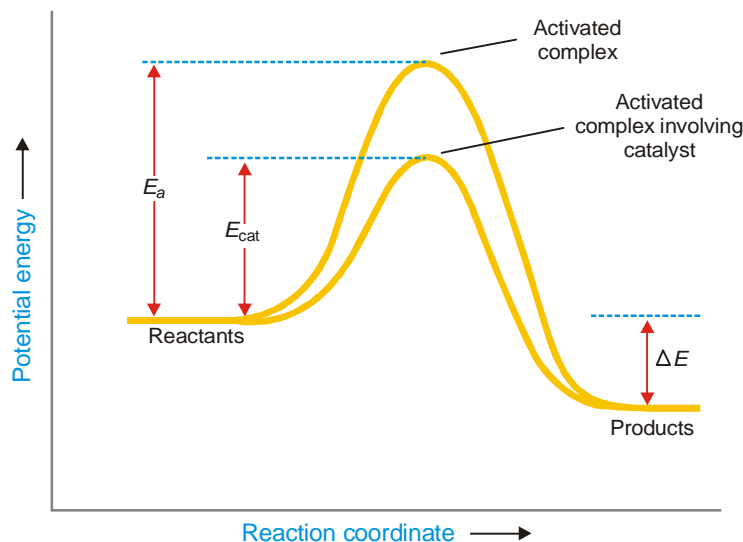


■ **Figure 20.14**  
A potential energy diagram for an endothermic reaction.

On the other hand, if the potential energy of the products is greater than that of the reactants, the energy released in going from the activated complex to products will be less than the activation energy and the reaction will be **endothermic**.

### ACTIVATION ENERGY AND CATALYSIS

We know that for each reaction a certain energy barrier must be surmounted. As shown in the energy diagram shown in Fig. 20.15, the reactant molecules must possess the activation energy,  $E_a$ , for the reaction to occur.

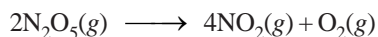


■ **Figure 20.15**  
Energy diagram for a catalysed and uncatalysed reaction showing a lowering of activation energy by a catalyst.

The catalyst functions by providing another pathway with lower activation energy,  $E_{cat}$ . Thus a much large number of collisions becomes effective at a given temperature. Since the rate of reaction is proportional to effective collisions, the presence of a catalyst makes the reaction go faster, other conditions remaining the same. It may be noted from the above diagram that although a catalyst lowers the activation energy, the energy difference,  $\Delta E$ , between products and reactants remains the same.

### LINDEMAN'S THEORY OF UNIMOLECULAR REACTIONS

A number of unimolecular reactions, for example,



are found to be of the first order. It is difficult to account for such reactions using the collision theory and the absolute reaction rate theory. If two molecules must collide in order to provide necessary activation energy, a second order rate law should result. In 1922, Lindeman explained this anomaly by assuming that **there existed a time lag between activation and reaction of molecules**. During this time lag, the activated molecules could either react or be deactivated. Thus,



If the time lag is long, step (3) is slow, the reaction should follow first order kinetics. However, if  $A$  reacts as soon as formed, step (2) is the slow step, then the reaction should be second order.

The proof of Lindeman's theory is provided by studying the effect of change of pressure on the reaction. At high pressure the rate of deactivation will be dominant. On the other hand, at sufficiently low pressure all the activated molecules will react before they can be deactivated. Therefore the reaction kinetics should change from first order to second order with decreasing pressure. Several gases are known to exhibit this behaviour.

## EXAMINATION QUESTIONS

- Define or explain the following terms :
  - Rate of reaction
  - Molecularity of a reaction
  - Half life of a reaction
  - Order of a reaction
  - Rate constant
  - Arrhenius equation
- Derive mathematical expression for the rate constant of a reaction ( $A + B \rightarrow \text{Products}$ ) of the second order.
- The first order rate constant for the decomposition of  $N_2O_2$  of  $0^\circ C$  is  $5.2 \times 10^{-6} \text{ min}^{-1}$ . If the energy of activation is 6200 joules per mole, calculate the rate constant at  $25^\circ C$ .  
**Answer.**  $7.385 \times 10^{-6}$
- Define order of a reaction, molecularity of a reaction and half life period. Show that for first order reactions the half life period is independent of the initial concentration.
  - The rate constant of a reaction is  $1.2 \times 10^{-3} \text{ sec}^{-1}$  at 303 K. Calculate the rate constant at 313 K, if the activation energy for the reaction is  $44.12 \text{ kJ mol}^{-1}$ .  
**Answer.**  $1.47 \times 10^{-3}$
- Explain why the rate of a reaction cannot be measured by dividing the amount of reactants reacted by the time taken.
  - What is activation energy? How is it determined?
- For the kinetics of bimolecular reactions briefly discuss the "Collision Theory".
  - Derive an expression for the half life period of the following reaction:  
 $A \rightarrow B$ , rate  $\propto [A]$
  - With the help of two examples, show that the rate can be independent of initial concentration of the reactants. What is the order of such reactions?
  - If the rate constant at one temperature alongwith the activation energy is given, how can the rate constant at any other temperature be determined?
- Explain Arrhenius equation. Discuss Arrhenius concept of activation energy. Give graphical representation of activation energy diagram. *(Jiwaji BSc, 2000)*
- Explain, with examples, zero-order reaction. Write rate law expression for it.
  - The reaction,  $A + B + C \rightarrow \text{Products}$ , is found to obey the rate law
 
$$r = \frac{-d[A]}{dt} = k [A]^2 [B]^{3/2} [C]^{-1/2}$$
 What is the order of overall reaction? *(Purvanchal BSc, 2000)*
- Derive an expression for rate constant of a bimolecular gaseous reaction on the basis of collision theory. *(Allahabad BSc, 2001)*
- Distinguish between reaction rate and rate constant of a reaction. Derive the integrated rate law for first order reaction. *(kathmandu BSc, 2001)*
- Explain briefly the collision theory of reaction rates. What are its limitations and how far they are overcome by theory of absolute reaction rates?

- (b) Write unit of rate constant for zero order reaction. *(Jamia Millia BSc, 2001)*
12. (a) A reactant R is converted into product by the following mechanism :  

$$R \rightarrow x \rightarrow P$$
where both the steps are of first order. Find out how the concentration of x varies with time and give a physical interpretation of the resulting expression.  
(b) A solution containing equal concentrations of ethyl acetate and NaOH is 25% saponified in 5 minutes. What will be the % saponification after 10 minutes.  
**Answer.**  $1.11 \times 10^{-5}$  *(Vidyasagar BSc (H), 2002)*
13. Deduce the rate expression for second order reaction where both the concentration terms are same. What is half-life period of the second order reaction? *(Arunachal BSc (H), 2002)*
14. (a) Explain various methods of determining the order of a reaction.  
(b) Derive an expression for the dependence of rate constant of a reaction with temperature.  
(c) Explain how the acid catalysed hydrolysis of an ester is followed experimentally to show it to follow first order kinetics.  
(d) What are zero order reactions? Give one example. *(Sri Venkateswara BSc, 2002)*
15. If 15% of a substance decomposes in first ten minutes in a first order reaction, calculate how much of it would remain undecomposed after one hour?  
**Answer.** 37.75% *(Vidyasagar BSc, 2002)*
16. Discuss the kinetics of hydrolysis of ethyl acetate in acidic medium. *(Jamia Millia BSc, 2002)*
17. Write short notes on :  
(a) Activation energy (b) Energy barrier *(MD Rohtak BSc, 2002)*
18. Derive the rate equation for the first order reaction and show that :  
(i) Half-life is independent of initial concentration.  
(ii) The rate constant is independent of concentration. *(MD Rohtak BSc, 2002)*
19. The velocity constant for a certain reaction is  $5.25 \times 10^{-3}$  at 303 K and  $11.1 \times 10^{-3}$  at 314 K. Calculate the energy of activation of the reaction.  
**Answer.** 53.849 kJ *(Mumbai BSc, 2002)*
20. (a) Describe the expression for the rate constant of the reaction  $A + B \rightarrow \text{Products}$ . The initial concentrations of A and B are different.  
(b) Describe the graphical method for the determination of order of reaction.  
(c) Obtain the unit of the second order rate constant from the rate expression. *(HS Gaur BSc, 2002)*
21. The energy of activation for a reaction is 105 kJ mol<sup>-1</sup>. Calculate the specific reaction rate for the reaction at 300 K, if the frequency factor is  $2.5 \times 10^{15}$  sec<sup>-1</sup>.  
**Answer.**  $1.3 \times 10^{-3}$  sec<sup>-1</sup> *(Mumbai BSc, 2002)*
22. (a) Derive the integrated Arrhenius equation of activation energy. How is the energy of activation determined from the plot?  
(b) The value of rate constant for the decomposition of nitrogen pentoxide ( $N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2$ ) is  $4.346 \times 10^{-5}$  at 25°C and  $4.87 \times 10^{-3}$  at 65°C. Calculate the energy of activation for the reaction. ( $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ )  
**Answer.** 103.585 kJ *(Arunachal BSc (H), 2002)*
23. (a) Discuss the collision theory of Bimolecular reactions.  
(b) Define collision number. *(Nagpur BSc, 2002)*
24. (a) Name different methods to determine the order of a reactions and describe the half-life method in detail.  
(b) Give theory of absolute reaction rates. *(Jamia Millia BSc, 2002)*
25. If the half-life of a first order reaction in A is 15 min., how long it will take for [A] to reach 10 percent of the initial concentration?  
**Answer.** 2990 sec *(Arunachal BSc, 2002)*

26. The rate constant of a second order reaction is  $5.70 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$  at  $25^\circ\text{C}$  and  $1.64 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$  at  $40^\circ\text{C}$ . Calculate the activation energy of the reaction. ( $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ )  
**Answer.** 54.645 kJ (Mizoram BSc (H), 2002)
27. Explain the term collision frequency. On what factors does it depend? What is meant by collision diameter?  
 (Guru Nanak Dev BSc, 2002)
28. The rate constant for a first order reaction is  $1.54 \times 10^{-3} \text{ sec}^{-1}$ . Calculate its half-life period.  
**Answer.** 450 sec (Allahabad BSc, 2002)
29. How is the order of the reaction determined by Differential method and Half-life method?  
 (Arunachal BSc, 2002)
30. A second order reaction, in which the initial concentration of both the reactants is the same, is 25% completed in 600 sec. How long will it take for the reaction to go to 75% completion?  
**Answer.** 5400 sec (Jamia Millia BSc, 2002)
31. Explain the following :  
 (i) If a reaction is pseudo order, the half life is always defined with respect to the species present in the smallest amount.  
 (ii) Under certain situation the rate of reaction and specific reaction rate become identical.  
 (Delhi BSc, 2002)
32. (a) Derive the Arrhenius equation and discuss how it is useful to calculate the energy of activation.  
 (b) Give one example each for pseudo unimolecular, second order, third order and zero order reactions.  
 (Madurai BSc, 2002)
33. Explain, with examples, the functions of catalytic promoters and poisons in chemical reactions.  
 (Panjab BSc, 2002)
34. The activation energy of a non-catalysed reaction at  $37^\circ\text{C}$  is  $83.68 \text{ kJ mol}^{-1}$  and the activation energy for the same reaction catalysed by enzymes is  $25.10 \text{ kJ mol}^{-1}$ . Calculate the ratio of the two rate constants.  
**Answer.** 0.9975 (Kalyani BSc, 2003)
35. (a) Derive an expression for rate constant ( $k$ ) for the reaction  $A + B \rightarrow \text{Products}$  on the basis of collision theory. Express the value of  $k$  in  $\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .  
 (b) The rate constants for a reaction at  $27^\circ\text{C}$  and  $37^\circ\text{C}$  are  $4.5 \times 10^{-5} \text{ sec}^{-2}$  and  $9.0 \times 10^{-5} \text{ sec}^{-2}$ . Evaluate the activation energy of the reaction.  
**Answer.** 53.598 kJ (Punjabi BSc, 2003)
36. Write short notes on:  
 (i) Transition state theory of reaction rates  
 (ii) Parallel reactions  
 (iii) Opposing reactions (Allahabad BSc, 2003)
37. A  $\ln k$  versus  $1/T$  graph was plotted to calculate the activation energy of a reaction using Arrhenius equation for the effect of temperature on reaction rate. The slope of the straight line was found to be  $-2.55 \times 10^4$ . Calculate the activation energy of the reaction.  
**Answer.**  $21.2007 \times 10^4 \text{ J}$  (Guru Nanak Dev BSc, 2003)
38. Calculate the activation energy of a reaction whose reaction rate at  $27^\circ\text{C}$  gets doubled for  $10^\circ$  rise in temperature ( $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ )  
**Answer.** 53.598 kJ (Arunachal BSc, 2003)
39. What do you understand by the term: 'rate determining step' of a complex reaction? What is steady-state hypothesis?  
 (Arunachal BSc, 2003)
40. What would be the units of the rate constant in the following rate law :  
 $\text{rate} = k [A][B]$   
 if the concentration is expressed in moles litre $^{-1}$  and time in seconds. (Delhi BSc, 2003)



41. Show that

(i) for a first order reaction  $t_{\frac{1}{2}} = \frac{0.693}{k}$

(ii) for a second order reaction  $t_{\frac{1}{2}} = \frac{1}{k_2 a}$  (Allahabad BSc, 2003)

42. Derive the equation

$$k = \frac{1}{t} \frac{x}{a(a-x)}$$

for a second order reaction where 'k' is second order rate constant, 'x' is in the amount of product formed after time 't' and 'a' is the initial amount of reactants. What is the unit of k in the equation?

(Nagpur BSc, 2003)

43. Write down the rate and the differential rate expression for  $A + 2B \rightarrow \text{Products}$ .

(Guru Nanak Dev BSc, 2003)

44. Explain the following with examples:

(a) Parallel Reactions

(b) Reversible Reactions

(c) Consecutive Reactions

(Purvanchal BSc, 2003)

45. Derive the rate expression for an opposing reaction in which the forward as well as reverse reactions are both first order.

(Kalyani BSc, 2003)

46. (a) What are pseudo and true unimolecular reactions? Explain with examples.

(b) A first order reaction is 15% complete in 20 minutes. What is the half-life period of the reaction?

**Answer.** (b) 85 min

(Purvanchal BSc, 2003)

47. (a) Derive an expression for the rate constant of a second order reaction, involving one reactant only. Also write how the equation you, derive, is employed in the graphical method to confirm second order.

(b) Describe the activated complex theory of bimolecular reactions. What are the advantages of this theory over collision theory?

(Guru Nanak Dev BSc, 2004)

48. (a) Derive a second order rate equation for the reaction



Explain that half-life period depends upon initial concentration of the reactants.

(b) Calculate the activation energy of a reaction whose rate constant at 27°C gets doubled for 10°C rise in temperature.

**Answer.** (b) 12804.5 cal

(Agra BSc, 2004)

49. (a) Derive an expression for the rate constant for 2nd order reaction assuming the initial concentration to be the same.

(b) 50% of a first order reaction is completed in 23 minutes. Calculate the time required to complete 90% of the reaction.

**Answer.** (b) 76.43 min

(Madras BSc, 2004)

50. A first order reaction is 15% complete in 20 minutes. How long will it take to be 60% complete?

**Answer.** 112.79 min

(Patna BSc, 2004)

51. Calculate the half-life period for the first order reaction whose rate constant is  $1.052 \times 10^{-3} \text{ sec}^{-1}$ .

**Answer.** 659 sec

(Indore BSc, 2004)

52. An acid solution of sucrose was hydrolysed to the extent of 54% after 67 minutes. Assuming the reaction to be of first order, calculate the time taken for 80% hydrolysis.

**Answer.** 124.4 min

(Allahabad BSc, 2005)

53. A second order reaction in which both the reactants have the same concentration is 25% complete in 10 minutes. How long will it take for the reaction to go to 90% completion ?  
**Answer.** 2700 min (Purvanchal BSc, 2005)
54. For a certain reaction, it takes 5 minutes for the initial concentration of  $0.5 \text{ mol lit}^{-1}$  to become  $0.25 \text{ mol lit}^{-1}$  and another 5 minutes to become  $0.125 \text{ mol lit}^{-1}$ . (a) What is the order of the reaction ? (b) What is the rate constant of the reaction ?  
**Answer.** (a) One (b)  $0.136 \text{ min}^{-1}$  (Mizoram BSc, 2005)
55. If the half life of a first order in A is 2 min, how long will it take A to reach 25% of its initial concentration.  
**Answer.** 4 min (Delhi BSc, 2006)
56. A reaction that is first order with respect to the reactant A has a rate constant of  $6 \text{ min}^{-1}$ . If we start  $[A] = 5.0 \text{ mol lit}^{-1}$  when would  $[A]$  reach the value of  $0.05 \text{ mol lit}^{-1}$  ?  
**Answer.** 0.7676 min (Mysore BSc, 2006)
57. The rate of a particular reaction becomes three times when the temperature is increased from 298 K to 308 K. Calculate the energy of activation for the reaction.  
**Answer.**  $83.8 \text{ kJ mol}^{-1}$  (Himachal BSc, 2006)
58. Calculate the half life of a first order reaction where the specific rate constant is (a)  $200 \text{ sec}^{-1}$  (b)  $2 \text{ min}^{-1}$ .  
**Answer.** (a)  $0.00346 \text{ sec}^{-1}$  ; (b)  $0.3465 \text{ min}^{-1}$  (Panjab BSc, 2006)

### MULTIPLE CHOICE QUESTIONS

1. Which of the following includes all the aims of kinetics?  
 (i) to measure the rate of a reaction  
 (ii) to be able to predict the rate of a reaction  
 (iii) to be able to establish the mechanism by which a reaction occurs  
 (iv) to be able to control a reaction  
 (a) (i), (ii) and (iii) (b) (i) and (ii)  
 (c) (i) and (iii) (d) (i), (ii), (iii) and (iv)  
**Answer.** (d)
2. Reaction rates can change with  
 (a) temperature (b) the addition of a catalyst  
 (c) reactant concentrations (d) all of these  
**Answer.** (d)
3. Reaction rates generally  
 (a) are constant throughout a reaction  
 (b) are smallest at the beginning and increase with time  
 (c) are greatest at the beginning of a reaction and decrease with time  
 (d) no such generalisations can be made  
**Answer.** (d)
4. Consider the reaction in which nitric oxide is oxidized to nitrogen dioxide,  
 $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ , for which the rate law is  $= k [\text{NO}]^2 [\text{O}_2]$ . If this reaction takes place in a sealed vessel and the partial pressure of nitric oxide is doubled, what effect would this have on the rate of reaction?  
 (a) the reaction rate would triple (b) the reaction rate would double  
 (c) the reaction rate would quadruple (d) there would be no effect on the reaction rate  
**Answer.** (c)

5. Which three factors affect the rate of a chemical reaction?  
 (a) temperature, pressure and humidity  
 (b) temperature, reactant concentration and catalyst  
 (c) temperature, reactant concentration and pressure  
 (d) temperature, product concentration and container volume  
**Answer.** (b)
6. For first-order reactions the rate constant,  $k$ , has the unit(s)  
 (a)  $1 \text{ mol}^{-1}$  (b)  $\text{time}^{-1}$   
 (c)  $(\text{mol/l})^{-1} \text{ time}^{-1}$  (d)  $\text{time mol l}^{-1}$   
**Answer.** (b)
7. What are the units of the rate constant for a reaction in solution that has an overall reaction order of two? (M is molarity, s is seconds.)  
 (a)  $\text{M}^{-1} \text{ s}^{-1}$  (b)  $\text{M}^{-1}$   
 (c)  $\text{s}^{-1}$  (d)  $\text{M s}^{-1}$   
**Answer.** (a)
8. The reaction  $\text{A} \rightarrow \text{B}$  is a second-order process. When the initial concentration of A is 0.50 M, the half-life is 8.0 minutes. What is the half-life if the initial concentration of A is 0.10 M?  
 (a) 1.6 minutes (b) 8.0 minutes  
 (c) 40.0 minutes (d) 16.0 minutes  
**Answer.** (c).
9. The quantity  $k$  in a rate law expression  
 (a) is independent of concentration (b) is called the Arrhenius constant  
 (c) is dimensionless (d) is independent of the temperature  
**Answer.** (a)
10. The first-order rate constant for the decomposition of  $\text{N}_2\text{O}_5$  to  $\text{NO}_2$  and  $\text{O}_2$  at  $70^\circ\text{C}$  is  $6.82 \times 10^{-3} \text{ s}^{-1}$ . Suppose we start with 0.300 mol of  $\text{N}_2\text{O}_5(\text{g})$  in a 0.500 L container. How many moles of  $\text{N}_2\text{O}_5$  will remain after 1.5 min?  
 (a) 0.081 mol (b) 0.555 mol  
 (c) 0.325 mol (d) 0.162 mol  
**Answer.** (d)
11. As the temperature of a reaction is increased, the rate of the reaction increases because the  
 (a) reactant molecules collide with greater energy  
 (b) reactant molecules collide less frequently  
 (c) reactant molecules collide less frequently and with greater energy  
 (d) activation energy is lowered  
**Answer.** (d)
12. In a series of reactions, which is the rate-determining step?  
 (a) the simplest reaction (b) the main reaction involving the major reactant  
 (c) the slowest reaction (d) the fastest reaction  
**Answer.** (c)
13. Beaker A contains a 1 gram piece of zinc and beaker B contains 1 gram of powdered zinc. If 100 milliliters of 0.1 M HCl is added to each of the beakers, how is the rate of reaction in beaker A compared to the rate of reaction in beaker B?  
 (a) the rate in A is greater due to the smaller surface area of the zinc  
 (b) the rate in A is greater due to the greater surface area of the zinc  
 (c) the rate in B is greater due to the smaller surface area of the zinc  
 (d) the rate in B is greater due to the greater surface area of the zinc  
**Answer.** (d)

14. The decomposition of ethylene oxide at 652 K  
 $(\text{CH}_2)_2\text{O}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g})$   
 is first-order with  $k = 0.0120 \text{ min}^{-1}$ . The activation energy of the reaction is 218 kJ/mol. Calculate the rate constant of the reaction at 525 K.
- (a)  $7.11 \times 10^{-7} \text{ min}^{-1}$  (b)  $202 \text{ min}^{-1}$   
 (c)  $8.7 \times 10^{-6} \text{ min}^{-1}$  (d)  $-14.2 \text{ min}^{-1}$   
**Answer.** (a)
15. Here is a second order reaction  $\text{A} \rightarrow \text{P}$ . If the initial concentration of A 0.0818 M goes down 30.0% in 3.15 minutes, what is the rate constant for the reaction?
- (a)  $0.0078 \text{ l mol}^{-1} \text{ s}^{-1}$  (b)  $1.7 \text{ l mol}^{-1} \text{ s}^{-1}$   
 (c)  $9.1 \text{ l mol}^{-1} \text{ s}^{-1}$  (d)  $16 \text{ l mol}^{-1} \text{ s}^{-1}$   
**Answer.** (b)
16. For a first-order reaction of the form  $\text{A} \rightarrow \text{P}$ ,  $t_{1/2} = 9$  hours. If the concentration of A is 0.0013 M right now, what is the best estimate of what it was the day before yesterday?
- (a) 0.0026 M (b) 0.0065 M  
 (c) 0.0052 M (d) 0.042 M  
**Answer.** (d)
17. The rate law relates the rate of a chemical reaction to
- (a) the concentrations of reactants (b) the temperature  
 (c) the activation energy (d) the reaction mechanism  
**Answer.** (a)
18. Rate laws for chemical reactions are determined
- (a) by examining the coefficients in the balanced chemical equation  
 (b) from the equilibrium constant  
 (c) from the rates of the forward and reverse reactions of the system at equilibrium  
 (d) by experiment  
**Answer.** (d)
19. For a reaction,  $\text{A} \rightarrow \text{products}$ , a graph of  $[\text{A}]$  versus time is found to be a straight line. What is the order of this reaction?
- (a) zero order (b) first order  
 (c) second order (d) third order  
**Answer.** (a)
20. To study the rate of a reaction, it is necessary to
- (a) identify the reactants  
 (b) know the relative amounts of reactants used  
 (c) know the overall chemical equation for the reaction  
 (d) all of the above are necessary  
**Answer.** (d)
21. Why do most chemical reaction rates increase rapidly as the temperature rises?
- (a) the fraction of the molecules with kinetic energy greater than the activation energy increases rapidly with temperature  
 (b) the average kinetic energy increases as temperature rises  
 (c) the activation energy decreases as temperature rises  
 (d) more collisions take place between particles so that the reaction can occur  
**Answer.** (a)

22. The rate constant for a reaction depends upon each of the following, EXCEPT:
- (a) solvent for solutions (b) temperature  
(c) concentration of reactants (d) nature of reactants
- Answer.** (c)
23. All of the following are true statements concerning reaction orders EXCEPT:
- (a) the rate of a zero-order reaction is constant  
(b) after three half-lives, a radioactive sample will have one-ninth of its original concentration  
(c) the units for the rate constant for first order reactions are  $\text{sec}^{-1}$   
(d) if doubling the concentration of a reactant doubles the rate of the reaction, then the reaction is first order in that reactant
- Answer.** (b)
24. The powers in the rate law are determined by
- (a) the principle of detailed balance  
(b) the physical states of the reactants and products  
(c) experiment  
(d) the coefficients in the balanced chemical reaction
- Answer.** (c)
25. Consider the reaction  $3A \rightarrow 2B$ .  
The average rate of appearance of B is given by  $[B]/t$ . How is the average rate of appearance of B related to the average rate of disappearance of A?
- (a)  $-2[A]/3t$  (b)  $[A]/t$   
(c)  $-[A]/t$  (d)  $-3[A]/2t$
- Answer.** (a)
26. Which one of the following is incorrect for the reaction  $A \rightarrow B$ ?
- (a) the half-life of a second-order reaction depends on the initial concentration  
(b) the half-life is the time for one half of the reactant to be consumed  
(c) the second-order rate constant can be found by plotting  $1/[A]^2$  versus time, where  $[A]$  is the concentration of reactant  
(d) the initial rates for a second-order reaction depend on the concentration of the reactant squared
- Answer.** (c)
27. Consider the reaction in which ammonia is synthesized from nitrogen and hydrogen gases :
- $$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$$
- How is the rate of formation of ammonia related to the rate of consumption of hydrogen?
- (a) the rate of formation of ammonia is half the rate of consumption of hydrogen  
(b) the rate of formation of ammonia is twice the rate of consumption of hydrogen  
(c) the rate of formation of ammonia is equal to the rate of consumption of hydrogen  
(d) the rate of formation of ammonia is two-thirds the rate of consumption of hydrogen
- Answer.** (d)
28. Which concentration plot is linear for a first-order equation? (A is one of the reactants).
- (a)  $[A]$  versus time (b) square root of  $[A]$  versus time  
(c)  $\ln[A]$  versus time (d)  $[A]^2$  versus time
- Answer.** (c)
29. A reaction in which all reactants are in the same phase is called
- (a) elementary (b) bimolecular  
(c) homogeneous (d) heterogeneous
- Answer.** (c)

30. As temperature increases, the reaction rate .....
- (a) decrease than increase (b) decreases  
(c) increases (d) stays the same
- Answer.** (c)
31. For the reaction  $2\text{NO}_2 + \text{O}_3 \rightarrow \text{N}_2\text{O}_5 + \text{O}_2$  the following observations are made :  
Doubling the concentration of  $[\text{NO}_2]$  doubles the rate, and doubling the concentration of  $[\text{O}_3]$  doubles the rate. What is the rate law for the reaction?
- (a) rate =  $k [\text{NO}_2]$  (b) rate =  $k [\text{NO}_2]^2 [\text{O}_3]$   
(c) rate =  $k [\text{NO}_2]^2 [\text{O}_3]^2$  (d) rate =  $k [\text{NO}_2] [\text{O}_3]$
- Answer.** (d)
32. The half-life of a first-order process
- (a) depends on the reactant concentration raised to the first power  
(b) is inversely proportional to the square of the reactant concentration  
(c) is inversely proportional to the reactant concentration  
(d) is totally independent of the reactant concentration
- Answer.** (d)
33. The reaction,  $2\text{NO}(\text{g}) \rightarrow \text{N}_2(\text{g}) + \text{O}_2(\text{g})$ , proceeds in a single elementary step. This reaction is thus
- (a) the molecularity cannot be determined from the given information  
(b) termolecular  
(c) bimolecular  
(d) unimolecular
- Answer.** (c)
34. Why is a minimum energy needed for an effective collision?
- (a) energy is needed to break bonds  
(b) energy is needed to orient the particles correctly  
(c) a minimum energy is needed, so that the particles will collide many times per second  
(d) enough energy is needed to give off heat in a reaction
- Answer.** (a)
35. Species that are formed in one step of reaction mechanism and used up in another step are called
- (a) catalysts (b) intermediates  
(c) inhibitors (d) activated complexes
- Answer.** (b)
36. For a certain reaction, the rate =  $k [\text{NO}]^2 [\text{O}_2]$ , when the initial concentration of NO is tripled, the initial rate
- (a) decreases by a factor of nine (b) increases by a factor of three  
(c) increases by a factor of six (d) increases by a factor of nine
- Answer.** (d)
37. Which of the following statements associated with mechanisms of chemical reactions is incorrect?
- (a) intermediates do not appear in the net chemical equation or overall rate law  
(b) the first step in a mechanism always determines the rate of the reaction  
(c) in elementary reactions, coefficients give the order with respect to reactants and products  
(d) a plausible mechanism must account experimentally determined rate law
- Answer.** (b)
38. What happens in a steady state?
- (a) product is being formed faster than reactants are regenerated  
(b) heat is evolved

- (c) the concentration of an intermediate is constant  
 (d) nothing is happening

**Answer.** (c)

39. What happens when molecules collide with less than the activation energy needed for the reaction?  
 (a) they stick together but do not react  
 (b) they react, but more slowly  
 (c) they react if the bonds are arranged in the correct orientation  
 (d) they do not react; they simply bounce off of each other

**Answer.** (d)

40. Why do fine iron wires burst into flame when lighted, while an iron frying pan does not?  
 (a) the finely divided iron has lower internal free energy than the frying pan  
 (b) the frying pan has much greater mass than the finely divided wires  
 (c) the frying pan is more dense than the wires  
 (d) the wires have greater surface area, enabling more iron particles to react more quickly

**Answer.** (d)

41. Which of the following terms describes a process in which two particles come together to form an activated complex?  
 (a) reaction mechanism  
 (b) elementary process  
 (c) rate determining step  
 (d) unimolecular

**Answer.** (b)

42.  $A + B + C \rightarrow$  products is :

- (a) unimolecular  
 (b) trimolecular  
 (c) bimolecular  
 (d) tetramolecular

**Answer.** (b)

43. Based on the collision model, the atoms at the top of the potential energy "hill" are called:

- (a) top of the hill  
 (b) activation energy  
 (c) transition state  
 (d) steric factor

**Answer.** (c)

44. According to chemical kinetic theory, a reaction can occur

- (a) if the reactants collide with the proper orientation  
 (b) if the reactants possess sufficient energy of collision  
 (c) if the reactants are able to form a correct transition state  
 (d) all of the above

**Answer.** (d)

45. What does termolecular refer to?

- (a) 2 molecules colliding  
 (b) 4 molecules colliding  
 (c) 3 molecules colliding  
 (d) 1 molecule dissociating

**Answer.** (c)

46. What is the order of the absorption process for alcohol through the lining of the stomach and small intestine?

- (a) zero order  
 (b) first order  
 (c) second order  
 (d) third order

**Answer.** (b)

47. The decomposition of nitrogen dioxide to nitrogen and oxygen is second-order with a rate constant  $k = 12.5 \text{ M}^{-1} \text{ s}^{-1}$ . What is the half-life for the reaction if  $[\text{NO}_2]_0 = 0.00260 \text{ M}$ ?

- (a) 0.0554 sec  
 (b) 30.8 sec

- (c) 385 sec (d) 61.5 sec

**Answer.** (b)

48. A first order reaction requires 8.96 months for the concentration of reactant to be reduced to 25.0% of its original value. What is the half life of the reaction?

- (a) 4.48 months (b) 2.24 months  
(c) 8.96 months (d) 17.9 months

**Answer.** (a)

49. In a reaction, the initial concentration of the reactant is 2.34 M. The equilibrium mixture contains 1.12 M of the reactant. Equilibrium was achieved in 523 sec. What is the average rate of the reaction?

- (a)  $4.45 \times 10^{-3}$  M/sec (b)  $2.14 \times 10^{-3}$  M/sec  
(c)  $2.33 \times 10^{-3}$  M/sec (d) 429 M/sec

**Answer.** (c)

50. The half-life for a first order reaction is 2768 years. If the concentration after 11,072 years is 0.0216 M, what was the initial concentration?

- (a) 0.0690 M (b) 0.345 M  
(c) 0.173 M (d) 1.000 M

**Answer.** (b)

51. For the hypothetical gas-phase reaction  $3A(g) \rightarrow 2B(g)$ , the number of moles of A present at 25 min is found to be 0.022. If the initial number of moles of A and B were 0.050 mol and 0.00 mol, respectively, how much B is present at 25 min?

- (a) 0.022 mol (b) 0.056 mol  
(c) 0.028 mol (d) 0.019 mol

**Answer.** (d)

52. The number of undecayed nuclei in a sample of Bromine-87 decreased by a factor of 4 over a period of 112 sec. What is the rate constant for the decay of Bromine-87?

- (a) 56 sec (b)  $6.93 \times 10^{-1}$  sec<sup>-1</sup>  
(c)  $1.24 \times 10^{-2}$  sec<sup>-1</sup> (d)  $6.19 \times 10^{-3}$  sec<sup>-1</sup>

**Answer.** (c)

53. The half-life of radioactive sodium is 15.0 hours. How many hours would it take for a 64 g sample to decay to one-eighth of its original concentration?

- (a) 3 (b) 15  
(c) 30 (d) 45

**Answer.** (d)

54. The decomposition of NOBr is second-order with respect to NOBr and second-order overall. If the initial concentration of NOBr is 0.102 M and the rate constant is  $25 \text{ M}^{-1} \text{ min}^{-1}$ , what is [NOBr] after 1.0 min?

- (a) 9.8 M (b)  $2.9 \times 10^{-2}$  M  
(c)  $4.0 \times 10^{-2}$  M (d) 35 M

**Answer.** (b)

55. For a reaction of the type  $A + B + C$  going to product, the following observations are made: Doubling the concentration of A doubles the rate, doubling concentration of B has no effect on the rate, and tripling the concentration of C increases the rate by a factor of 9. What is the rate law for the reaction?

- (a) rate =  $k [A]^2 [B] [C]^2$  (b) rate =  $k [A] [C]^2$   
(c) rate =  $k [A]^2 [B] [C]$  (d) rate =  $k [A] [B] [C]$

**Answer.** (b)

56. If we have the reaction  $A(g) \rightarrow 2B(g)$  and the number of moles of A is as follows,

time	0	5 min	10 min
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moles A                      0.100              0.085              0.070

what is the number of moles of B at 10 min?

- (a) 0.030 mol                                      (b) 0.140 mol  
(c) 0.060 mol                                      (d) 0.200 mol

**Answer:** (c)

57. From a plot or reasonable estimate, what is the instantaneous rate of change of A versus time at 10 min?

Time	0	2.50	5.00	7.50	10.0	12.5
[A]	0.500	0.389	0.303	0.236	0.184	0.143

- (a)  $-0.0209$                                       (b)  $-0.0164$   
(c)  $-0.0316$                                       (d)  $-0.0184$

**Answer:** (d)

58. A reaction requires 279 minutes in order to reach equilibrium. The concentration of one reactant changed from 2.13 M to 0.24 M. What is the average rate of the reaction?

- (a)  $7.63 \times 10^{-3}$  M/min                      (b)  $6.77 \times 10^{-3}$  M/min  
(c) 2.13 M/min                                      (d) 148 M/min

**Answer:** (b)

59. In a first-order reaction,  $A \rightarrow$  products,  $[A] = .0620$  M initially and 0.520 M after 15.0 min. What is the half-life,  $t_{1/2}$ , of this reaction?

- (a) 7.50 min                                      (b) 46.5 min  
(c) 29.6 min                                      (d) 59.2 min

**Answer:** (d)

60. In a first-order reaction,  $A \rightarrow$  product,  $[A] = 0.620$  M initially and 0.520 M after 15.0 min. What is the value of the rate constant?

- (a)  $9.12 \times 10^{-2}$  min $^{-1}$                       (b)  $5.09 \times 10^{-3}$  min $^{-1}$   
(c) 0.0117 min $^{-1}$                                       (d) 0.154 min $^{-1}$

**Answer:** (c)

61. In a lab, each of the following factors will vary to affect reaction rate EXCEPT:

- (a) catalyst used                                      (b) concentration of reactants  
(c) identity of reactants                              (d) oxygen availability

**Answer:** (d)

62. In a first-order reaction,  $A \rightarrow$  products,  $k = 0.0150$  min $^{-1}$ . If  $[A]$  is 0.400 M initially, what will  $[A]$  be after 2.00 h?

- (a) 0.388 M                                      (b)  $1.92 \times 10^{-3}$  M  
(c) 0.487 M                                      (d) 0.0661 M

**Answer:** (d)

63. In a second-order reaction the rate constant is  $4.0 \times 10^{-4}$  M $^{-1}$  s $^{-1}$ . What will be the concentration of reactant after 10 min if the initial concentration is 0.800 M?

- (a) 1.49 M                                      (b) 0.671 M  
(c) 0.629 M                                      (d) 0.300 M

**Answer:** (b)

64. In the reaction  $2A + B \rightarrow 2C + D$ ,  $-\Delta[A]/t$  is found to be 5.0 M min $^{-1}$ . What is the rate of change of B?

- (a) 2.5 M/min                                      (b) 10 M/min  
(c) 25 M/min                                      (d) 5.0 M/min

**Answer:** (a)

65. The reaction  $A \rightarrow P$  is a second-order process with  $t_{1/2} = 23.0$  minutes at an initial concentration of  $A = 0.500$  M. What is the concentration of A after 1.00 hour elapses?

- (a) 0.263 M                                      (b) 0.139 M

- (c) 0.0822 M (d) 0.175 M

**Answer.** (b)

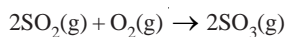
66. The thermal decomposition of  $\text{N}_2\text{O}_5(\text{g})$  to form  $\text{NO}_2(\text{g})$  and  $\text{O}_2(\text{g})$  is a first-order reaction. The rate constant for the reaction is  $5.1 \times 10^{-4} \text{ s}^{-1}$  at 318 K. What is the half-life of this process?
- (a)  $3.9 \times 10^3 \text{ s}$  (b)  $2.0 \times 10^3 \text{ s}$   
 (c)  $1.0 \times 10^{-3} \text{ s}$  (d)  $1.4 \times 10^3 \text{ s}$

**Answer.** (d)

67. If the reaction,  $2\text{A} + 3\text{D} \rightarrow \text{products}$ , is first-order in A and second-order in D, then the rate law will have the form : rate =
- (a)  $k [\text{A}] [\text{D}]^2$  (b)  $k [\text{A}]^2 [\text{D}]$   
 (c)  $k [\text{A}]^2 [\text{D}]^2$  (d)  $k [\text{A}] [\text{D}]$

**Answer.** (a)

68. If the reaction below is carried out in a closed, rigid container, how could you best follow the rate of the reaction?



- (a) monitor the density of the mixture (b) monitor the temperature  
 (c) monitor the pressure (d) monitor the change in concentration

**Answer.** (c)

69. Which of the following does NOT affect the rate of a chemical reaction?
- (a) enthalpy of the reaction (b) concentration of reactants  
 (c) temperature (d) surface area

**Answer.** (a)

70. Which of the following rate laws is third-order overall?
- (a) rate =  $k [\text{A}]^3 [\text{B}]^1$  (b) rate =  $k [\text{A}]^3 [\text{B}]^3$   
 (c) rate =  $k [\text{A}]^5 [\text{B}]^2$  (d) rate =  $k [\text{A}] [\text{B}]^2$

**Answer.** (d)

71. For a certain reaction, a plot of  $\ln [\text{A}]$  versus  $t$  gives a straight line with a slope of  $-1.46 \text{ s}^{-1}$ . The order of the reaction in A is:
- (a) 0 (b) 3  
 (c) 2 (d) 1

**Answer.** (d)