Indira Gandhi National
Open University
School of Sciences

BCHCT-137

COORDINATION CHEMISTRY, STATES OF MATTER AND CHEMICAL KINETICS

Block

4

CHEMICAL KINETICS

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BLOCK 4: CHEMICAL KINETICS

In the previous block of this course, you have learnt about different states of matter in terms of their structure and properties. In this block you would learn about Chemical kinetics-an important domain of physical chemistry that deals with the time aspect of chemical reactions. This block consists of two units

Unit13, titled, ‘Chemical kinetics-I’deals with the basic aspects of chemical kinetics like, different types of rates, their measurement and factors affecting them. In addition, it covers differential and integral rate laws, order, and half-life of a reaction.

Unit 14, titled, ‘Chemical kinetics-II’ deals withthe methods for the determination of order of reaction, temperature dependence of rate of reaction and theories of reaction rate. In the context of temperature dependence of rate, we will discuss about Arrhenius equation and its significance. We will explain the collision theory and activated complex theoryin details and compare the collision theory and Arrhenius equation.

Expected Learning Outcomes

After studying this block, you should be able to:

- define and differentiate between different types of rates of reaction;
- describe different methods of following the progress of a chemical reaction;
- list and explain various factors affecting the rates of chemical reactions;
- explain the terms like, differential and integrated rate laws, order of reaction and outline their significance;
- derive and analysis integrated rate equations for zeroth, first and second order reactions;
- list and describe different methods for the determination of order of a reaction;
- discuss the effect of temperature on the reaction rate and calculate the activation energy of a reaction by using Arrhenius equation;
- list the assumptions of collision theory and derive an expression for rate constant; and
- explain the activated complex theory of biomolecular reactions;

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UNIT 13

Chemical Kinetics–I

Structure

13.1 INTRODUCTION

In the previous units of this course, you have learnt about different states of matter in terms of their structure and properties. In this and the next unit you would learn about chemical kinetics, a domain of physical chemistry that deals with the time aspect of chemical reactions. We would begin the unit by defining chemical kinetics and outlining its significance. This will be followed by defining, explaining and outlining the significance of different types of rates that are used in chemical kinetics. We would also take up different methods of measuring rates of chemical reactions and the factors affecting the rate of a reaction.

We would then take up rate laws i.e., the expressions for the concentration dependence of rate of a reaction and the time dependence of concentration in a chemical reaction. In this context we would define the terms like, rate constant and order and outline their significance. We would also derive and analyse expressions for integrated rate equations for reactions following zeroth, first and second order reaction kinetics.

In the next unit we would take up different methods of determination of order of reaction and the theories of reaction rates.

Expected Learning Outcomes

After studying this unit, you should be able to:

- define chemical kinetics and outline its significance;
- state different ways of expressing the rate of a chemical reaction;
- differentiate between different types of rates of reaction;
- describe different methods of following the progress of a chemical reaction;
- list and explain various factors affecting the rates of chemical reactions;
- explain the terms, differential and integrated rate laws and outline their significance;
- define order of a reaction and outline its significance;
- derive and analyse integrated rate equations for zeroth, first and second order reactions; and
- present the data obtained from a kinetics experiment through suitable equations and graphs, and calculate the rate constant and order of reaction.

13.2 CHEMICAL KINETICS AND ITS SIGNIFICANCE

In the context of a chemical reaction there are three fundamental questions that need to be answered before the reaction can be put to use. These are, "Is the reaction feasible?" i.e., whether the desired reaction would take place or not, secondly if it does, "How far would it go?" which way would the equilibrium be – towards the reactants or the products and thirdly, "How long would the reaction take?" or when would we get the product(s)? The first two questions can be answered on the basis of thermodynamics – the value of Gibbs energy change of the reaction can be used to determine the feasibility of the chemical reaction and the value of equilibrium constant is indicative of the extent of the reaction in a given direction.

Chemical Kinetics concerns the 'time aspect' of a reaction or the rate at which the reaction takes place and the factors affecting it. It also provides information about the mechanism by which the reactants are converted into products.

The answer to the third question, however, falls in the domain of chemical kinetics which concerns the 'time aspect' of the reaction or the rate at which the reaction takes place and the mechanism by which the reactants are converted to the products. For example, the reaction between hydrogen and oxygen gases to give water has a highly negative value of standard Gibbs energy change (ΔG^0 (298 K) =–237 kJ mol $^{-1}$) i.e., it is highly feasible reaction. However, we can keep a mixture of these two gases at room temperature for years without getting even a trace of water which implies that the rate of this reaction is very slow.

The study of reaction rates or kinetics of a reaction is of utmost importance to an industrial chemist who intends to prepare a significant amount of a given product in a reasonable amount of time. Further, the results of a rate measurement can be expressed in terms of a rate law which can provide clues to the mechanism of the reaction. This in turn, helps in understanding the course of the reaction and its manipulation to achieve better yields. Let us learn how do we define the rate of a chemical reaction and what are different ways of expressing them?

13.3 RATE OF A CHEMICAL REACTION

We often use the concept of *rate* in our day-to-day life. It implies change in some parameter in unit time. For example, the rate at which water flows from a tap can be expressed in gallons or litres per minute. The speedometer on our automobiles indicates the rate of travel or speed of the vehicle in km/h. It refers to the distance travelled by the vehicle per unit time (an hour). The speed keeps varying during the course of a journey and at any given time we can note it from the speedometer. However, in common use we talk about the rate (or speed) slightly differently. We take the total distance travelled and divide it with the time taken to cover that distance to compute the speed. A person travelling from say Chandigarh to Delhi, a distance of about 250 km, in 4 h is said to have travelled at an average speed of (250 /4) km h^{-1} or 62.5 km h^{-1}. Other common examples could be the rate of bank interest, rate of inflation and rate of population growth etc.

A speedometer is actually a rate meter.

The rates referred above are average rates i.e., change in some parameter over a specified period of time while the one given by the speedometer is instantaneous rate i.e., the rate (speed) at a given instant. In the example of journey from Chandigarh to Delhi, the reading on the speedometer at a specific time, say while crossing Panipat would be the instantaneous rate at that time.

Different chemical reactions proceed at different rates. Certain reactions get to equilibrium in a few minutes or seconds, while certain others may take days or even years. That is, the rate of a chemical reaction can be rapid or slow. For example, the addition of a solution of silver nitrate to a solution of sodium chloride gives a precipitate almost instantaneously while rusting of iron takes place in days to years depending upon the environmental conditions. Further, the conversion of graphite to diamond takes millions of years. In studying the kinetics or the rate of a reaction different ways of representing the rates are used. These are: average rate, instantaneous rate and initial rate. The concept of rate of a reaction is very crucial for a proper understanding the domain of chemical kinetics; therefore, we need to define these rates precisely. Let us see how we define different types of rate for a reaction?

km/L; kilometre per litre

Average Rate= $\frac{\text{Change in a quantity}}{\text{time taken for the change}}$

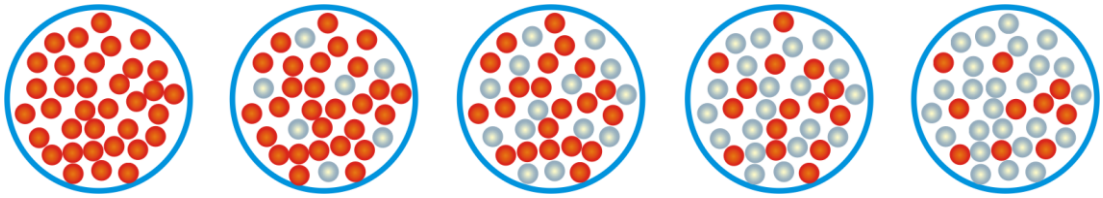
13.3.1 Defining Rate

Let us consider a simple reaction,

$$A \rightarrow B \qquad \ldots(13.1)$$

The progress of this reaction can be followed in terms of change in concentrations of either the reactant A or the product B. As the reaction

proceeds the concentration of the product increases with time whereas that of the reactant decreases with time as shown below. Here, A and B are indicated in terms of grey and red spheres respectively.



Time→

Initially, we have only the reactant molecules. As the reaction proceeds, the number of reactant molecules (A) goes on decreasing whereas that of the product (B) goes on increasing. Graphically, these changes can be represented as shown in Fig.13.1.

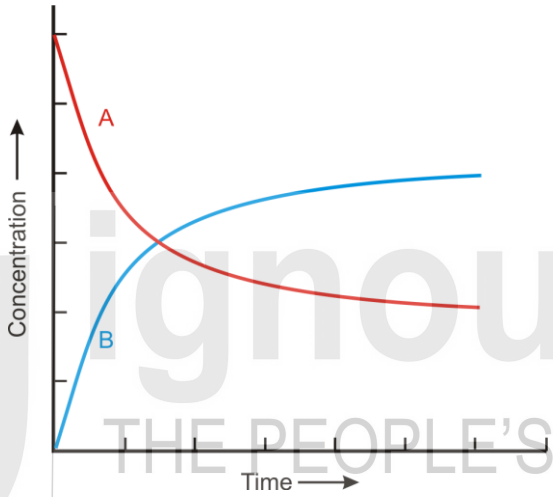


Fig. 13.1:The variation of concentration of the reactant (A) and the product (B) as a function of time for the reaction, A→ B.

In describing a change in a parameter, the symbol, 'Δ' is used. It is pronounced as delta and it refers to the difference between the final value and the initial value of a property or a quantity.

The average rate is defined as the ratio of the change in the concentration to the time taken for the change, i.e.,

$$\text{Average rate} = \frac{\text{Change in the concentration}}{\text{Time taken for the change}} \quad \ldots(13.2)$$

Let us say that in a time interval Δt (delta 't'), the change in the concentration of the product B is Δ[B]. Then the reaction rate will be given as follows:

$$\text{Reaction rate} = \frac{\Delta[B]}{\Delta t} \quad \ldots(13.3)$$

Here, the square brackets refer to the concentration of the species contained in it.

If, on the other hand, we measure the change in the concentration of the reactant A, then the rate would be given as

$$\text{Reaction rate} = -\frac{\Delta[A]}{\Delta t} \quad \ldots(13.4)$$

You may note here that in this case we have put a minus sign before the expression. The introduction of minus sign ensures that the rate is positive. You know that the rate of a reaction cannot be negative (it can only be positive or zero i.e., either the reaction occurs at a certain rate or it does not occur at

all). If we had not used the minus sign then the rate as defined (Eq. 13.2) would have become negative as Δ[A] is negative.

Let us take another simple reaction,

$$2A + 3B \longrightarrow C + 4D \qquad \ldots(13.5)$$

The progress of this reaction can be monitored in terms of change in the concentrations of different reactants or products. If in time interval Δt the change in the concentration of the product C is Δ[C] the reaction rate as defined above, Eq. (13.3) would be given as follows:

$$\text{Reaction rate} = \frac{\Delta[C]}{\Delta t} \qquad \ldots(13.6)$$

The rate of above reaction can equally well be expressed in terms of the 'change in the concentration of the product 'D'. We see from the stoichiometry of the reaction that four moles of 'D' are produced in the time required for producing one mole of C, i.e., D is produced four times as fast as C. So, if we have to define rate in terms of [D], then we must divide it by four which is its stoichiometric coefficient in the balanced chemical equation. This is so because a given reaction proceeds at a given rate, i.e., the rate of a reaction is unique. The reaction cannot have different rates in terms of different reactants or products. In other words, the rate in terms of the product D, would be,

$$\text{Reaction rate} = \frac{1}{4}\frac{\Delta[D]}{\Delta t} \qquad \ldots(13.7)$$

As C and D are both products, their concentration increases as the reaction progresses i.e., Δ[C] andΔ[D] are positive. As discussed above, if we wish to state the rate of the reaction in terms of any of the reactants, then we multiply the rate expression by -1. In other words, we would write the rate of reaction given in Eq. (13.5) as,

$$\text{Reaction rate} = -\frac{1}{2}\frac{\Delta[A]}{\Delta t} \quad \text{or} \quad = -\frac{1}{3}\frac{\Delta[B]}{\Delta t} \qquad \ldots(13.8)$$

- The rate of reaction is always positive.
- Every reaction has a unique rate
- The rate of reaction can be expressed in terms of any reactant or the product

Note that 2 and 3 are the stoichiometric coefficients of A and B, respectively in the reaction. So, we see that in the above example, we have four equivalent ways of expressing the rate of the given reaction i.e.,

$$\text{rate} = \frac{\Delta[C]}{\Delta t} = \frac{1}{4}\frac{\Delta[D]}{\Delta t} = -\frac{1}{2}\frac{\Delta[A]}{\Delta t} = -\frac{1}{3}\frac{\Delta[B]}{\Delta t} \qquad \ldots(13.9)$$

As the units of Δc_i are mol dm^{-3} while that of Δt is second; the units of rate, as defined in Eq. 13.9, are mol dm^{-3} s^{-1}.

In general, the average rate is defined as

$$\text{rate} = \frac{1}{\nu_i}\frac{\Delta c_i}{\Delta t}(\text{For products}) = -\frac{1}{\nu_i}\frac{\Delta c_i}{\Delta t}(\text{For reactants}) \qquad \ldots(13.10)$$

Where, Δc_i is the change in the concentration of the i^{th} species (reactant or product) ; ν_i is the stoichiometric coefficient of the i^{th} species in the balanced chemical equation andΔt is the change in time. As Δc_i has units of mol dm^{-3} and Δt has units of *s* therefore, the rate as defined above would have units of **mol dm^{-3} s^{-1}** or mol/(dm^3.s).

Instantaneous rate

Instantaneous rate is the rate of a reaction at any particular time.

There is another way of defining rate called instantaneous rate. You would recall that in the context of speedometer we said it measures speed of the vehicle at a given instant (instantaneous speed). The same holds true for the rates of chemical reactions also. It refers to the rate of reaction at a given (specified) time. It is defined as

$$\text{Instantaneous rate} = \frac{1}{\nu_i}\frac{dc_i}{dt}(\text{for products}) = -\frac{1}{\nu_i}\frac{dc_i}{dt}(\text{for reactants}) \quad ..(13.11)$$

The instantaneous rate for a given reaction can be represented (like the average rate) in a number of equivalent ways. Let us take the example of formation of ammonia from nitrogen and hydrogen,

$$N_2\,(g) + 3H_2(g) \rightarrow 2NH_3(g) \qquad \ldots(13.12)$$

The rate of this reaction can be measured in terms of either as the rate of appearance of NH_3 or as the rates of disappearance of N_2 or H_2. In terms of the above definition (Eq. 13.10) the instantaneous rate for the reaction can be given as any of the following equivalent expressions.

$$r_{(\text{inst.})} = \frac{1}{2}\left(\frac{dc_{NH_3}}{dt}\right) = -\frac{1}{3}\left(\frac{dc_{H_2}}{dt}\right) = -\left(\frac{dc_{N_2}}{dt}\right) \qquad \ldots(13.13)$$

$$r_{(\text{inst.})} = \frac{1}{2}\left(\frac{d[NH_3]}{dt}\right) = -\frac{1}{3}\left(\frac{d[H_2]}{dt}\right) = -\left(\frac{d[N_2]}{dt}\right) \qquad \ldots(13.14)$$

It is important to understand the difference between the rate of appearance of product (or disappearance of reactant) and the rate of the reaction. In the example discussed above, $\left(\frac{dc_{NH_3}}{dt}\right)$ is the rate of appearance of ammonia i.e., the rate at which ammonia is produced. However, the rate of reaction as written would be $\frac{1}{2}\left(\frac{dc_{NH_3}}{dt}\right)$. Similarly, $\left(\frac{dc_{H_2}}{dt}\right)$ is the rate of disappearance of hydrogen whereas the rate of reaction in terms of disappearance of hydrogen would be $-\frac{1}{3}\left(\frac{dc_{H_2}}{dt}\right)$.

Relationship between Average and Instantaneous Rates

In a kinetics experiment, the basic kinetic data is the variation of the concentration of a reactant (or a product) as a function of time i.e., concentration-time data. Let us take the example of reaction between Zn metal and hydrogen ions to understand the difference between the average and instantaneous rates. The reaction can be given as

$$Zn\,(s) + 2H_3O^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) + 2H_2O\,(l) \qquad \ldots(13.15)$$

The reaction can be followed by measuring the number of moles of hydrogen gas produced as a function of time.

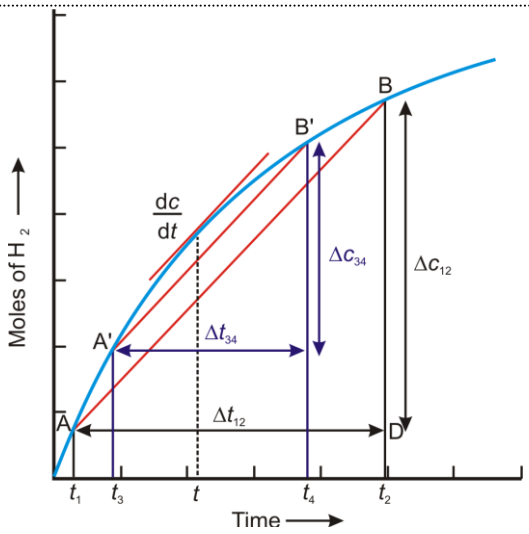


Fig.13.2: The average and instantaneous rate: As $\Delta t \rightarrow 0$, average rate → instantaneous rate.

A typical curve for the reaction between Zinc and acid showing the number of moles of hydrogen produced as a function of time is given in Fig. 13.2.We can see that the rate of formation of hydrogen does not remain constant throughout the progress of reaction. It is quite fast to begin with and gradually becomes slow. This can be inferred from the variation in the steepness of the curve. If from time t_1 to t_2 the concentration of H_2 changes from c_1 to c_2 the average rate within this time is given as the slope of the cord AB (tan <BAD = BD/ AD). This may approximately be thought of as the rate of the reaction at the middle of the time interval i.e., $(t_1 + t_2) / 2$.

For time t_3 to t_4 the length of the cord (A′B′) decreases. As the value of Δt goes on decreasing (as shown in the figure) the length of the cord becomes smaller and smaller till at a specific time t where the cord becomes tangent to the curve at a point where A and B coincide. The slope of the tangent to the curve at this point is called as the **instantaneous rate** of the reaction at the time t. Mathematically speaking; the instantaneous rate is the average rate in the limits of $\Delta t \rightarrow 0$. You may note here that in the definition of instantaneous rate we use derivatives. You would recall from your school mathematics that the derivative of a function (Y) with respect to variable (x) is defined as

$$\frac{dy}{dx} = \lim_{\Delta x \to 0} (\Delta y / \Delta x)$$

The symbol $\Delta t \rightarrow 0$ means that Δt approaches zero.

For time variable can write, $$\frac{dy}{dt} = \lim_{\Delta t \to 0} (\Delta y / \Delta t) \qquad \ldots(13.16)$$

You may note here that the term in the bracket represents the average rate of change in y whereas the term on left hand side gives the instantaneous rate. Thus, the average rate approaches the instantaneous state, as Δt approaches zero (i.e., $\Delta t \rightarrow 0$).

13.3.2 Calculation of Reaction Rate

You may be curious to know as to how the reaction rates are calculated. Let us take the following reaction:

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g) \qquad \ldots(13.17)$$

To determine the rate, we measure the concentration of the reactants or product (s) as a function of time. The observed values of the concentration of the reactants and the products for this reaction as a function of time are given in Table 13.1.

Table 13.1: Concentrations of NO_2, NO and O_2 as a function of time at 673 K

Time/s	$[NO_2]$/M	[NO]/M	$[O_2]$/M
0	0.0100	0.0000	0.0000
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033

Based on the experimental concentration versus time data given in Table 13.1, we plot graphs of concentration variation with time as given in Fig. 13.3. We can use these graphs to calculate the rate of reaction with respect to different components.

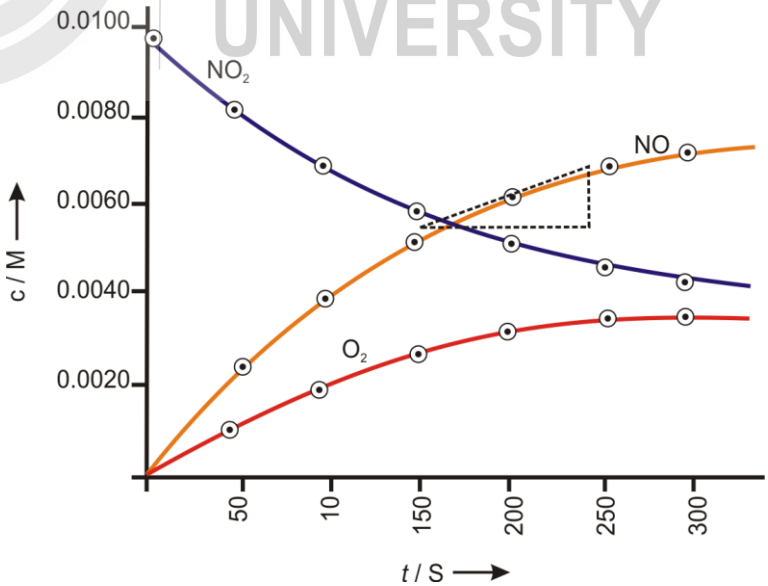


Fig. 13.3: Concentration against time plots for NO_2, NO, and O_2 based on the data given in Table 13.1

Let us consider the curve representing concentration against time plot for NO_2. You may note the falling nature of the curve which is characteristic of concentration against time plot for a reactant. Suppose we wish to determine the rate at a time of 200s. Since it is the rate at a particular time, i.e., it is instantaneous rate, we can write the rate as

$$\text{Rate} = -\frac{1}{2}\frac{d[NO_2]}{dt} \qquad \ldots(13.18)$$

where, $\frac{d[NO_2]}{dt}$ is the rate of consumption of NO_2 and it can be obtained by determining the slope of the curve at 200s that is,
Rate of consumption of NO_2 at 200 s

= (Slope of the tangent line at t = 200 s)= (-1.31×10^{-5}) M s^{-1}

We can get the rate of reaction as

$$\text{Rate} = \frac{1}{2}\frac{d[NO_2]}{dt} = -\frac{1}{2}(-1.31\times10^{-5})\text{M s}^{-1} = (6.55\times10^{-6})\text{M s}^{-1} \qquad \ldots(13.19)$$

Now let us take up the curve representing concentration versus time plot for NO. You may note the increasing nature of the curve which is characteristic of concentration against time plot for a product. Suppose we wish to determine the rate at a time of 200 s i.e., we wish to know the rate at 200 s. Since it is again the instantaneous rate, we can write the rate as

$$\text{Rate} = \frac{1}{2}\frac{d[NO]}{dt} \qquad \ldots(13.20)$$

Where, $\frac{d[NO]}{dt}$ is the rate of formation of NO and it can be obtained by determining the slope of the tangent to the concentration versus time curve at 200s; that is,

Rate of formation of NO at t = 200 s

= (Slope of the tangent to the curve at t = 200 s) = (1.30×10^{-5}) M s^{-1}

We can get the rate in terms of formation of NO as

$$\text{Rate} = \frac{1}{2}\frac{d[NO]}{dt} = \frac{1}{2}(-1.30\times10^{-5})\text{M s}^{-1} = (6.50\times10^{-6})\text{M s}^{-1} \qquad \ldots(13.21)$$

Similarly, we can determine the rate of reaction in terms of the formation of O_2. It comes out to be (6.25 × M s^{-1}).You may verify the same by calculating it yourself as explained above. Based on these calculations you can note that the rate of reaction is approximately the same whether it is determined in terms of NO_2, NO or O_2. This is as expected because as stated above, the rate of a reaction is unique (a reaction occurs at a given rate) though it may be expressed in different ways.

We have so far learnt about two kinds of rates, the average rate and instantaneous rate defined by Eq. 13.9 and Eq.13.10 respectively. There is another term called **initial rate**. It is the rate in the initial stages of the reaction i.e., at time '*t*' close to zero. It is defined as the rate of the reaction as soon as the reactants are mixed. It is the instantaneous rate of the reaction at a time very close to zero. One way to obtain the initial rate is to plot concentration versus time graph and draw tangent at t=0. The slope of this tangent will give the initial rate. However, since it is quite a tedious process, so usually it is obtained by dividing the change in concentration of reactant / product

From the slope of the tangent line drawn (corresponding to a particular time) to the concentration (c) against time (t) curve for a component, we can obtain the rate of the reaction.
Rate of reaction

$$= \frac{-(\text{slope of tangent to the } c \text{ against } t \text{ curve for the reactant})}{\text{Stoichiometric coefficient of the reactant}}$$

$$= \frac{-(\text{slope of tangent to the } c \text{ against } t \text{ curve for the product})}{\text{Stoichiometric coefficient of the product}}$$

The concentrations of components are given in molarity (M) unit.
1 M = 1 mol dm^{-3}

(Δ [reactant /product]) in a brief time interval (Δt) immediately after the mixing of reactants with Δt. That is, we measure an average rate over a very short time from the beginning of the reaction. This method takes advantage of the fact that for a very short time interval in the beginning of the reaction, the concentration versus time curve and the tangent to the curve at t=0, almost coincide with each other (Fig. 13.4).

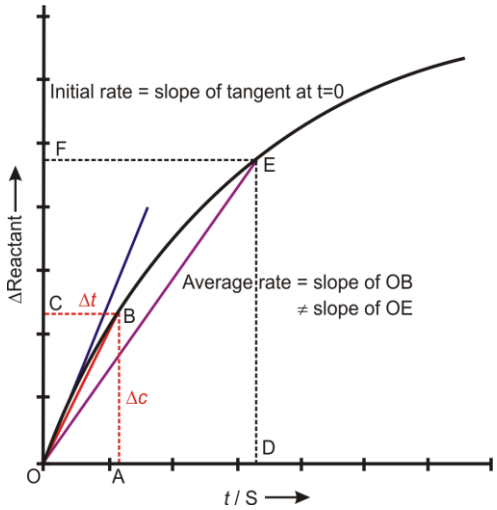


Fig. 13.4: Illustration of Initial rate being approximately equal to the average rate for very small value of Δt.

We will talk more about initial rate later. For now, we would like to take up different methods of measuring rates of reaction. However, before that answer the following simple questions to assess your learning.

SAQ 1

At 323 K, the rate of reaction for the decomposition of N_2O_5 at a particular instant is 2.74 x 10^{-4} M s^{-1}. Calculate the rate of formation of O_2. The reaction is represented below:

$$2N_2O_5\ (g) \rightarrow 4NO_2 + O_2\ (g)$$

SAQ 2

In the decomposition reaction of hydrogen iodide, given below

$$2HI\ (g) \rightarrow H_2\ (g) + I_2\ (g)$$

what is the relationship between the rate of reaction in terms of decomposition of HI and in terms of formation of H_2 (g)?

SAQ 3

Write the expressions for the (i) average (ii) instantaneous rates of the reaction,

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

in terms of concentration of N_2(g) and NH_3(g).

13.3.3 Measurement of Rate of Reaction

As was indicated earlier, we generally deal with reactions in homogeneous medium. We had seen that for homogenous reactions, it is convenient lo represent rate in terms of concentration of reactants or products. So, generally the measurement of rate involves the determination of concentration of a species among the reactants or products as a function of time. A number of experimental methods are available for the determination of concentration as a function of time. These methods depend primarily on the nature of species involved. Let us take up a few of those methods.

i) **Measurement of pressure or volume of a gas:** In some reactions, one of the reactants or products is a gaseous species. In such cases, the measurement of pressure or the volume of the gas produced or consumed provides an elegant method of assessing its concentration. This can be used in obtaining the rate of reaction. For example, the decomposition of H_2O_2can be conveniently followed by measuring the volume of O_2(g) evolved as a function of time.

When more than one of the components is in gaseous phase, the partial pressures of the species is to be calculated with the help of reaction stoichiometry.

$$H_2O_2(aq) \rightarrow H_2O(l) + O_2(g) \qquad \ldots(13.22)$$

ii) **Titrimetry**: It is one of the most commonly used methods to follow the progress of a reaction. If any of the reactants or products can be suitably titrated without any interference from other species in the reaction mixture, then this method is useful. For example, the progress of the reaction given above (Eq. 13.21) can equally well be followed by titrating equal volumes of the reaction mixture at different time intervals against $KMnO_4$ solution. H_2O_2 and $KMnO_4$ react as follows:

$$5H_2O_2(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g) \qquad \ldots(13.23)$$

In many instances, we can follow the reaction by measuring a physical property the value of which is directly proportional to the concentration of a reactant or product. The instrumental methods which make use of the variation in the physical property for measuring the concentration have an added advantage that the concentration can be measured directly without disturbing the reaction mixture. Let us take up a few cases.

iii) **Conductometry and potentiometry:** In some cases, the progress of the reaction is characterised by a continuous change in the conductance, emf or pH of the reaction mixture. In such cases, a suitable instrumental method can be devised to follow the reaction. For example, the saponification of ethyl ethanoate (ethyl acetate) given below can be followed conductometrically i.e., by conductance measurement.

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COO^- + C_2H_5OH + Na^+ \qquad \ldots(13.24)$$

As the reaction proceeds, the conductance of the solution decreases due to the replacement of highly mobile hydroxyl ions with less mobile acetate ions. The concentration of sodium ions remains constant

therefore they are not considered. The progress of this reaction can, therefore, be followed by measuring the conductance of the reaction mixture.

iv) **Spectrophotometry or colorimetry:** In some reactions, one of the components has a distinct absorption band in the visible or ultra-violet region of the spectrum. The progress of such a reaction can be followed in terms of absorbance at a characteristic wavelength. For example, iodination of 2-propanone (acetone) given below can be followed colorimetrically as it has a characteristic absorption band around 565 nm.

$$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI \quad \ldots(13.25)$$

In a mixture containing acetone and iodine in presence of acid, the concentration of iodine decreases with the passage of time. This can be determined by measuring the absorbance of solution as a function of time.

v) **Polarimetry:** If in a reaction, an optically active substance is either consumed or produced, then the progress can be followed with the help of a polarimeter that measures the optical rotation of the solution. Study of inversion of sucrose is one of the experiments based on polarimetry. The hydrolysis of sucrose in presence of a mineral acid takes place according to the following equation.

Polarimeter is an instrument used for measurement of optical rotation of a given sample.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{fructose}}{C_6H_{12}O_6(aq)} \quad \ldots(13.26)$$

The reactant sucrose is dextrorotatory whereas the hydrolysis products viz., glucose and fructose are dextrorotatory and laevorotatory respectively. Further the laevorotation(-92^o) of fructose is more than the dextrorotation (52.5^o) of glucose. Therefore, as the hydrolysis proceeds the dextrorotatory sucrose gradually changes into the laevorotatory mixture and this change can be followed by using a polarimeter that measures the optical rotation of the solution. As the sign of optical rotation changes, the reaction is called inversion of sucrose.

NMR : Nuclear magnetic resonance
ESR : Electron spin resonance

Besides these, a number of highly sophisticated instruments like NMR, ESR and mass spectrometer are also used to study reaction kinetics. This is beyond the scope of our study. So upto now, we have learnt about rate of a reaction, its expression, significance and measurement. Let us now see what are the factors that affect the rate of a reaction? Before that, attempt the following simple question to assess your understanding of these concepts.

SAQ 4

State the name of a suitable experimental method that can be followed to monitor the reaction rate in each of the following cases:

i) $H_2(g) + Br_2(g) \rightarrow HBr(g)$

Hint: Bromine absorbs in the visible region, while hydrogen and hydrogen bromide do not.

ii) $CH_3COOC_2H_5$ (aq) + OH^- (aq) → CH_3COO^- (aq) + C_2H_5OH (aq)

iii) CH_3CHO (g) → CH_4 (g) + CO(g)

13.3.4 Factors Affecting the Rate of a Reaction

Reaction rates can be affected in a number of ways. There are four common factors that can affect the rate of a reaction. These are

- Nature of the reactants
- Concentration of reactants
- Temperature
- The use of a catalyst

Let us discuss these one by one

Nature of the Reactants

According to the collision theory of reaction rates (you would have learnt about it in your school and would learn in detail about it in the next unit) the reactants produce products by its molecule colliding with one another. The more often they collide, more likely the chance that the product will form. In the gaseous state the molecules move around quite rapidly and are more likely to collide and form product. Therefore, in the gaseous state the reactions usually occur rapidly. The reacting molecules dispersed in a solution are the next most favorable way for product to form at a reasonable speed. On the other hand, the reactions do occur in pure liquids or in solid form, but the rates tend to be rather slow because the reacting molecules are quite restricted in their movement among one another, and therefore, do not come into contact very often. The relative rates vary roughly as:

The chalk powder reacts much faster with HCl whereas the piece of chalk reacts relatively slowly. This can be observed in terms of the rate of evolution of hydrogen gas.

Gases > solutions > pure liquids > solids

In reactions involving solids the reaction occurs at the boundary surface of the solids. Greater the contact between the reactants at the solid boundary surface greater is the rate of the reaction. Therefore, subdividing a solid into smaller particles increases the reaction rate. The effect of surface area of the reactant on the rate of the reaction can be seen in the reaction of a piece of chalk or powder of chalk with hydrochloric acid. The reaction with chalk powder will be much faster than that of with the piece of chalk (You may try to do it yourself in the lab when you get an opportunity).

Concentration of Reactants

The dependence of the rate of reaction on the concentration of the reactants and products has no unique relationship. Generally, the rate of reaction increases with the increase in the concentration of the reactants. The rates of some reactions increase much more than those of the others on increasing the concentration of the reactants. However, some reactions become slower on

increasing the concentration of the reactants and sometimes even the concentration of the products also affect the rate of the reaction. The exact relationship between the concentration of reactants and products and the reaction rates are defined by the kinetic rate laws which are to be determined experimentally for every reaction. We shall deal with these in the next section.

Temperature

The rate of a reaction generally increases with the increase in the temperature. As a rule of the thumb the rate becomes about double for every increase of 10°C in the temperature. A temperature dependence study of the rate of a reaction can provide useful thermodynamic parameters about the reaction. We shall deal with the details of temperature dependence of reaction rates in the next unit.

Use of a Catalyst

A catalyst is defined as a substance which alters the rate of a reaction but doesn't undergo any permanent chemical change in itself. It might undergo temporary change in the molecular structure, but ultimately the catalyst molecule is restored to its original structure before the product is formed. Catalysts provide an alternative path of lower energy of activation so that product might be formed at a lower temperature or at higher rate. In some cases, if a suitable catalyst is not there then the reaction would occur so slowly that practically product formation would not be feasible. From a molecular point of view the catalyst provides a surface for the reactant molecules to position themselves with one another so that when they do collide, they will do so much more effectively.

13.4 RATE LAWS

In kinetics we generally study the reactions under conditions where the rate of the forward reaction is significant, but the reverse reaction rate is low. This is made possible, if we study the reaction upto a point where the product amounts are not high. For example, in the decomposition of NO_2, there could be a decrease in the concentration of NO_2 upto a particular time. Afterwards, enough nitric oxide and oxygen are formed, and the reverse reaction could also take place leading to the formation of NO_2. As mentioned before, in general, the rates of reactions are complex functions of the concentrations of the reactants and the products at a given temperature. However, there are some reactions in which the rates are proportional to the simple powers of the concentrations of the reactants. Let us take some examples to illustrate it.

1. Decomposition of N_2O_5

N_2O_5 decomposes as per the following equation.

$$2N_2O_5\ (g) \rightarrow 4NO_2(g) + O_2(g) \qquad \ldots(13.27)$$

The results of the study of decomposition of N_2O_5 at different concentrations of N_2O_5 at 323 K are compiled in Table 13.2.

Table 13.2: Rates for the decomposition of N_2O_5 for different concentrations of N_2O_5at 323 K

(i) Initial concentration of $[N_2O_5]$/M	(ii) Rate/M s^{-1}	(iii) $\frac{\text{Rate}}{[N_2O_5]}$ / s^{-1}
0.300	2.73×10^{-4}	9.1×10^{-4}
0.150	1.73×10^{-4}	9.1×10^{-4}
0.100	9.10×10^{-5}	9.1×10^{-4}

From columns (i) and (ii), of Table 13.2 you can see that the rate for the decomposition of N_2O_5 decreases with the decreases in the concentration of N_2O_5. The column (iii) gives the ratio of the rate of the reaction to the concentration of N_2O_5. This shows that for all the three concentrations, the ratio of the rate of the reaction to the concentration of N_2O_5 is a constant i.e.,

$$\frac{\text{Rate}}{[N_2O_5]} = k \qquad \ldots(13.28)$$

On rearranging, we can write, rate = $k\,[N_2O_5]$ …(13.29)

This shows that the rate of this reaction is proportional to the concentration N_2O_5 where, k is the proportionality constant. Let us take another example,

2. Decomposition of hydrogen iodide at a constant temperature.

$$2HI(g) \rightarrow H_2(g) + I_2(g) \qquad \ldots(13.30)$$

The instantaneous rates of this reaction at different concentrations of HI are given in Table 13.3

Table 13.3: Rates for the Decomposition of HI for different concentrations and rate to concentration ratios at 323 K

(i) [HI]/M	(ii) Rate/M s^{-1}	(iii) $\frac{\text{Rate}}{[HI]}$ / s^{-1}	(iv) $\frac{\text{Rate}}{[HI]^2}$ / $M^{-1}\,s^{-1}$
3.00×10^{-2}	3.60×10^{-5}	1.2×10^{-3}	4.00×10^{-2}
2.00×10^{-2}	1.60×10^{-5}	8.0×10^{-4}	4.00×10^{-2}
1.50×10^{-2}	9.01×10^{-6}	6.0×10^{-4}	4.00×10^{-2}

From Table 13.3, you can see that the rate of decomposition of HI decreases with decreases in the concentration of HI, as in the decomposition of N_2O_5. However, it is evident from column (iii) that the ratio of the rate to the concentration of HI (rate / [HI]) is not a constant but, as per column (iv), the rate / $[HI]^2$ is a constant i.e.,

$$\text{Rate} / [HI]^2 = k \qquad \ldots (13.31)$$

On rearranging, we can write, rate = $k\,[HI]^2$ … (13.32)

This shows that the rate of reaction is proportional to the square of the concentration of HI.

13.4.1 Differential rate Laws: Concentration Dependence of Rate

For many chemical reactions, the relationship between the reaction rate and the concentration can be expressed in a simple way as in Eq. 13.24 or Eq. 13.27. Such a relationship is called the **differential rate law.** Thus, *a differential rate law is an equation expressing the relationship between the instantaneous reaction rate and the concentrations of the reactants in a reaction.* In general, the rate of reaction may depend on the concentration of one or more reacting species. Further, the proportionality between rate and concentration may be direct or inverse. The actual dependence of rate on the concentration of various species measured by any of the methods described above is expressed as differential rate law or differential rate equation.

Rate law and rate constant

In general, the rate law for a simple reaction with one reactant may be of the following type:

$$\text{Reaction rate} = k\,[\text{Reactant}]^p \qquad \ldots (13.33)$$

From Eq. 13.33, it can be seen that if [reactant] = 1, then rate=*k*. For this reason, *k* is called the specific rate.

Where, the proportionality constant *k* is called the **rate constant** or **rate coefficient** or the **specific rate constant of reaction**. Thus, by definition, the rate constant is independent of concentration, but it may depend on other factors like temperature and presence of catalyst etc. In this equation, *n* is called the order to the reaction.

Comparing Eq. (13.33) with Eq.(13.29) and Eq.(13.32), we conclude that

i) p = 1 in Eq. 13.29; i.e. decomposition of N_2O_5 is a **first order** reaction. The significance of this statement is that the reaction rate is proportional to the first power of concentration of N_2O_5.

$$\text{i.e. Rate} = k\,[N_2O_5]^1 \qquad \ldots (13.34)$$

where, *k* is the **first order rate constant**

ii) p = 2 for the decomposition of HI; i.e. the decomposition of HI is a **second order reaction.** Again, this means that the decomposition rate of HI is proportional to the second power or square of the concentration of HI.

$$\text{i.e. Rate} = k\,[HI]^2 \qquad \ldots (13.35)$$

where, *k* is the **second order rate constant**

The rate constant can be visualised as the rate of reaction when all the species in rate equation are at unit concentration. For this reason, the rate constant is also known as the **specific rate constant**.

Units for Rate Constant

For a rate equation expressed as: rate = k $[A]^p$; the order for the reaction is p and the units for rate are mol dm^{-3} s^{-1}. We can derive the units for the rate constant (*k*) for reaction of different orders.

The units of rate constant depend on the overall order of the reaction. It has the dimensions of concentration $^{(\text{I-order})}$ time $^{-1}$ i.e., concentration$^{(1-n)}$ time^{-1}.

For a **zero-order** reaction: rate = $k\,[A]^0$

Since $[A]^0$=1; rate =*k*

Therefore, *k* would have the units of rate i.e., **mol dm^{-3} s^{-1}** …(13.36)

For a **first order** reaction: rate = $k[A]^1$; =>*k* =rate/ [A]

Since the units of rate are mol dm^{-3} s^{-1} and that of [A] are mol dm^{-3}

k would have units of mol $dm^{-3}s^{-1}$/mol dm^{-3} = **s^{-1}** …(13.37)

Similarly for a **second order** reaction; rate = $k\,[A]^2$;

$[A]^2$ has units (mol $dm^{-3})^2$; *k* would have units of rate/ (mol $dm^{-3})^2$

or mol dm^{-3} s^{-1}/ (mol $dm^{-3})^2$ or dm^3 mol^{-1} s^{-1} or **(mol $dm^{-3})^{-1}$ s^{-1}** …(13.38)

Order of Reaction and Stoichiometry

The rate laws as well as the order of the reaction must be determined experimentally; these cannot be predicted from the stoichiometry of the reaction. The stoichiometry of reaction gives the relationship between the amounts of the reactants and the amounts of the products. The stoichiometry of a reaction must be differentiated from the order of a reaction. Let us consider the following examples.

Example 13.1: The gas-phase decomposition of N_2O_5 yields NO_2 and O_2 at a given temperature as per the following reaction.

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

The experimentally observed rate law for the reaction is: rate = *k* $[N_2O_5]$

We see that the stoichiometric coefficient of N_2O_5 in the reaction is 2 whereas the order of reaction with respect to N_2O_5 is 1.

Example 13.2: The balanced equation for the decomposition of nitrous oxide is given below:

$$2N_2O(g) \rightarrow)2N_2(g) + O_2(g)$$

The experimentally determined rate law is rate = *k* $[N_2O]$

In this example, the stoichiometric coefficient of N_2O is 2 whereas the order of reaction with respect to N_2O is 1.

In the above examples, the order of reaction and the stoichiometry are not identical. But there are cases where the order and stoichiometric coefficient are identical. One of the examples can be seen in the following reaction:

Example 13.3: For the decomposition of HI reaction,

$$2HI\,(g) \rightarrow H_2\,(g) + I_2\,(g)$$

The experimentally determined rate law is

Rate = $k\,[HI]^2$

In this reaction the order of reaction with respect to HI is two and the stoichiometric coefficient of HI is also 2.

From the above examples, you can see that the stoichiometric coefficient and the order of the reaction with respect to a species need not be the same always. You must bear in mind the following points while arriving at a rate law:

i) The order of the reaction must be determined experimentally; the experimental methods will be discussed in the next unit.

ii) In the case of simple reactions, the concentrations of the reactants appear in rate law; but the concentrations of the products do not appear in the rate law. It is so because generally the rate measurements are done under the conditions where the reverse reaction rate is negligibly low.

iii) The order of a reaction need not be identical with the stoichiometric coefficient of the reactant.

So far, we have considered the reactions involving only one reactant. In case of reactions involving many reactants, the rate of a reaction may depend on the concentrations of more than one reactant.

In general, for a reaction

$$A + B + C \rightarrow \text{products} \qquad \ldots(13.39)$$

The experimentally determined rate law may be represented as,

$$\text{rate} = k[A]^p\,[B]^q\,[C]^r \qquad \ldots (13.40)$$

In this expression, [A], [B]... etc., represent the molarities of the species in the brackets. The exponent of a reactant concentration in the rate law represents the **order of the reaction** with respect to that reactant. The sum of the exponents of the concentration terms in the rate law is called the **overall order**. The exponents p, q, r .., in the experimentally determined rate law are generally small positive integers. However, in certain cases, these may be fractional or even negative also.

For the rate law given in Eq. 13.40, we say that the reaction is of p^{th} order with respect to A and of q^{th} order with respect to B and so on. The overall order of the reaction is $p+q+r$.....Let us take one more example.

Example 13.4: For the following reaction,

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

The experimentally determined rate law has been found to be

$$\text{Rate} = k[BrO_3^-][Br^-][H^+]^2$$

Thus, the reaction is first order in BrO_3^-, first order in Br^- and second order in H^+. The overall rate of the reaction is four (1+1+2=4).

For the following reaction

$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$

let us compare the order of reaction and the stoichiometric coefficient for each reactant.

	BrO_3^-	Br^-	H^+
Order	1	1	2
Coeff.	1	5	6

It may be noticed that the stoichiometric coefficient and the respective order of reaction are not identical.

It is reiterated again that the rate law is to be arrived at from the experimental measurement of dependence of the rate of a reaction on the concentration of reactants and not from the stoichiometric equation.

In a kinetic experiment, we normally measure concentration as a function of time. So, we would like to have a relationship between concentration and time. Such a relationship is provided by the integrated rate laws. Let us see how we obtain these rate laws? However, before that, try the following simple questions to assess your understanding.

SAQ 5

State the units of the rate constants for zeroth order, first order and second order reactions.

SAQ 6

The experimentally determined rate law for the following reaction,

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

is, rate = $k\,[NO]^2\,[Cl_2]$

What is the i) order of reaction with respect to $[Cl_2]$?

ii) overall order of reaction, and iii) units for k?

13.4.2 Integrated Rate Laws: Time Dependence of Concentration

Differential rate laws given above represent the rate of the reaction as a function of concentration of reactants. Except for zero-order rate law (for which the rate is independent of concentration) the rate of a reaction will change as the reaction proceeds because the concentrations of reactants and products change with the progress of the reaction. The results of rate determination would depend on when the rate has been determined. It is, therefore, desirable to have an expression that describes the change in the reactant concentration as a function of time. Such an expression can be obtained by the mathematical process of integrating the differential rate equations.

The integrated rate equation can be used to predict the concentration of the reactant at any time. The integrated rate equations have an additional advantage that these provide different ways of plotting the experimental data which in fact can be used to determine the order of the reaction. Let us derive the integrated rate equations for reactions with some simple orders and learn about their characteristics.

I. Zeroth order reactions

The differential rate law for a zeroth order reaction is of the following form,

$$\frac{-\mathrm{d[A]}}{\mathrm{dt}} = k[\mathrm{A}]^0 \quad \ldots (13.41)$$

Any number raised to the power zero is equal to 1.

Since $[\mathrm{A}]^0 = 1$, $\frac{-d[\mathrm{A}]}{dt} = k$ … (13.42)

This implies that for a zeroth order reaction, the reaction rate is independent of the concentration of the reactant. That is, a zero-order rate law can be observed only if the actual reactant concentrations do not change as the reaction proceeds, which is uncommon, and so zero-order rate laws are also not common. However, some examples of zero-order reactions are given below:

i) Decomposition of ammonia on a hot platinum surface.

$$2\mathrm{NH_3(g)} \xrightarrow{\mathrm{Pt}} 2\mathrm{N_2(g)} + 3\mathrm{H_2(g)} \quad \ldots (13.43)$$

ii) Decomposition of nitrous oxide on a hot platinum surface.

$$2\mathrm{N_2O(g)} \xrightarrow{\mathrm{Pt}} 2\mathrm{N_2(g)} + \mathrm{O_2(g)} \quad \ldots (13.44)$$

iii) Decomposition of hydrogen iodide on finely divided gold at 320 K.

$$2\mathrm{HI(g)} \xrightarrow{\mathrm{Au}} \mathrm{H_2(g)} + \mathrm{I_2(g)} \quad \ldots (13.45)$$

Let us derive the integrated rate law for a zeroth order reaction.

For a general reaction

$$\mathrm{A} \rightarrow \text{products} \quad \ldots (13.1)$$

If the order is zero, the differential rate law would be

$$\frac{-d[\mathrm{A}]}{dt} = k \quad \ldots (13.46)$$

Rearranging, we get

$$-\mathrm{d[A]} = \kappa \mathrm{d}t \quad \ldots (13.47)$$

Integrating Eq. (13.47) we get,

$$-\int \mathrm{d[A]} = \kappa \int \mathrm{d}t \;\Rightarrow -[A] = kt + \text{constant} \quad \ldots (13.48)$$

Where, [A] is the concentration of the reactant at time *t*. At the start of the reaction i.e., when $t = 0$, the concentration of A equals the initial concentration of reactant i.e., [A] is equal to $[\mathrm{A}]_0$.

Substituting in Eq. (13.48), we get

$$-[A]_0 = \text{constant of integration} \quad \ldots (13.49)$$

Substituting the value of the constant of integration back in Eq.(13.48) we get

$$-[A] = kt - [A]_0 \quad \ldots (13.50)$$

This can be rearranged to

$$[A]_0 - [A] = kt \quad \ldots (13.51)$$

or $$[A] = [A]_0 - kt \quad \ldots (13.52)$$

or $$[A] = -kt + [A]_0 \quad \ldots (13.53)$$

which are the integrated rate law expressions for a zero-order reaction. Comparing Eq.(13.53) with the equation of a straight line y=mx + c, we see that this will give a straight-line plot if measured values of reactant concentration, [A] are plotted against time. The slope of the plot will be equal to –*k*, the negative of **zero-order rate constant,** and the intercept would be the initial concentration, $[A]_0$;Fig. 13.5.

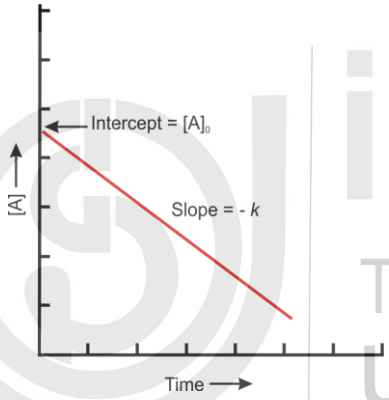


Fig. 13.5: Plot of integrated rate law for zero-order reaction

Let us take an example to see the application of integrated rate law expression for zero order reactions

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Example 13.5: The decomposition of hydrogen iodide on gold at 323 K is zeroth order reaction and the rate constant for it is found to be 1.20×10^{-4} M s^{-1}.

a) If the initial concentration of hydrogen iodide is 0.500 M, calculate its concentration after 3.00×10^3 s.

b) How long will it take for all of the hydrogen iodide to decompose?

Solution: **a)** Using Eq. 13.52, $[A] = [A]_0 - kt$

Substituting the value

$$A = (0.500 - (1.20 \times 10^{-4} \times 3.00 \times 10^3))M = 0.140 \text{ M}$$

(b) If hydrogen iodide completely decomposed, then [A] = 0

The Eq. (13.52) under these conditions becomes

$$0 = [A]_0 - kt$$

On rearranging, we get

$$\text{or} \quad t = \frac{[A]_0}{k}$$

Substituting the values, we get

$$\frac{0.500\text{M}}{1.20 \times 10^{-4}\ \text{Ms}^{-1}} = 4.17 \times 10^3\ \text{s}$$

Hence, the reaction will be complete after 4.17 x 10^3 s.

Half-Life of a Zeroth Order Reaction

The time taken for the concentration of a reactant to fall to half its initial value is called the **half-life** of a reaction. It is denoted by the symbol, $t_{1/2}$. We can derive an expression useful for calculating the half-life of a substance undergoing zeroth order reaction using Eq. (13.52); $[A] = [A]_0 - kt$. At half life, the concentration of the reactant A will be half of its initial value i.e,

At $t = t_{t/2}$:[A]= $[A]_0/2$ … (13.54)

Substituting in Eq. (13.52), we get

$$[A]_0/2 = [A]_0 - kt_{1/2} \quad \text{… (13.55)}$$

Rearranging, and simplifying we get

$$t_{1/2} = \frac{[A]_0}{2k} \quad \text{… (13.56)}$$

This means that the half-life of a zeroth order reaction is directly proportional to the initial concentration of the reactant. You may note that since the concentration of the reactant decreases to half after one half-life, the second half life would be half of the first half life and this trend would continue. In other words, the half life period for a Zeroth order reaction keeps on decreasing as shown in Fig. 13.6.

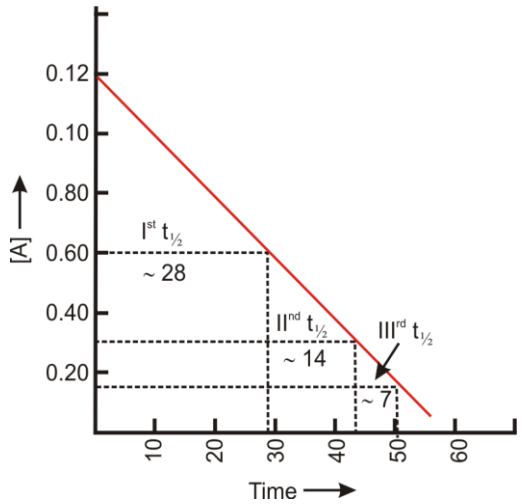


Fig. 13.6: [A] versus t plot for zero-order reaction showing decreasing half-lives.

Let us take an example to see the importance of Eq. (13.56).

Example 13.6: The decomposition of hydrogen iodide on gold at 323 K follows Zeroth order kinetics. Calculate the half-life for the reaction by using the data from the example 5.

Solution: According to Eq.(13.56) the half-life for a Zeroth order reaction is given as

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

Substituting the values of $[A]_0$ and k from example 5 we get

$$t_{1/2} = \frac{[A]_0}{2k} = \frac{0.500\,M}{2 \times 1.20 \times 10^{-4}\,Ms^{-1}} = 2.08 \times 10^3\ s$$

Thus, the half-life of the reaction would be 2.08 x 10^3 s.

II. Integrated Rate Law for First Order Reactions

Let us consider the following reaction, which is experimentally found to be first order.

$$A \rightarrow Products \qquad \ldots (13.1)$$

We can write the differential rate law using Eq.(13.33) as

$$rate = \frac{-d[A]}{dt} = k[A]^1 \qquad \ldots (13.57)$$

Where k is the first order rate constant and n = 1. This means that the rate of consumption of A at any given time is directly proportional to the first power of the concentration of A at that time. In order to obtain the integrated rate for first order reaction, we have to know the concentrations of A at the start of the reaction and at a time t as mentioned below:

At time = 0 (i.e., at the start), the concentration of A = $[A]_0$

At time = t, the concentration of A = $[A]_t$

Using these limits of concentration and time, we can integrate Eq. 13.50 after rearranging it as follows:

$$\int_{[A]_0}^{[A]_t} \frac{-d[A]}{[A]} = \int_0^t k\,dt \qquad \ldots (13.58)$$

i.e., $$-\{\ln[A]\}_{[A]_0}^{[A]_t} = k[t]_0^t \qquad \ldots (13.59)$$

$$-\{\ln[A]_t - \ln[A]_0\} = k(t-0) \qquad \ldots (13.60)$$

$$\ln[A]_0 - \ln[A]_t = kt \qquad \ldots (13.61)$$

Hence, $$\ln\frac{[A]_0}{[A]_t} = kt \qquad \ldots (13.62)$$

Eq. (13.62) can be written in the exponential forms as follows:

$$[A]_t = [A]_0\, e^{-kt} \quad \ldots (13.63)$$

$\ln \frac{[A]_0}{[A]_t} = kt$

Taking antilog we get

$\frac{[A]_0}{[A]_t} = e^{kt}$

$\frac{[A]_t}{[A]_0} = e^{-kt}$

Rearranging,

$[A]_t = [A]_0\, e^{-kt}$

Corresponding to Eq. 13.63, we can draw the concentration versus time plot for first order reaction as shown in Fig. 13.7. Such a curve is called an exponential decay curve. In an exponential decay curve, there is a steep decrease in concentration initially. It is followed by a slower decrease in concentration subsequently. Note that the decay curve goes parallel to x - axis after longer time intervals indicating that the reaction will take infinite time for completion.

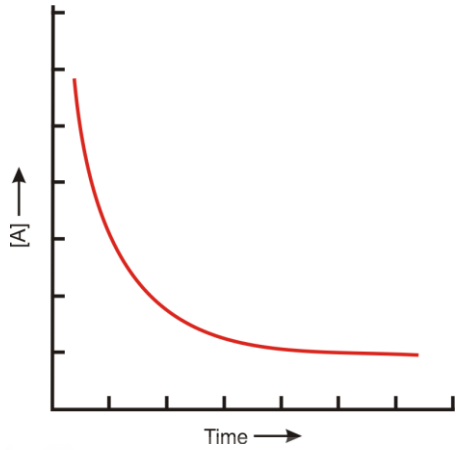


Fig. 13.7: Exponential decay of the concentration of reactant in a first order reaction.

Remember the following formula:
ln x = 2.303 log x

Radioactive decay is a good example of first order reaction. Let us come back to Eq. (13.62). It is more convenient to work with logarithms to the base 10 (known as common logarithms). Hence, we can rewrite Eq. (13.62) as follows:

$$2.303 \log \frac{[A]_0}{[A]_t} = kt \text{ or } k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t} \quad \ldots (13.64)$$

Eq. (13.64) is useful in calculating the concentration of the reactant at a time t (i.e., $[A]_t$) provided, its initial concentration (i.e., $[A]_0$), k and t are known. Also, k can be calculated, if $[A]_0$, and $[A]_t$ and t are known. Further, we can test whether a reaction follows first order or not by using the graphical method.

Graphical Method of Calculating First Order Rate Constant

In order to facilitate graphical representation, Eq. 13.64 is modified as follows:

$$\log \frac{[A]_0}{[A]_t} = \frac{kt}{2.303} \quad \ldots (13.65)$$

Hence, $$\log[A]_0 - \log[A]_t = \frac{kt}{2.303} \quad \ldots (13.66)$$

i.e., $$-\log[A]_t = \frac{kt}{2.303} - \log[A]_0 \quad \ldots (13.67)$$

$$\log[A]_t = \frac{-k}{2.303} t + \log[A]_0 \quad \ldots (13.68)$$

By comparing Eq. (13.65) or Eq. (13.68) with the equation for a straight line,

$$y = mx + c \quad \ldots (13.69)$$

we can infer that by plotting log $[A]_t$or log $\{[A]_t/[A]_0\}$ or log $\{[A]_0/[A]_t\}$ against time, a straight line must be obtained for a first order reaction. Such plots for first order reactions are shown in Figs. 13.8. the rate constant can be obtained by using the slope of the line so obtained.

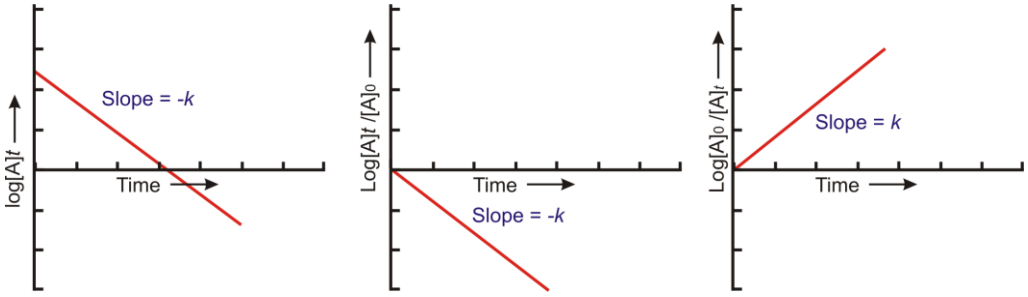


Fig. 13.8: Plots for integrated rate equation for a first order reaction.

Knowing the concentration of a reactant undergoing first order reaction at a particular time, it is possible to calculate its concentration at another time interval using the following equation that can be obtained from, Eq. 13.65

$$\log\frac{[A]_{t_1}}{[A]_{t_2}} = \frac{k}{2.303}(t_2 - t_1) \qquad \ldots (13.70)$$

Here, $[A]_{t1}$ and $[A]_{t2}$ are the concentrations of the reactant at time t_1 and t_2 respectively. The graphical representations of straight line plots for the first order reactions are quite useful in solving the problems based on first order reactions. We will illustrate it with the help of some examples. We will take three different cases.

From Eq. 13.65 we can derive Eq. 13.70 by substituting the concentrations of A at time intervals t_1 and t_2 as follows:

At time = t_1

Concentration of A = $[A]_{t_1}$.

At time = t_2

Concentration of A = $[A]_{t_2}$.

$$\log\frac{[A]_0}{[A]_{t_1}} = \frac{k\,t_1}{2.303}$$

$$\log\frac{[A]_0}{[A]_{t_2}} = \frac{k\,t_2}{2.303}$$

Hence,

$$\log\frac{[A]_0}{[A]_{t_2}} - \log\frac{[A]_0}{[A]_{t_1}} = \log\frac{k}{2.303}(t_2 - t_1)$$

i.e.,

$$\log\frac{[A]_{t_1}}{[A]_{t_2}} = \frac{k}{2.303}(t_2 - t_1)$$

Case-I

The concentration versus time data for the reactant is given. Checking whether the given data corresponds to a reaction showing first order kinetics. Let's take an example.

Example 13.7: On heating cyclopropane to 770 K, it is converted into propene. In one experiment, the following data were obtained:

t /s	0	300	600	900
$\frac{[\text{Cyclopropane}]}{\text{M}}$	1.50×10^{-3}	1.24×10^{-3}	1.00×10^{-3}	8.3×10^{-4}

Using graphical method, test whether the above data satisfy first order rate equation. Calculate the rate constant also.

Solution: As shown above, a graph between log $[A]_t$ versus t must be a straight line with negative slope for a reaction following first order kinetics. Therefore, using the given data, we calculate the log [cyclopropane]/M values and tabulate them along with the corresponding t values as given below.

t/s	0	300	600	900
Log[Cyclopropane]	–2.82	–2.91	–3.00	–3.08

Then we plot a graph between log [cyclopropane] (on y-axis) and time (on x-axis). The plot for the given data is given in Fig. 13.9.

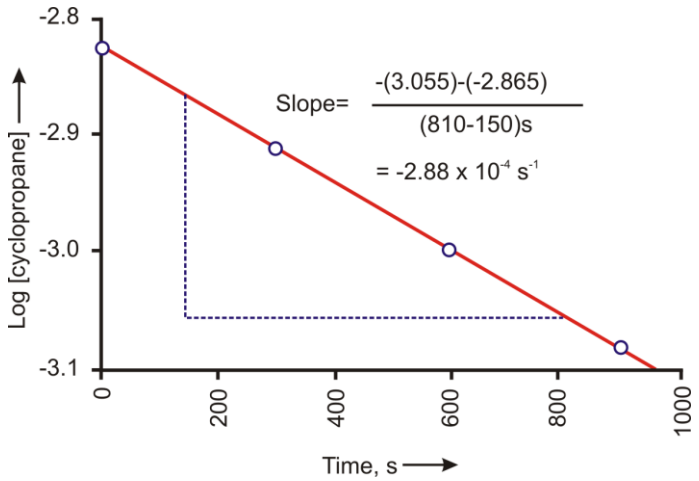


Fig. 13.9: log [cyclopropane] against *t* plot for the data given in the question.

As the graph is a straight line, it confirms that the reaction follows first order kinetics. Now in order to calculate the value of rate constant, we make use of the fact that the slope of the curve is equal to -*k* / 2.303.

The slope of the line = $-k / 2.303 = -2.88 \times 10^{-4}\ s^{-1}$

Simplifying, we get the value of rate constant as

$$k = -2.303 \times \text{slope} = -2.303 \times (-2.88 \times 10^{-4})\ s^{-1}$$

➔ $k = 6.63 \times 10^{-4}\ s^{-1}$

Case-II

The concentration versus time data for the reactant A is not given directly. Instead, the values of parameters such as partial pressure, absorbances, volume, titre values etc. which are proportional to the concentration of the reactant may be given. Our aim again is to check whether the given data corresponds to a reaction showing first order kinetics. In such cases, the measurements made at zero time and given time *t* may be used in place of $[A]_0$ and $[A]_t$ respectively. For example, we can substitute the partial pressure of the reactant instead of its concentration in Eq. 13.65 as follows and obtain a modified expression as follows

$$\log \frac{(p_A)_0}{(p_A)_t} = \frac{kt}{2.303} \qquad \ldots (13.71)$$

Where $(p_A)_0$ and $(p_A)_t$ are the partial pressures of the reactant A at the start and, after a time, *t.* Let's take an example to see the application of Eq. (13.71)

Example 13.8: Azomethane ($CH_3 - N = N - CH_3$) decomposes at 600 K as per the following equation:

$$CH_3 - N = N - CH_3(g) \rightarrow C_2 - H_6(g) + N_2(g)$$

The rate of reaction was followed by measuring the partial pressure of azomethane (p_A) at different time intervals and the observed data is given below:

t/s	0	1000	2000	3000	4000
p_A / Pa	10.9	7.6	5.3	3.7	2.6

Using the data, test whether the reaction follows first order kinetics and also calculate the rate constant.

Solution: You would recall from Unit 8 that the concentration (c_A) of a substance A in a gaseous mixture can be related to its partial pressure (p_A) as follows:

$$p_A = c_A RT \text{ or } p_A \propto c_A$$

So we can use partial pressure of azomethane instead of concentration as shown in Eq. 13.71. Rearranging Eq. 13.71, we get,

$$\log(p_A)_t = \log(p_A)_0 - \frac{kt}{2.303}$$

Where, $\log (p_A)_0$ and $\log (p_A)_t$ are the logarithms of the partial pressures of azomethane at the start of the reaction, and after a time, t. We tabulate the data accordingly:

t/s	0	1000	2000	3000	4000
$\log[(p_A)_t$ /Pa]	1.04	0.88	0.72	0.57	0.41

Then we plot a graph between $\log (p_A)_t$ (on y-axis) and time (on x-axis). The plot for the given data is given in Fig. 13.10.

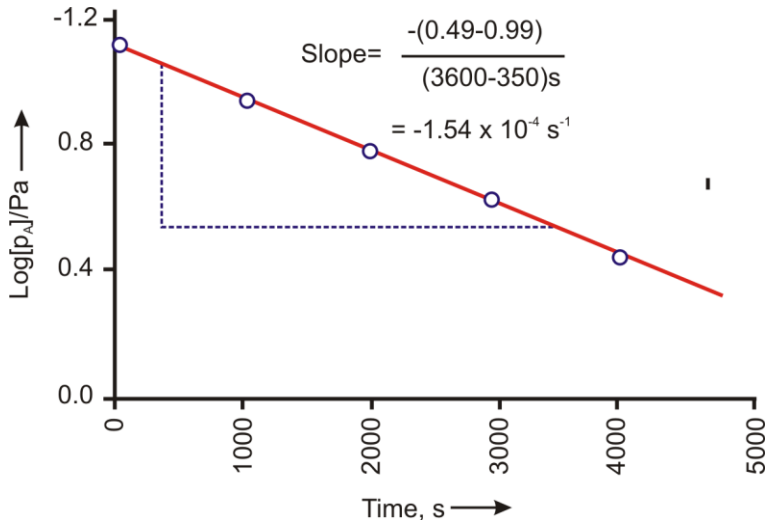


Fig. 13.10: log $(p_A)_t$ versus time plot for the for the data given in the question.

As the graph is a straight line, it confirms that the decomposition of azomethane follows first order kinetics. Now in order to calculate the value of rate constant, we make use of the fact that the slope of the curve is equal to $-k/2.303$.

$$\text{Slope} = -1.54 \times 10^{-4}\ \text{s}^{-4}$$

The value of rate constant would be

$$k = -2.303 \times \text{Slope}$$
$$= -2.303 \times (-1.54 \times 10^{-4}\ \text{s}^{-1})$$
$$= 3.55 \times 10^{-4}\text{s}^{-1}$$

Case-III

Sometimes the rate measurements are made in terms of the concentrations of the product formed. If the stoichiometry of the reaction is such that one molecule of the product is formed when one molecule of the reactant is consumed, then the concentration of the product at $t = \infty$ must be equal to initial concentration of the reactant. Let us assume that the concentration of the product at any given time is x, then x also represents the decrease in the concentration of the reactant after a time, t. Thus, $[A]_0$= concentration of the product at $t = \infty$ and $[A]_t = [A]_0$-x. Using these relationships, Eq.(13.65) could be written as,

$$\log \frac{[A]_0}{[A]_0 - x} = \frac{kt}{2.303} \quad \ldots (13.72)$$

Let us take an example to understand the significance of Eq. (13.72).

Example 13.9: The rate of hydrolysis of benzene diazonium chloride (C_6H_5N = NCl) in its aqueous solution as given below.

$$C_6H_5N_2Cl + H_2O \xrightarrow{\Delta} C_6H_5OH + N_2 + HCl$$

was followed by measuring the volume of nitrogen evolved at different time intervals. The reaction was found to be first order. Using the data given below, calculate the first order rate constant.

Time / s	0	1500	3000	4500	∞
$\frac{\text{Volume of } N_2}{\text{cm}^3}$	0	6.4	12.1	17.6	81

Solution: As you can note that in this example, the rate measurement is done in terms of the concentration of a product. The volume (V_t) of nitrogen produced at any given time, t, is proportional to the concentration of benzene diazonium chloride reacted (x). The

volume at $t = \infty$ (i.e., V_∞) indicates the volume of nitrogen produced by the complete hydrolysis of benzene diazonium chloride and, it is proportional to the initial concentration of benzene diazonium chloride i.e., $[A]_0$.

Thus, $[A]_0 \propto V_\infty$; $x \propto V_t$ and $([A]_0 - x) \propto V_\infty - V_t$

Hence $$\frac{[A]_0}{[A]_0 - x} = \frac{V_\infty}{V_\infty - V_t}$$

Using this relationship in Eq. 13.65, we get

$$\log \frac{V_\infty}{V_\infty - V_t} = \frac{kt}{2.303}$$

Rearranging, we get

$$\log(V_\infty - V_t) = \log V_\infty - \frac{kt}{2.303}$$

Thus, a plot between $(V_\infty - V_t)$ and t would be a straight line for a first order reaction with slope = $-k/2.303$ and intercept as log V_∞. Using the data given above $(V_\infty - V_t)$ and log $(V_\infty - V_t)$ values are tabulated for different t values.

Time / s	0	1500	3000	4500
$(V_\infty - V_t)/cm^3$	81	74.6	68.9	63.4
log $[(V_\infty - V_t)/cm^3]$	1.908	1.873	1.838	1.802

Then we plot a graph between log $(V_\infty - V_t)$ (on y-axis) and time (on x-axis). The plot for the given data is given in Fig. 13.11.

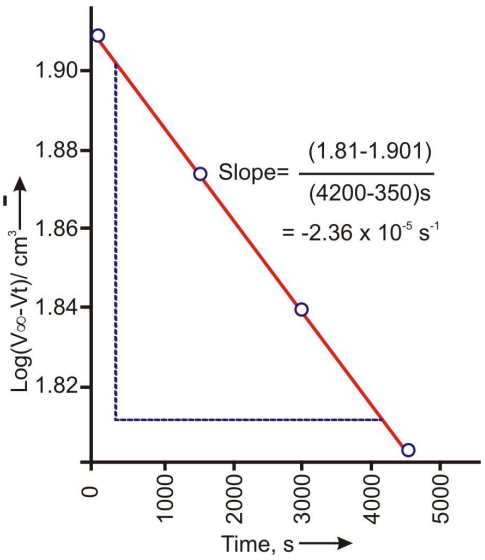


Fig. 13.11: log $(V_\infty - V_t)$ against t plot for the hydrolysis of benzene diazonium chloride as per for the data given in the question.

from Fig. 13.11,

$$\text{slope} = -2.36 \times 10^{-5}\ \text{s}^{-1}$$

We know that the rate constant, $k = -2.303 \times \text{slope}$

Substituting the value of slope, we get

$$k = -2.303 \times (-2.36 \times 10^{-5}\ \text{s}^{-1})$$

$$k = 5.44 \times 10^{-5}\ \text{s}^{-1}$$

Thus, the rate constant for the decomposition of benzene diazonium chloride is found to be $= 5.44 \times 10^{-5}\ \text{s}^{-1}$

Half-Life of First Order Reactions

As stated before, the time taken for the concentration of a reactant to reduce to half its initial value is called the half-life of a reaction. It is denoted by the symbol, $t_{1/2}$. Let us derive an expression for calculating the half-life of a substance undergoing first order reaction using Eq. (13.65) i.e.,

$$\log \frac{[A]_0}{[A]_t} = \frac{kt}{2.303} \quad \ldots (13.65)$$

We must bear in mind that when

$$t = t_{1/2}, [A]_t = [A]_0 / 2$$

Using these relationships in Eq. (13.65), we get,

$$\log \frac{[A]_0}{[A]_0 / 2} = \frac{kt_{1/2}}{2.303} \quad \ldots (13.73)$$

Simplifying,

$$\log 2 = \frac{kt_{1/2}}{2.303} \quad \ldots (13.74)$$

Rearranging, we get

$$t_{1/2} = \frac{2.303 \log 2}{k} = \frac{0.693}{k} \quad \ldots (13.75)$$

From Eq. 13.75, you may note that $t_{1/2}$ does not depend on initial concentration of the substance in the case of a first order reaction. This means that for a given first order reaction, half-life period is the same, whatever be the initial concentration. This fact can be shown graphically as given in Fig. 13.12. Further, we see that the half-life for a first order reaction is inversely proportional to the rate constant i.e., higher the rate constant smaller the half-life.

For a first order reaction, the amount of the reactant remaining after *n* half-life periods is given by the formula:

$$\left\{\begin{array}{l}\text{Concentration}\\ \text{of the reactant}\\ \text{remaining after}\\ n \text{ half - lives}\end{array}\right\} = \left(\frac{1}{2}\right)^n \times \left\{\begin{array}{l}\text{Initial}\\ \text{concentration}\\ \text{of the reactant}\end{array}\right\}$$

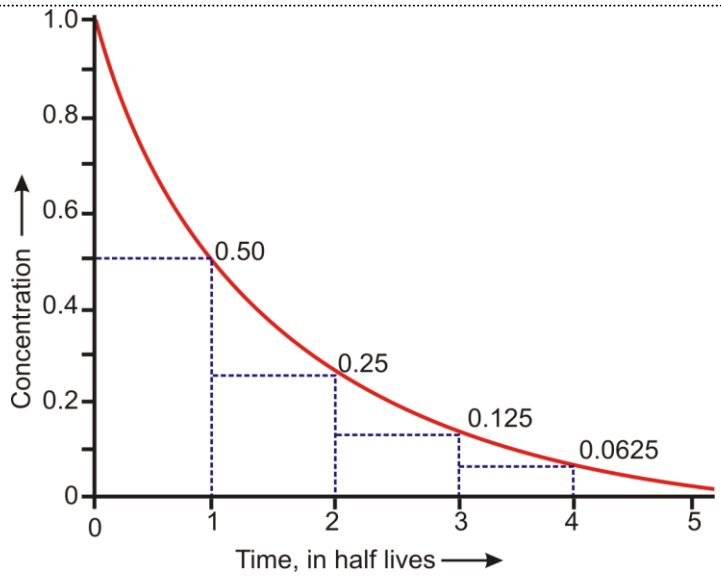


Fig. 13.12: [A] versus *t* plot for first-order reaction showing constancy of the half-lives.

Let us take an example to learn about calculating the $t_{½}$ of a reaction from the given value of the rate constant.

Example 13.10: The first-order rate constant for the decomposition of N_2O_5 at 340 K is found to be $5.20 \times 10^{-3}\ s^{-1}$. Calculate the time required for the concentration of N_2O_5 to reduce to (a) one-half and (b) one-fourth of its initial value.

Solution:

a) Using Eq. 13.75 , $t_{1/2}$(first order) = 0.693/k

Substituting the value of the rate constant, we get

$$= \frac{0.693}{5.20 \times 10^{-3} s^{-1}}$$

$t_{1/2}$= 133 s

Hence, time taken for the concentration of $N_2O_5$to reduce to one half (50%) is 133 s.

b) You have learnt above that for a first order reaction the half-life is independent of concentration. That is, it does not depend on concentration. In one half-life the concentration reduces to 50% in the next half-life it will be reduced to 50% of the 50% i.e., 25% (one fourth). In other words, the time required for the decrease in the concentration of N_2O_5 to one-fourth of its initial value will be twice the half-life period, i.e., 266 s.

Having studied the equations useful in calculating the first order rate constant and the half-life period of the reaction, let us derive similar equations for second order reactions.

III. Integrated Rate Laws for Second Order Reactions

There are two types of second order reactions.

i) A single reactant forms the product and the reaction rate depends on the second power of the reactant concentration.

$$A \rightarrow \text{ Products} \qquad \ldots (13.1)$$

The rate equation will be

$$\text{rate} = -\frac{d[A]}{dt} = k[A]^2 \qquad \ldots (13.76)$$

Where, k is the second order rate constant. Two examples of this type are given below:

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g) \qquad \ldots (13.77)$$

$$2HI(g) \rightarrow H_2(g) + I_2(g) \qquad \ldots (13.78)$$

ii) Two different reactant molecules could react to give products through a second order reaction.

$$A + B \rightarrow \text{Products} \qquad \ldots (13.79)$$

The rate equation is,

$$\text{Reaction rate} = k[A][B] \qquad \ldots (13.80)$$

That is, the order is 1 each w.r.t. both the reactants. Note that the stoichiometric ratio of the reactants is 1:1. This may be incidental. You must remember that the actual rate law is determined experimentally. Some examples of this type are given below.

$$H_2(g) + I_2(g) \rightarrow 2HI(g) \qquad \ldots (13.81)$$

$$CH_3Br(aq) + OH^-(aq) \rightarrow CH_3OH(aq) + Br^-(aq) \qquad \ldots (13.82)$$

$$CH_3COOC_2H_5(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + C_2H_5OH(aq) \qquad \ldots (13.83)$$

Again the study of these reactions could be simplified if the initial concentrations of both the reactants $[A]_0$ and $[B_0]$ are the same.

i.e. $[A]_0 = [B]_0$ and so $[A]_t = [B]_t$

where [A] and [B] are concentrations of the reactants at any given time, *t.*

Then, Eq. 13.80 takes the same form as Eq. 13.76.

$$\text{Rate} = \frac{-d[A]}{dt} = cA][B] = k[A][A] = k[A]^2 \qquad \ldots (13.84)$$

Thus, we could see that the rate equation takes the same form for a second order reaction, it the reaction is

i) second order in a single reactant or

ii) first order in each of the two reactants such that the concentrations of the two are same throughout the reaction.

However there could be another case where the initial concentration of the two reactants A and B are different then the resulting integrated rate law will be different. Such a case, is not being taken up here. Here, we will derive the integrated rate law only for the case (i) and case (ii) with equal initial concentrations of the reactants.

We start with the differential rate law,

$$\frac{-d[A]}{dt} = k[A]^2 \qquad \ldots (13.76)$$

The integrated form of this equation can be obtained using the following limiting conditions:

At time = 0 (i.e., at the start), the concentration of A = $[A]_0$. At time = t, the concentration of A = $[A]_t$.

Applying these limits on the rearranged form of Eq. 13.76, we get,

i.e. $$-\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = \int_0^t k\,dt \qquad \ldots (13.85)$$

i.e. $$-\left[-\frac{1}{A}\right]_{[A]_0}^{[A]_t} = k(t-0) \qquad \ldots (13.86)$$

$$\left[\frac{1}{[A]_t} - \frac{1}{[A]_0}\right] = kt \qquad \ldots (13.87)$$

or $$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \qquad \ldots (13.88)$$

or $$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \qquad \ldots (13.89)$$

The second order rate constant can be calculated by plotting $1/[A]_t$ against t. A straight line graph must be obtained if the reaction is second order in the reactant. The slope of the straight line gives the second order rate constant.

$$slope = k \qquad \ldots (13.90)$$

Let us now take up the expression for half-life of a second order reaction.

Half-Life of a Second Order Reaction

For reactions following second order rate as per Eq. 13.76, an equation could be derived which is useful in calculating the half-life period.

At the half-life period ($t = t_{t/2}$), $[A]_t = [A_0]/2$. Using this in Eq. 13.88,

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

i.e. $$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{1/2} \quad \ldots (13.91)$$

Rearranging and simplifying, we get

$$t_{1/2} = \frac{1}{k[A]_0} \quad \ldots (13.92)$$

From Eq. 13.79, we understand that $t_{1/2}$ is inversely proportional to initial concentration for a second order reaction.

Each successive half-life is double the preceding half-life in a second order reaction. In a first order reaction, all successive half-life periods are same.

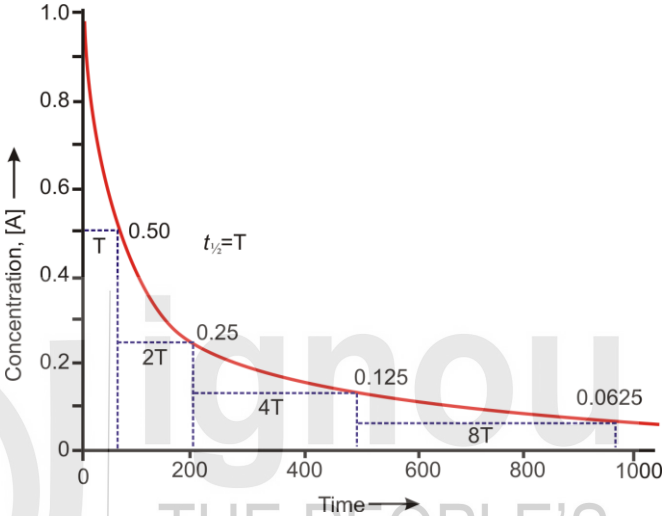


Fig. 13.13: $[A]_t$ versus t plot for second-order reaction showing increasing half-lives.

As initial concentration of the reactant decreases, $t_{1/2}$ increases. If for the decrease in concentration of A to 50% of its initial value, time required is T s, then for the change from 50% A to 25% A, it will require T s and so on. The increase in successive half-lives for a second order reaction can be represented by Fig. 13.13.

Let us take up an example to understand the importance of Eq. (13.92)

Example 13.11: At 700 K, the second order rate constant for the reaction,

$$2HI(g) \rightarrow H_2(g) \rightarrow I_2(g)$$

is 1.83×10^{-3} M^{-1} S^{-1}.

Calculate the time taken for 1.00×10^{-2} M HI to reduce to (a) one-half and (b) one-eighth of its initial concentration.

Solution:

a) We know that the time required for the reactant concentration to reduce to its half, is equal to the half-life of the reaction. Therefore, we first calculate the t½ for the reaction

Using Eq. 13.92,

$$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{1.83\times10^{-3}\times1.00\times10^{-2}}\ s$$

$$= 5.46 \times 10^4\ s.$$

b) Time needed for the decrease in concentration of HI to one-eights of its initial value would be three half-lives as shown below

First half life: $[A]_0 \rightarrow [A]_0/2$

Second half life: $[A]_0/2 \rightarrow [A]_0/4$

Third half life: $[A]_0/4 \rightarrow [A]_0/8$

We know that for a second order reaction each successive half life is double of the preceding half-life. If the first half life is T, the second half life would be 2T and the third half-lifewould be 4T and so on. Since in our case the time required is three half-lives, the total time will be equal to 7T (T +2T+4T=7T) where T is the first half life.

As in part a) we have determined the first $t_{1/2}$ i.e., T to be = 5.46×10^4 s, the time required for the initial concentration to reduce to its one eighth would be seven times this value. That is,

$$7 \times 5.46 \times 10^4\ s = 3.82 \times 10^5\ s$$

The differential and integrated rate laws for zeroth, first and second order rate equations are summarised in Table 13.2. $[A]_o$ and $[A]_t$ represent the concentration of the reactant A at the start and, after the time, *t*.

Table 13.2: Rate laws and other important data for reaction of the type A $\rightarrow$products showing different orders

Order of reaction	Differential rate law	Integrated rate equation	Expression for $t_{1/2}$	Type of plot	Unit for *k*
Zeroth order	rate = k	$[A]_t = -kt + [A]_0$	$[A]_0/2k$	$[A]_t$ against t	$M\ s^{-1}$
First order	rate = k [A]	$\log[A]_t = \frac{-kt}{2.303} + \log[A]_0$	$0.693/k$	$\log[A]_t$ against t	s^{-1}
Second order	rate = k $[A]^2$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$1/k[A]_0$	$1/[A]_t$ against t	$M^{-1}\ s^{-1}$

Let us sum up what have we discussed in this unit. However, before that answer the following simple question to assess your understanding.

SAQ 7

The decomposition of HI is a second order reaction. At 700 K, the rate constant for the reaction is 1.83×10^{-3} M^{-1} s^{-1}. If the initial concentration of HI is 1.0×10^{-1} M determine its half-life.

13.5 SUMMARY

In this unit we started by introducing the domain of chemical kinetics and outlined its significance. Then we defined and explained different ways of representing the rates of reaction. These are average rate- the change in concentration over a period of time, instantaneous rate – the rate at a given instant of time and the initial rate- the instantaneous rate at time close to zero. Different methods like, measurement of pressure or volume of a gas, titrimetry, conductometry, colorimetry etc. that can be used to follow the progress of the reaction were also explained. Reaction rates can be affected in a number of ways and there are four factors like, nature of the reactants, concentration of reactants, temperature and use of a catalyst that affect the rate of a reaction.

The rates of chemical reactions are found to be a function of the concentrations of one or more reacting species. These dependences of rate on the concentration of different reactants or products is represented in terms of a rate equation or a rate law. These rate laws are empirical relationships i.e., obtained from experimental data, and may or may not conform to the basic stoichiometry of the reaction. The exponent of a reactant in the rate law represents the order of the reaction with respect to that reactant. The sum of the exponents of the concentration terms in the experimentally determined rate law is called the overall order of the reaction .The proportionality constant '*k*' in the rate equation is called the rate constant. The units of rate constant depend on the overall order of the reaction and have the dimensions of $concentration^{(1\text{-}order)}$. $time^{-1}$.

The integrated rate equations obtained by integrating the differential rate equations represent change in concentration as a function of time. These equations can be used to predict the concentration at any time and provide different ways of plotting the experimental data which can be used to determine the order of the reaction. The integrated rate equations for the reactions showing zero-order, first order and second order kinetics were derived and analysed. Their importance was established with the help of examples. The half-life of a reaction refers to the time taken by the original concentration to reduce to its one half. The expressions for half-lives of zeroth, first and second order reactions were also derived and analysed.

13.6 TERMINAL QUESTIONS

1. In the formation of ammonia,

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

The rate of consumption of hydrogen gas at a particular instant is 4.78×10^{-4} M s^{-1}. What is the rate of formation of ammonia?

2. The rate constant for the decomposition of N_2O_5 at 340 K is found to be $5.20 \times 10^{-3} s^{-1}$. This reaction follows first order kinetics. If the initial rate of decomposition of N_2O_5 is 2.60×10^{-4} M s^{-1}, calculate the initial concentration of N_2O_5.
3. What is the time required for 87.5% decomposition of N_2O_5 at 340 K? Use data from the previous question.
4. What is the half-life period for the first order decomposition of azomethane at 600 K if $k = 3.55 \times 10^{-4}$ s^{-1}?
5. A substance decomposes by first order kinetics. If 15% of a substance decomposes in first ten minutes, calculate how much of it would remain undecomposed after one hour?
6. If the half-life of a first order reaction in A is 15 min., how long will it take for [A] to reach 10 percent of the initial concentration?

13.7 ANSWERS

Self-Assessment Questions

1. Using Eq. 13.2, $\text{Rate} = \frac{d[O_2]}{dt}$

$= 2.74 \times 10^{-4}$ M s^{-1}

2. $\frac{1}{2}\left(\frac{-d[HI]}{dt}\right) = \frac{d[H_2]}{dt}$

3. Average rate $= -\frac{\Delta[N_2]}{[\Delta t]} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$

Instantaneous rate $= -\frac{d[N_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

4. i) spectrometry

ii)pH measurement, conductometry or titration

iii) measurement of pressure of gas

5.

Order	**Unit of *k***
zeroth order	M s^{-1}
first order	s^{-1}
second order	M^{-1} s^{-1}

6. The order w.r.t. Cl_2 = 1

Overall order = 3

Unit of *k* = M^{-2} s^{-1}

7. For a second order reaction the half life =

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

We are given

k = 1.83×10^{-3} M^{-1} s^{-1} and

$[A]_0 = 1.0 \times 10^{-1}$ M

Substituting the values, we get

$$t_{1/2} = \frac{1}{1.83\times10^{-3}\times1.0\times10^{-1}} = 4.46\times10^{3}\ s$$

Terminal Questions

1. $$\frac{1}{3}\left(\frac{-d[H_2]}{dt}\right) = \frac{1}{2}\frac{d[NH_3]}{dt}$$

Hence,

$$\frac{d[NH_3]}{dt} = \frac{2}{3}\left(\frac{-d[H_2]}{dt}\right) = \frac{2}{3}\times4.78\times10^{-4}\ M\ s^{-1}$$

$$= 3.19\times10^{-4}\ M\ s^{-1}$$

2. $$\frac{-d[N_2O_5]}{dt} = k[N_2O_5]$$

Hence,

$$[N_2O_5] = \frac{1}{k}\frac{-d[N_2O_5]}{dt} = \frac{2.60\times10^{-4}\ M\ s^{-1}}{5.20\times10^{-3}\ s^{-1}}$$

= 5.00×10^{-2} M

3. $[A]_t = 12.5\%[A]_0 = [A]_0/8$

Using Eq. 13.64, $$t = \frac{2.303}{k}\log\frac{[A]_0}{[A]_0/8}$$

$$= \left(\frac{2.303}{5.20\times10^{-3}}\log8\right)s = 400\ s$$

4. Using Eq. 13.75, $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3.55\times10^{-4}}s = 1950\ s$

5. According to Eq. (13.65) for a first order reaction: $\log\frac{[A]_0}{[A]_t} = \frac{kt}{2.303}$

We are given that in 10 minutes 15 % of the substance is decomposed. This means that the remaining amount of the substance is 85 % of initial concentration, $[A]_0$ i.e., $[A]_{t=10} = 0.85\ [A]_0$

Substituting in the equation we get

$$\log\frac{[A]_0}{0.85[A]_0} = \frac{k \times 10}{2.303}$$

Simplifying and solving, we get

$$k = \frac{2.303}{10}\log\frac{1}{0.85} = 0.0162 \text{ min}^{-1}$$

Now we need to find out the amount remaining after 1 hr, i.e., 60 min. we again use Eq. 13.65.

Let the amount remaining, $[A]_{60} = x\,[A]_0$

Substituting in the equation

$$\log\frac{[A]_0}{x[A]_0} = \frac{0.0162 \times 60}{2.303} = 0.4221$$

Taking antilog

$$\frac{1}{x} = 2.643$$

Solving, we get x = 0.38 i.e, 38 % of the substance would remain after I hour.

6. We are given $t_{½}$ which can be used to get the value of rate constant by using Eq. (13.75). Then we can use equation (13.65)

According to Eq. (13.75)

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

Rearranging and substituting the value of half life we get,

$$k = \frac{0.693}{15 \text{ min}} = 0.0462 \text{ min}^{-1}$$

Now, we need to calculate the time for the concentration to reach 10 % i.e., 0.10 $[A]_0$.

Using Eq.(13.65)

$$\log\frac{[A]_0}{0.10[A]_0} = \frac{0.0462\,t}{2.303}$$

Solving, we get t = 49.8 minutes

Thus, it will take 49.8 minutes for the concentration to reach 10% of the initial concentration.

UNIT 14

Chemical Kinetics–II

Structure

14.1 INTRODUCTION

In the previous unit you have learnt about the introductory aspects of chemical kinetics, viz., different definitions of rate, their significance, measurement and factors affecting them. In addition, you have also learnt about the differential and integrated rate laws, order and half-life of a reaction. In this unit we will continue our discussion on chemical kinetics and take up a few important aspects. These are the methods for the determination of order of reaction, temperature dependence of rate of reaction and theories of reaction rate.

We will begin by discussing different methods employed for the determination of order of a reaction on the basis of the kinetic data. These will be supplemented with suitable examples. Thereafter, we would take up the temperature dependence of reaction rates and in this process we will bring in Arrhenius equation and discuss its significance. Then we will take up the theories of reaction rates. Herein we will explain in detail the collision theory and activated complex theory. We would also compare the collision theory and Arrhenius equation.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ list different methods for the determination of the order of a reaction;
- ❖ describe different methods used for determining the order of the reaction;
- ❖ discuss the effect of temperature on the reaction rate in terms of Arrhenius equation;
- ❖ calculate the activation energy of a reaction by using Arrhenius equation;
- ❖ list the assumptions of collision theory and derive an expression for rate constant;
- ❖ compare the Arrhenius equation and collision theory and outline the significance of preexponential term in Arrhenius equation; and
- ❖ explain the activated complex theory of biomolecular reactions;

14.2 DETERMINATION OF THE ORDER OF A REACTION

In the previous unit you have learnt about the rate laws. You would recall that in order to write the rate law, we must know the order of reaction with respect to each reactant. In this section, we discuss the following methods for determining the order of reaction.

1) Method of Initial Rates
2) Graphical or Trial and Error Method
3) Half-Life Method
4) Isolation Method

Let us discuss these one by one

1) Method of Initial Rates

You would recall from the previous unit that the initial rate is the rate of reaction as soon as the reactants are mixed. It is the instantaneous rate at a time very close to zero. One way to obtain the initial rate is to plot concentration versus time graph for the reaction and draw a tangent at $t = 0$. The slope of this tangent gives the initial rate. But usually, it is obtained by dividing the change in reactant concentration, Δ [reactant] in a very short time interval (Δt) immediately after the mixing of reactants and dividing it by the time interval. That is, we measure the average rate over a short time period. This method takes advantage of the fact that for a very short time interval in the beginning of the reaction, the concentration versus time curve and the tangent at $t = 0$, almost coincide with each other.

To understand the utility of initial rate in determining the order of a reaction, let us consider the following reaction,

$$A + B \longrightarrow \text{products} \qquad \ldots(14.1)$$

for which let us assume the rate law to be,

$$\text{rate} = k[A]^p [B]^q \qquad \ldots(14.2)$$

For a given set of concentrations of A and B, the initial rate is determined. The experiment is repeated with a different concentration of one of the components, while that of the other remains the same. Comparison of these two rates gives the order of the reaction with respect to the species for which the concentration has been changed. It can be shown as follows.

Let us assume that the R_1 is the rate when the initial concentrations of A and B are a_1 and b_1, respectively. Also, let us assume that, R_2 is the rate when we vary the initial concentration of A, from a_1 to a_2, while the concentration of B remains as b_1. That is,

$$(\text{Rate})_1 = R_1 = k(a_1)^p (b_1)^q \qquad \ldots(14.3)$$

$$(\text{Rate})_2 = R_2 = k(a_2)^p (b_1)^q \qquad \ldots(14.4)$$

Dividing R_2 by R_1 we get,

$$R_2 / R_1 = (a_2 / a_1)^p \qquad \ldots(14.5)$$

Taking logarithms, we get,

$$\log R_2 / R_1 = \log (a_2 / a_1)^p = p \log(a_2 / a_1) \qquad \ldots(14.6)$$

Rearranging we get,

$$p = \frac{\log(R_2 / R_1)}{\log(a_2 / a_1)} \qquad \ldots(14.7)$$

Another experiment is also to be performed in which the initial concentration of B is varied (to b_3) keeping that of A as constant (as a_1). In such a case

$$(\text{Rate})_3 = R_3 = k(a_1)^p (b_3)^q \qquad \ldots(14.8)$$

Dividing R_3 by R_1, we get, $R_3 / R_1 = (b_3 / b_1)^q$ …(14.9)

Taking logarithms, we get

$$\log (R_3 / R_1) = q \log(b_3 / b_1) \qquad \ldots(14.10)$$

Rearranging, we get,

$$q = \frac{\log(R_3 / R_1)}{\log(b_3 / b_1)} \qquad \ldots(14.11)$$

Once the values of p and q are known, the overall order will be $p + q$. You can understand this method from the following example.

Example 14.1: For the reaction, $Cl_2(g) + 2NO(g) \rightarrow 2\,NOCl(g)$, the initial concentration, $[Cl_2]_0$ and $[NO]_0$ are given along with initial rates measured as: $\text{Rate} = \frac{-d[Cl_2]}{dt}$

$[Cl_2]_0$ / M	$[NO]_0$ / M	Initial rate / M s^{-1}
0.10	0.10	3.0×10^{-3}
0.20	0.10	6.0×10^{-3}
0.20	0.20	2.4×10^{-2}

Calculate (i) order of the reaction with respect to each of the reactants and overall order; (ii) what is the rate law? (iii) calculate the rate constant.

Solution:

i) We can write the rate law as $k[Cl_2]^p[NO]^q$.

Similar to Eqs. 14.3. 14.4 and 14.8, we can write the rate expressions as

$$R_1 = k(0.10)^p\ (0.10)^q = 3.0\times10^{-3}\ \text{Ms}^{-1}$$

$$R_2 = k(0.20)^p\ (0.10)q = 6.0\times10^{-3}\ \text{Ms}^{-1}$$

$$R_3 = k(0.20)^p\ (0.20)^q = 2.4\times10^{-2}\ \text{Ms}^{-1}$$

Using Eq. 14.7, we can calculate p as follows

$$p = \frac{\log\frac{3.0\times10^{-3}}{6.0\times10^{-3}}}{\log\frac{0.10}{0.20}} = \frac{-\log\frac{6.0}{3.0}}{-\log\frac{0.20}{0.10}} = \frac{-\log 2}{-\log 2} = 1$$

Using Eq. 14.11, we can calculate q as follows

$$q = \frac{\log\frac{6.0\times10^{-3}}{2.4\times10^{-2}}}{\log\frac{0.10}{0.20}} = \frac{-\log\frac{24}{6.0}}{-\log\frac{0.20}{0.10}} = \frac{-\log 4}{-\log 2} = \frac{-2\log 2}{-\log 2} = 2$$

Hence, the reaction is second order in NO and first order in Cl_2. The overall order is 2 + 1 = 3.

ii) The corresponding rate law is given below:

$$\text{Rate} = k[Cl_2][NO]^2$$

iii) The rate constant can be calculated by using any one of the three rate equations given above. Let us take R_1.

$$R_1 = 3.0\times10^{-3}\ \text{M s}^{-1} = k(0.10\text{M})(0.10\text{M})^2$$

$$k = \frac{3.0\times10^{-3}}{(0.10)^3}\text{M}^{-2}\,\text{s}^{-1} = 3.0\ \text{M}^{-2}\text{s}^{-1}$$

Care must be taken in applying the method of initial rates as the method of initial rates is applicable to simple reactions only. An elegant way to measure the initial rates is by clock reactions. Let us understand the principle of clock reactions.

Clock Reactions

Only those reactions in which the reaction mixture undergoes a colour change can be used as clock reactions. The colour change may 'be due to a reactant or-a pro duct or an added indicator.

In the case of some reactions, the time taken for the colour change of the reaction mixture can be used for measuring the initial rate. Such self-indicating reactions are known as **clock reactions**. Clock reactions are designed in such a way that the appearance of one of the products (in terms of which the reaction is being monitored) is slightly delayed. For this purpose, a small amount of a substance called a monitor-substance (z) is added. This by itself does not take part in the reaction but quickly consumes one of the products (in question) formed. Once whole of this monitor-substance has reacted, the product shows up. Normally, this product is coloured or gives a distinct colour with an 'indicator' added in the reaction mixture. For example, the kinetics of the reaction potassium persulphate and potassium iodide,

$$2KI + K_2S_2O_8 \rightarrow 2K_2SO_4 + I_2 \quad \ldots (14.12)$$

The monitor substance is added in a very small amount so that the reaction does not go beyond just a few percent before the product shows up.

can be studied as a clock reaction. A reaction mixture is prepared using potassium persulphate and potassium iodide in a higher concentration and sodium thiosulphate (monitor substance) is added in much lower concentration. A drop of starch is also added to the reaction mixture. The reaction mixture is colourless in the beginning and it turns blue after some time. Once the reaction starts iodine is formed immediately as a product. This could react with the starch indicator to give colour, but it reacts with the added sodium thiosulphate as per the following reaction:

$$2\,Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6 \quad \ldots (14.13)$$

$1/\Delta t$ is a measure of the initial rate.

The reaction of iodine with thiosulphate occurs in preference to its interaction with the indicator. Once all the added sodium thiosulphate is consumed the iodine react with starch and a blue colour is developed. The time interval, Δt, between the mixing of the reactants and the appearance of blue colour is noted. $1/\Delta t$ is a measure of the initial rate. The time of appearance of blue colour will depend on the amount of sodium thiosulphate added and the initial rate.

You would recall that we defined initial rate as average rate ($\Delta c / \Delta t$) for small values of Δt from $t = 0$. The amount of added monitor substance fixes the value of Δc, and the rate of the reaction is manifested in terms of Δt only. That is why such reactions are called **clock reactions**. If the rate is fast and the product shows up soon, then Δt is small (i.e., rate $\propto \frac{1}{\Delta t}$). Addition of monitor substance is like winding a clock. The more you wind (i.e., add more '*z*'), longer it would take for the product to show up. The order of the reaction with respect to KI (p) and the order of the reaction with respect to $K_2S_2O_8$ (q) can be calculated by using the following formula:

$$\log(1/\Delta t) = p \log [KI] + q \log[K_2S_2O_8] + \text{constant} \quad \ldots(14.14)$$

A plot of log ($1/\Delta t$) against log [KI] is made using Δt values obtained by varying [KI] and keeping [$K_2S_2O_8$] constant.

The slope of the straight line gives p. Similarly q is obtained from the slope of the straight line got by plotting log $(1/\Delta t)$ against log $[K_2S_2O_8]$. For the second plot, Δt is obtained by varying $[K_2S_2O_8]$ and keeping [KI] constant.

Experimentally it has been found that $p = 1$ and $q = 1$.

Hence, $$\frac{-d[K_2S_2O_8]}{dt} = k[KI][K_2S_2O_8] \quad \ldots(14.15)$$

You would perform the iodine clock reaction in the laboratory course BCHCL-138. The kinetics of following reactions can also be studied using clock reactions,

1) Acid catalysed iodination of acetone

2) Saponification of ester (using phenolphthalein indicator)

3) The Harcourt-Esson reaction:

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \longrightarrow I_2(aq) + 2H_2O(l)$$

2. Graphical or Trial and Error Method

This method of determination of order is based on the integrated rate equations discussed in the previous unit. In this method different graphs (as listed in column 3 of Table 14.2) are plotted from the concentration versus time data obtained in the experiment.

Table 14.2: Integrated rate equations and the straight line plots for different orders of the reaction A⟶ products.

Order	Integrated Rate equation	Straight line plot
Zero	$[A]_t = -kt + [A]_0$	$[A]_t$ versus t
First	$\ln([A]_t / [A]_o) = -kt$	$\ln [A]_t / [A]_o$ versus t $\ln([A]_0 / [A_t])$ versus t
Second	$1 / [A]_t = kt + 1 / [A]_0$	$1 / [A]_t$ versus t

The order is ascertained from the plot giving a straight line e.g., suppose that for a hypothetical set of data for an experiment the following plots are obtained (Fig.14.1).

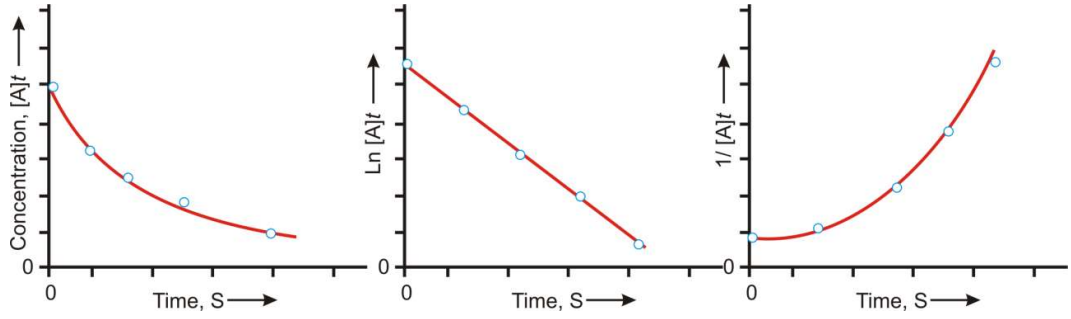


Fig. 14.1: Plots of a) $[A]_t$; b) $\ln[A]_t$; and c) $1/[A]_t$ versus time for a hypothetical reaction.

Referring to the Table 14.2, we can say that the order for this reaction is one as the straight line is obtained for $\ln[A]_t$ versus time graph. This method is of hit and trial nature. However, it is applicable for simple systems like A→ products. In case of reactions involving more than one reactant the analysis becomes complex and laborious.

Let us take an example to understand the application of graphical method in the determination of order of reaction.

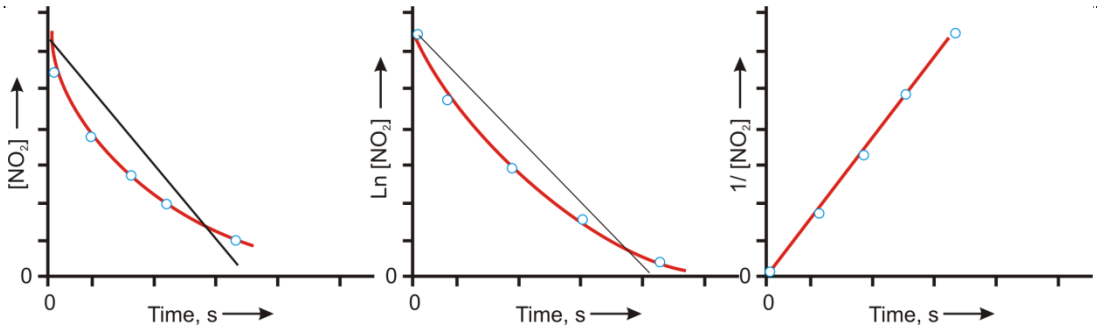
Example 2: The thermal decomposition of NO_2 [$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$] was studied at 330°C. The concentration of NO_2 as function of time was measured and the observed data is given as under. Determine the order of reaction by using graphical method.

Time / min	$[NO_2]$ / M
0	1.0×10^{-2}
1	6.8×10^{-3}
2	5.2×10^{-3}
3	4.2×10^{-3}
4	3.5×10^{-3}
5	3.0×10^{-3}
6	2.6×10^{-3}

Solution: as discussed above, in order to use graphical method, we plot concentration versus time, ln (concentration) versus time and reciprocal of concentration versus time plots from the given data and check which of these gives a straight line. Let us first compute the log concentration and reciprocal concentration values.

Time / min	$[NO_2]$ / M	ln $[NO_2]$	$1/[NO_2]$ / M^{-1}
0	1.0×10^{-2}	–4.61	100
1	6.8×10^{-3}	–4.99	147
2	5.2×10^{-3}	–5.26	192
3	4.2×10^{-3}	–5.47	238
4	3.5×10^{-3}	–5.65	286
5	3.0×10^{-3}	–5.81	333
6	2.6×10^{-3}	–5.95	385

Using the data, let us now plot the desired graphs corresponding to the zeroth, first and second order reactions. The plots are as under



You may note that the plot of reciprocal concentration versus time is observed as a straight line. Therefore, we can say that the thermal decomposition of NO_2 follows second order kinetics.

3. Integrated Rate Equation Method

This is another trial and error method for the determination of order of reaction. In this method we determine the order of reaction by substitution of experimental data into the integrated rate equations for different orders of reactions. The one giving a constant value for k determines the order with respect to that component.

4. Half-Life Method

In this method, the half-lives are determined using different initial concentrations of the reactant. If the half-life is independent of initial concentration, the reaction is first order. If the half-life is inversely proportional to the first power of initial concentration, the reaction is second order. If the half-life is directly proportional to the first power of initial concentration, the reaction is zeroth order.

In general, half-life period (t) is proportional to $[A]_0^{1-n}$ where $[A]_0$ is the initial concentration of the reactant and n is the order of the reaction.

If the half-life periods are t_1 and t_2 corresponding to the initial concentrations $[A]_1$ and $[A]_2$ of a reactant, then

$$\frac{t_2}{t_1} = \left(\frac{[A]_2}{[A]_1}\right)^{1-n} = \left(\frac{[A]_1}{[A]_2}\right)^{n-1} \quad \ldots(14.16)$$

Taking logs and simplifying,

$$n - 1 = \frac{\log(t_2/t_1)}{\log\{[A]_1/[A]_2\}} \quad \ldots(14.17)$$

or $$n = 1 + \frac{\log(t_2/t_1)}{\log\{[A]_1/[A]_2\}} \quad \ldots(14.18)$$

Let us take an example to learn how the order is determined by half-life method.

Example 14.3: For the decomposition of acetaldehyde in gas-phase at 791 K, the half-life periods are 328 s and 572 s corresponding to the

initial concentrations 9.72×10^{-3} M and 4.56×10^{-3} M respectively. What is the order of the reaction?

Solution: Using Eq. 14.18,

$$n = 1 + \frac{\log(572/328)}{\log(9.72\times10^{-3}/4.56\times10^{-3})} = 1 + \frac{0.2415}{0.3287} = 1.735$$

The order of the reaction is 1.735. Note that the order of the reaction is fractional.

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5. Isolation Method

In the case of reactions having more than one reactant, the rate law can be simplified if the concentrations of all reactants except one are taken in excess. So, when the reaction takes place it does so to a limited extent till the reactant in small amount is consumed whereby there is no effective change in the concentration of the reactants taken in excess. The reaction rate then depends on the reactant present in lesser quantity. The order of the reaction is determined by one of the methods given above. This procedure is repeated in turn with each of the reactants being in lesser amount while others are taken in excess. This procedure is called van't Hoff's isolation method.

For example, consider the reaction,

$$A + B \rightarrow \text{Products} \qquad \ldots(14.19)$$

For which the rate law is,

$$\text{rate} = k[A]^p[B]^q \qquad \ldots(14.20)$$

In the first set of experiment suppose B is taken in excess as compared to A then the concentration of B almost remains a constant throughout the experiment. The effective rate law becomes

$$\text{rate} = k_1[A]^p \qquad \ldots(14.21)$$

where, $k_1 = k$ (Initial concentration of B)^q …(14.22)

In such a case the rate depends on the concentration of A only. The value of 'm' can be obtained with the help of graphical method or any other suitable method. In the second set of experiments, [A] is taken as much larger as compared to [B].

The rate measurements are made and the order n is calculated using the rate law stated below.

$$\text{rate} = k_2[B]^q \qquad \ldots(14.23)$$

where,

$$k_2 = k \text{ (Initial concentration of A)}^p \qquad \ldots(14.24)$$

The overall order of the reaction is $p + q$.

Hydrolysis of ethyl ethanoate is a second order reaction

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH \quad \ldots(14.25)$$

Whose rate law is

$$\text{Rate} = k\,[CH_3COOC_2H_5]\,[H_2O] \quad \ldots(14.26)$$

When the hydrolysis is followed in aqueous solutions then there is practically no significant change in the concentration of H_2O and effective rate law becomes

$$\text{Rate} = k''[CH_3COOC_2H_5] \text{ where } k''=k[H_2O] \quad \ldots(14.27)$$

The reaction behaves like one following first order kinetics. Such reactions are termed as **pseudo-first order reactions**.

SAQ 1

For the alkaline hydrolysis of ethyl nitrobenzoate, the half-life periods and the initial concentrations are given below:

$[A]_0/10^{-2}$ M	5.00	4.00
$t_{½}$ / s	240	300

Calculate the order of reaction.

14.3 TEMPERATURE DEPENDENCE OF RATE CONSTANT

How does the temperature affect the rate of product formation in a reaction? The rate of product formation in a reaction increases when we increase temperature. From a thermodynamic point of view increasing the temperature increases the average kinetic energy of the reactant molecules. According to the collision theory the increased kinetic energy increases the impact energy upon collision with other molecules. This in turn increases the probability that more molecules will exceed the activation energy producing products at an increased rate. You may ask that how is this accomplished if concentrations are not altered?

You know that the differential rate law contains the concentration terms and the rate constant. Increasing the temperature will not alter the concentration in a significant way. Therefore, it is the rate constant that gets affected by increasing the temperature. Arrhenius investigated the relationship between rate constant and temperature of the reaction. He proposed the following empirical relationship between the rate constant, k, and temperature, T.

As the reaction rate varies with temperature, it also must be specified while stating the values of rate constant.

$$\ln k = \ln A - E_a / RT \quad \ldots(14.28)$$

or $$\log k = \log A - E_a / 2.303RT \quad \ldots(14.29)$$

Where, A is called the Arrhenius factor or frequency factor or pre-exponential factor and E_a is the activation energy. Activation energy is the minimum energy that the reactant molecules must have in order to react.

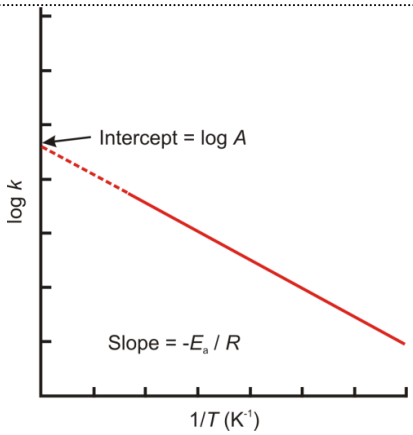

Fig. 14.2: Plot of log *k* against $\frac{1}{T}$.

If log k is plotted against 1/T, a straight line (Fig. 14.2) is obtained for many reactions. In such cases, the slope of the line is equal to $-E_a/2.303R$ and the intercept at 1/T = 0 gives the value of log A.

The unit of A depends on the unit of k. For first order reactions, A has s^{-1} unit which is the same as the unit of frequency. This could be a reason for its name, frequency factor. A is also called the pre-exponential factor since it precedes the exponential term in Eq. 14.30.

Eq. 14.28 can also be written in the exponential form as follows:

$$k = Ae^{-E_a/RT} \qquad \ldots(14.30)$$

A possible reason for the deviation from Arrhenius equation in some reactions is that A and E_a may also vary with temperature. The temperature dependence of Arrhenius factor will be discussed in collision theory. In the present discussion, we consider that A and E_a are constants for a reaction. If the activation energy is high for a reaction, it means that the temperature dependence of the reaction rate is also high. In such cases, even a small change of temperature results in a large change in the rate constant.

Although activation energy of a reaction can be calculated from log k vs 1/T plot, another way of obtaining it is to calculate rate constants (k_1 and k_2) at two different temperatures (T_1 and T_2). Assuming E_a and A to be constant and using Eq. 14.29, we can write

$$\log k_1 = \log A - E_a/2.303RT_1 \qquad \ldots(14.31)$$

and $$\log k_2 = \log A - E_a/2.303RT_2 \qquad \ldots(14.32)$$

Subtracting the terms in Eq. 14.31 from those in Eq. 14.32,

$$\log \frac{k_2}{k_1} = \frac{-E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \ldots(14.33)$$

$$= \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \ldots(14.34)$$

i.e., $$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\frac{(T_2 - T_1)}{T_1T_2} \qquad \ldots(14.35)$$

The Eq. (14.35) can be used to see how a small change in temperature affects the rate. Let us assume that for a reaction having activation energy of 50 kJ / mole the temperature changes from 27 to 37 degrees celsius. Let us see how does the rate change on doing so?

Converting the two temperatures to kelvin scale we get,

T_1 = 27 + 273 = 300 K and T_2 = 37 + 273 = 310 K

Substituting, the values of activation energy, T_1, T_2 and R in the Eq.14.35, we get,

log (k_2/k_1) = [50 kJ mol^{-1}/2.303 (8.314 ×10^{-3} kJ K^{-1}mol^{-1})] (1/300 K–1/310 K)

Simplifying and solving, we get

log (k_2/k_1) = 0.2808

Take the antilog of both sides:

Antilog [log k_2/k_1] = Antilog 0.2808

This gives: k_2/k_1 =1.91

In other words, increasing the temperature by 10 degrees nearly doubles the rate by doubling the rate constant. Eq. (14.35) is an important equation. It contains five parameters. If we know any four of them, we can find the fifth parameter. Let us take an example wherein we calculate the activation energy by using the data on rate constants at two different temperatures. The activation energy then can be used to calculate the frequency factor by using Eq. (14.30).

Example 14.4: The rate constant for the decomposition of SO_2Cl_2 at 552 K and 600 K are 1.01 × 10^{-6} s^{-1} and 3.85 × 10^{-5} s^{-1} respectively. Calculate the activation energy and the frequency factor for the reaction, assuming them to be independent of temperature.

Solution: From Eq. (14.35),

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

Substituting the values, we get

$$E_a = \left(\frac{2.303 \times 8.314 \times 552 \times 600}{48} \log \frac{3.85 \times 10^{-5}}{1.01 \times 10^{-6}} \right) \text{J mol}^{-1}$$

$$E_a = 2.09 \times 10^5 \text{ J mol}^{-1}$$

To calculate the frequency factor, we take log of Eq. (14.30), we get

$$\log A = \log k + E_a / 2.303 RT$$

Substituting for $T = 600\text{K}$, $E_a = 2.09 \times 10^5 \text{ Jmol}^{-1}$ and $k = 3.85 \times 10^{-5} \text{ s}^{-1}$ in it and simplifying, we get

$$= -4.4145 + \frac{2.09 \times 10^5}{2.303 \times 8.314 \times 600}$$

$$\log A = -4.4145 + 18.1924 = 13.7779$$

Taking antilogs

$$A = \text{Antilog } 13.7779$$

$$\Rightarrow A = 6.00 \times 10^{13}\ \text{s}^{-1}$$

Thus, the activation energy and the frequency factors are

2.09×10^5 Jmol^{-1} and 6.00×10^{13}s^{-1} respectively.

We can understand the significance of the terms, E_a, A, and $e^{-E_a/RT}$ during the discussion on collision theory of reaction rates. Let us take up the theories of reaction rates. However, before that answer the following simple question to assess your understanding.

SAQ 2

The energy of activation for a reaction is 10^5 kJ mol^{-1}. If the frequency factor is 2.5×10^{15} s^{-1} calculate the specific reaction rate for the reaction at 300 K.

SAQ 3

The gas-phase reaction between methane (CH_4) and sulphur (S_2) can be given as

$$CH_4(g) + 2S_2(g) \rightarrow CS_2(g) + 2H_2S(g)$$

The rate constants for this reaction at 550°C and 625°C are observed to be 1.11 M^{-1} s and 6.41 M^{-1} s respectively. Calculate the activation energy,E_a for this reaction.

14.4 THEORIES OF REACTION RATES

Arrhenius equation as discussed above provides an empirical explanation to the effect of temperature on the reaction rates. We need to have a theoretical explanation for the same at the molecular level. A number of theories have been proposed for explaining the reaction rates. We will take up two of these theories here. These are:

- Collision theory
- Activated complex theory

Let us begin with collision theory

14.4.1 Collision Theory

Collision theory is applicable to bimolecular reactions in gas phase. You would recall from the Unit 8 that according to the kinetic theory of gases the molecules of gases are in constant state of motion and frequently collide with each other. It is, therefore, logical to assume that the chemical reactions occur as a result of collisions between reacting molecules and the rate of reaction is proportional to the number of collisions. This is the basis of collision theory. The theory has the following postulates.

- The molecules are hard spheres and there are no intermolecular interactions between them. (you would recall it to be one of the assumptions of kinetic theory of gases)
- The collisions between the molecules are crucial for the reaction to occur and the rate is proportional to the number of collisions.
- Only the molecules that have a certain minimum amount of energy called activation energy undergo reaction.
- The molecules need to collide in a proper orientation for the collision to be effective.

Let us consider the following gas-phase bimolecular elementary reaction to understand collision theory

$$X + Y \rightarrow \text{Products} \qquad \ldots(14.36)$$

As stated above, according to the collision theory, the rate of a bimolecular reaction would depend on the following

- The total collision frequency and
- Boltzmann factor (to account for the molecules having energy greater than activation energy, E_a.)

Let us first calculate the collision frequency

Total Collision Frequency

Total collision frequency (Z_{XY}) is the number of collisions between the molecules of X and the molecules of Y in unit time in unit volume. Only X–Y collisions are counted but not X–X or Y–Y collisions, since only X–Y collisions are responsible for the reaction indicated in Eq. 14.36.

In Sec. 8.11 of Unit 8of this course, we derived Eq. 8.52 for calculating the total collision frequency among the molecules of a single gas. The total collision frequency (Z) in general, can be derived using the following relationship:

$$Z = \begin{cases} \pi \times (\text{collision diameter})^2 \\ \times (\text{average relative speed of gas molecules}) \\ \times (\text{number density}) \\ \times (\text{number density}) \\ \times (\text{correction factor}) \end{cases} \qquad \ldots(14.37)$$

As per Eq. 8.47 of Sec. 8.9 of Unit 8, average speed of a mole of gas molecules $(\bar{u})$ $= \left(\frac{8RT}{\pi M_m}\right)^{1/2}$

$M_m = m.N_A$

$\Rightarrow m = \frac{M_m}{N_A}$ and

$k_B = \frac{R}{N_A}$

$\Rightarrow R = k_B.N_A$

i.e., average speed of a gas molecule $(\bar{u})$ $= \left(\frac{8k_BT}{\pi m}\right)^{1/2}$

While calculating the relative motion of particles, it is customary to use reduced mass in the place of mass of one molecule of the gas.

Hence average relative speed of the molecules of X and Y $= \left(\frac{8k_bT}{\pi\mu}\right)^{1/2}$

$\mu = \frac{M_X M_Y}{M_X + M_Y} \cdot \frac{1}{N_A}$

where M_X, M_Y and N_A are the molar mass of X, molar mass of Y and Avogadro constant.

For calculating the total collision frequency (Z_{XY}) among the molecules of X and Y, as per Eq. 14.37, we use the following relationships:

i) Collision diameter $= \sigma_{XY} = 1/2(\sigma_X + \sigma_Y)$ …(14.38)

where σ_X and σ_Y are the diameters of the molecules, X and Y, respectively. The collision diameter σ_{XY} is the distance of closest approach between a molecule of X and a molecule of Y.

ii) Average relative speed of molecules of X and Y $= \left(\frac{8k_bT}{\pi\mu}\right)^{1/2}$ …(14.39)

where k_b is the Boltzmann constant (subscript b is added to k to differentiate it from the rate constant), T is temperature and μ is reduced mass.

Note that $= \frac{1}{\mu} = \frac{1}{m_X} + \frac{1}{m_Y}$ …(14.40)

or $\mu = \frac{m_X m_Y}{m_X + m_Y}$ …(14.41)

where m_X and m_Y are the masses of one molecule each of X and Y, respectively.

iii) Let us now calculate the factor, (number density) × (number density). Since we have two types of molecules, X and Y, we have to consider number densities of both X and Y. Using Eq. 14.41,

(number density of X) × (number density Y)

$= N_A[X].N_A[Y] = N_A^2[X][Y]$ …(14.42)

In the case of collision between the molecules of X and Y (i.e., between molecules of different gases), there is no necessity for the correction factor. It is because we calculate the collisions between each molecule of X and each molecule of Y. Each collision is counted only once. So, omitting the correction factor and using Eqs. 14.37, 14.38, 14.39 and 14.42, we get

$$Z_{XY} = \pi\sigma_{XY}^2\left(\frac{8k_bT}{\pi\mu}\right)^{1/2} N_A^2[X][Y] \quad \ldots(14.43)$$

Thus, we have obtained a relationship useful in calculating the total collision frequency for the collisions between each molecule of X and each molecule of Y. Here, $\pi\sigma_{XY}^2$ is called the mean collision cross-section. Next, we study the significance of Boltzmann factor.

Boltzmann Factor

You must realize that not all collisions between the molecules of X and Y would result in the product formation. Only those collisions, in which, the energy of the colliding molecules equals or exceeds some critical value E_A (known as activation energy as per Arrhenius equation), are effective in bringing about the reaction between X and Y. If $E_A >> RT$, then the Boltzmann

Number density of a gas has been defined in Subsec. 8.8.2 of Unit 8.

Number density $= \frac{\text{Number of molecules of the gas}}{\text{Volume of the gas}}$

$= \frac{\text{Pressure of the gas}}{\text{Boltzmann constant} \times \text{temperature}}$

$= \frac{p}{RT}$

Also note that from Eq. 8.41, concentration of a gas $= \frac{\text{Number of moles of the gas}}{\text{Volume of the gas}}$

$= \frac{p}{RT}$

i.e., Concentration of a gas $= \frac{p}{N_A k_b T} = \frac{\text{Number density}}{N_A}$

where N_A is Avogadro constant, i.e., Number density of a gas = N_A× (concentration of the gas)

factor $e^{-E_a/RT}$, gives the fraction of the collisions in which the colliding molecules possess energy equal to or greater than the activation energy.

$$\text{Boltzmann factor} = e^{-E_a/RT} \quad \ldots (14.44)$$

Boltzmann factor is helpful in calculating the number of molecules possessing energy equal to or greater than a particular value. Boltzmann factor, in other words, is helpful in calculating the population of the energy levels.

$$[\text{X}] = \frac{\text{Number of moles of X}}{\text{Volume}}$$

$$= \frac{\text{Number of molecules of X}}{N_A \times \text{Volume}}$$

$$= \frac{\text{Number density of X}}{N_A}$$

Calculation of Reaction Rate

The product of the total collision frequency and the Boltzmann factor gives the **number of molecules of X or Y in unit volume that are reacting per unit time**. This follows from the definition of the terms, total collision frequency and the Boltzmann factor. In order to obtain the reaction rate in terms of concentration of X or Y (or the **number of moles of X or Y** in unit volume) consumed per unit time, we have to divide the product, $Z_{XY}\, e^{-E_a/RT}$ by Avogadro constant.

$$\text{Reaction rate} = \frac{-\text{d}[\text{X}]}{\text{d}t} = \frac{-\text{d}[\text{Y}]}{\text{d}t}$$

$$= \frac{Z_{XY}\, e^{-E_a/RT}}{N_A} \quad \ldots (14.45)$$

Using Eqs. 14.43 and 14.45,

$$\text{reaction rate} = \pi \sigma_{XY}^2 \left(\frac{8k_bT}{\pi \mu}\right)^{1/2} N_A^2\, [\text{X}][\text{Y}] e^{-E_a/RT} \times \frac{1}{N_A}$$

$$= \pi \sigma_{XY}^2 \left(\frac{8k_bT}{\pi \mu}\right)^{1/2} N_A\, [\text{X}][\text{Y}] e^{-E_a/RT} \quad \ldots(14.46)$$

By definition, the reaction rate for a bimolecular elementary reaction as per Eq. 14.36 is as follows:

$$\text{Reaction rate} = k[\text{X}][\text{Y}] \quad \ldots(14.47)$$

Comparing Eqs. 14.46 and 14.47, we get

$$k = \pi \sigma_{XY}^2 \left(\frac{8k_bT}{\pi \mu}\right)^{1/2} N_A e^{-E_a/RT} \quad \ldots(14.48)$$

Eq. 14.48 gives the theoretical value of the rate constant for bimolecular reaction as per collision theory.

14.4.2 Collision Theory and Arrhenius Theory – a Comparison

When you compare Arrhenius Equation with Eq. 14.48 you can see that the frequency factor *A* is given by,

$$A = \pi \sigma_{XY}^2 \left(\frac{8k_BT}{\pi \mu}\right)^{1/2} N_A \quad \ldots(14.49)$$

From Eq. 14.49, you can see that *A* is not independent of temperature as predicted by Arrhenius equation. However, over a short range of temperature,

the variation in A is not significant. Arrhenius factor can be written as a product of A' and $T^{1/2}$ where A' is a temperature-independent constant and T is temperature.

$$A = A'T^{1/2} \qquad \ldots(14.50)$$

Where, $$A' = \pi \sigma_{XY}^2 \left(\frac{8k_B}{\pi \mu}\right)^{1/2} N_A \qquad \ldots(14.51)$$

The factor $T^{1/2}$ indicates the temperature dependence of A as given in Eq. 14.49.

Hence,

$$\log A = \log A'T^{1/2} = \log A' + 1/2 \log T \qquad \ldots(14.52)$$

Using this in Eq. 14.29,

$$\log k = \log A' + 1/2 \log T - E_a / 2.303RT$$

or $$\log k - 1/2 \log T = \log A' - E_a / 2.303RT \qquad \ldots(14.53)$$

A better method of arriving at the experimental values of E_a and A is to plot [log k – ½ log T] against 1/T.

The slope of the plot gives E_a value since

or $$\text{slope} = -E_a / 2.303R \qquad \ldots(14.54)$$

The intercept gives log A' value. From A' values, A at any temperature can be found out since

$$A = A'T^{1/2} \qquad \ldots(14.55)$$

The value of A so obtained is the experimental value.

It was found that in the case of reactions between simple molecules, the agreement between the experimental value of A and the value obtained as per collision theory (Eq. 14.49) is fairly good. In the case of reactions involving complex molecules, there is a discrepancy between the two values of A. To explain the discrepancy between the two values of A, a refinement was suggested for Eqs. 14.48 and 14.49 in terms of steric factor.

Steric Factor

Although the molecular collisions may have requisite energy, the reaction will take place only if the molecules have proper orientation. In other words, the reacting species must have proper spatial orientation for the reaction to occur. In the case of complex molecules, the probability of attaining proper orientation for the reaction is much less as compared to simple molecules. To stress the need for the proper spatial requirement, **steric factor or probability factor** (P) was also added to the right-hand side of Eq.14.48.

Hence $$k = P\pi \sigma_{XY}^2 \left(\frac{8k_bT}{\pi \mu}\right)^{1/2} N_A e^{-E_a/RT} \qquad \ldots(14.56)$$

$$A = P\pi\sigma_{XY}^2\left(\frac{8k_bT}{\pi\mu}\right)^{1/2} N_A \quad \ldots(14.57)$$

Also, $$P = \frac{A_{experimental}}{A_{theoretical}} \quad \ldots(14.58)$$

The steric factor is smaller for reaction between complex molecules. We expect the steric factor to be less than unity. But many fast reactions are known for which the steric factor is much greater than unity. Collision theory cannot explain such cases. Let us now study the **Activated Complex Theory** which gives a better method of calculating reaction rates.

14.4.3 Activated Complex Theory

The activated complex theory or the theory of absolute reaction rates assumes the formation of activated complex ($A^{\ddagger}$) from the reactants (X and Y) as a preceding step for the formation of the product, P.

$$X + Y \rightleftharpoons A^{\ddagger} \quad \ldots(14.59)$$

$$A^{\ddagger} \rightarrow P \quad \ldots(14.60)$$

The main features of the activated complex theory are given here.

The reactant molecules come into contact with each other. In this process, a few bonds get distorted; some bonds start forming with the exchange or release of atoms or groups. The composite molecule so formed from the reactants prior to the formation of the product is called the activated complex. The activated complex then decomposes to give the product. The reaction sequence could be represented as in Fig.14.3.

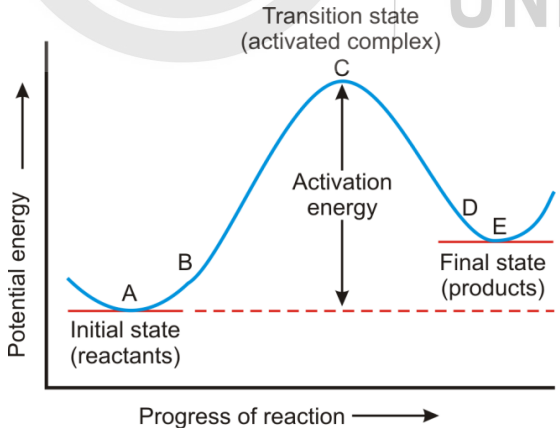

Fig. 14.3: Graphical representation of the change in potential energy as a function of reaction coordinate.

The total potential energy of the system is depicted in the *y*-axis and the **reaction coordinate** in the *x*-axis. Reaction coordinate is the sequence of simultaneous changes in bond distances and bond angles. Such changes result during the formation of the products from the reactants.

Consider the reaction between a molecule of H_2 and a molecule of I_2. To start with, let us imagine that the two molecules are far apart, and the total potential energy of the system is the sum of the potential energies of H_2 and I_2. This

Activated complex is the configuration of the atoms which the reactant molecules have near the top of the energy barrier that separates the reactants from the products. Transition state is the highest point in the potential energy curve.

part of the reaction course is represented by the point A of the curve in Fig. 14.3. As the two molecules approach each other to such an extent that the orbitals begin to overlap (point B in the curve), H – H and I – I bonds begin to stretch, and H-I bond begins to form. The total potential energy starts increasing and this is represented by the rising portion of the curve BC. As the extent of H – H and I – I bond breakage and H – I bond formation increase, a point is reached when the potential energy is maximum (point C). The situation at point B, C and E is given below.

B C E

The activated complex, represented by point C is a composite molecule, and has the maximum potential energy. The maxima point in the potential energy curve is called the transition state. Even a Slight reorganisation of the bonds can enable the activated complex to pass through the transition state. The path along CD represents the course of the events which result in the complete breakage of H – H and I – I bonds along with the formation of H – I bond. The point E represents the total potential energy of two H – I molecules. Although a fraction of the activated complex molecules could form the reactants (along the path CB); the formation of the products is almost a certainty, once the activated complex is at the transition state. The fraction of activated complex converted into products is called the transmission coefficient and, in majority of cases, it is unity.

Energy Requirement for the Reaction

Now let us consider the energy criteria for the reaction. The energy requirement for the reactants to cross the energy barrier is to be met from translational or the vibrational energy of the molecules. At the transition state, there are vibrations along each bond involving all the constituent atoms. The activated complex has a particular bond that is unstable and likely to break. If the activated complex vibrates with the frequency corresponding to this vibrational mode, the activated complex decomposes into product.

Rate Constant Calculation using Activated Complex Theory

Based on statistical thermodynamics, Eyring developed the activated complex theory. The basic postulate of the theory is that there exists a quasi equilibrium between the activated complex and the reactants. Let us consider the bimolecular gas phase reaction,

$$X + Y \rightarrow \text{Products}$$

The first step is the formation of an activated complex $(A^{\ddagger})$ as shown below.

$$X + Y \rightleftharpoons A^{\ddagger} \qquad \ldots(14.61)$$

Here, $A^{\ddagger}$ represents the activated complex. The activated complex then decomposes to give the product, P

$$A^{\ddagger} \rightarrow P \qquad \ldots(14.62)$$

The rate of formation of the product depends on,

(i) the concentration of the activated complex and

(ii) the frequency with which it is converted into the product. This is the frequency of one of the vibrational modes of the bond with respect to which the activated complex is unstable. Using detailed calculations, it is possible to derive an expression useful in calculating the rate constant (k) of the elementary reaction, X + Y $\rightarrow$ P (for which the steps are given in Eqs. 14.61 and 14.62). We shall only state the final expression without going through the derivation in full.

$$k = \frac{RT}{p^0}.\frac{k_B T}{h}.K_p = \frac{Rk_B T^2}{p^0 h}.K_p \qquad \ldots(14.63)$$

Where

K_p = The equilibrium constant for the formation of the activated complex after adjusting for its vibration with respect to which it is unstable.

T = Temperature

k_B = Boltzmann constant

RT / p^0 is the correction term where p^0 is the standard pressure (1 bar)

h = Planck constant

R = Gas constant

Using van't Hoff isotherm

$$\Delta G^{\ddagger} = -RT \ln k_p \qquad \ldots(14.64)$$

Where, $\Delta G^{\ddagger}$ is molar Gibbs energy of activation.

Hence, $$K_p = e^{-\Delta G^{\ddagger}/RT} \qquad \ldots(14.65)$$

Using Eq. 14.65 in Eq. 14.63,

$$k = \frac{Rk_B T^2}{hp^0} e^{-\Delta G^{\ddagger}/RT} \qquad \ldots(14.66)$$

From thermodynamics, we can write

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad \ldots(14.67)$$

Where, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the molar enthalpy of activation and molar entropy of activation, respectively.

Using Eq. 14.67 in Eq. 14.66,

$$k = \frac{Rk_B T^2}{hp^0} e^{-(\Delta H^{\ddagger} - T\Delta S^{\ddagger})/RT} \qquad \ldots(14.68)$$

$e = 1 + \frac{1}{1!} + \frac{1}{2!} + \frac{1}{3!} + \ldots \cong 2.718$

Note that 1!, 2!, etc., are to be read as factorial 1, factorial 2, etc.

Also

1! = 1;

2! = 1 ×2;

3! = 1 × 2 × 3

Finally '….' In the above expression means that it is a continuous series.

$$k = \frac{Rk_B T^2}{hp^0} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R} \quad \ldots(14.69)$$

Using non-logarithmic form of Eq. 14.28, it is possible to find the following relationship for a bimolecular gas phase reaction (the derivation is beyond the scope of this course)

$$\Delta H^{\ddagger} = E_a - 2RT \quad \ldots(14.70)$$

Using Eqs. 14.69 and 14.70,

$$k = \frac{Rk_B T^2}{hp^0} e^{-(E_a - 2RT)/RT} e^{\Delta S^{\ddagger}/R}$$

$$k = \frac{Rk_B T^2}{hp^0} e^{-E_a/RT} e^2 e^{\Delta S^{\ddagger}/R} \quad \ldots(14.71)$$

Comparing Arrhenius equation (Eq. 14.30) with Eq. 14.71,

$$A = \frac{Rk_B T^2}{hp^0} e^2 e^{\Delta S^{\ddagger}/R} \quad \ldots(14.72)$$

Hence $e^{\Delta S^{\ddagger}/R} = \frac{hp^0}{Rk_b T^2 e^2} . A$

Substituting for the constants, we get

$$e^{\Delta S^{\ddagger}/R} = 7.8119 \times 10^{-11} \frac{A}{T^2} \quad \ldots(14.73)$$

Taking natural logarithms,

$$\Delta S^{\ddagger}/R = \ln 7.8119 \times 10^{-11} \frac{A}{T^2} \quad \ldots(14.74)$$

$$\Delta S^{\ddagger} = 2.303R(\log 7.8119 \times 10^{-11} + \log A/T^2) \quad \ldots(14.75)$$

$$= (19.15 \log A/T^2 - 193.6) \text{ J mol}^{-1}\text{K}^{-1} \quad \ldots(14.76)$$

Thus $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ can be calculated at any given temperature, if A and E_a are known from Arrhenius plot (Fig. 14.2).

While discussing collision theory or the activated complex theory, we consider only the gas-phase reactions. The study of reaction rates in solutions is complicated due to the role of the solvent. In this course, we shall not discuss the reaction rates in solutions.

Comparison of Collision Theory and Activated Complex Theory

To account for the discrepancy between the experimentally obtained value of A and the value calculated as per collision theory, we had to introduce steric factor in Eq. 14.56. The activated complex theory has the factor, $e^{\Delta S^{++}/R}$, which takes care of the steric factor automatically.

It is observed that $\Delta S^{\ddagger}$ is negative for many reactions. Such a negative value indicates decrease in disorderliness. This is understandable since during

collisions, the particles have to approach each other, thereby causing a decrease in randomness. The negative value of $\Delta S^{\ddagger}$ brings down the value of $e^{\Delta S^{\ddagger}/R}$ and hence of *A* as per Eq. 14.72. A large negative value for the entropy of activation is generally observed for reactions involving complex molecules. The demand for proper orientation is more in the case of a complex molecule and this causes larger reduction in randomness. Thus, the entropy of activation, and hence, the frequency factor could be expected to be much less for reactions involving complex molecules.

SAQ 4

The second order rate constants of a reaction are given below at two temperatures:

T / K	298	308
$10^5 \times k$ / M^{-1} s^{-1}	8.8	28

Calculate the activation energy of the reaction

SAQ 5

For the reaction

$$2NOCl \rightarrow 2NO + Cl_2$$

Arrhenius factor at 298 K is 9.4×10^9 $M^{-1}s^{-1}$. Calculate entropy of activation for this reaction at 298 K.

Let us sum up what have we discussed in this unit.

14.5 SUMMARY

In this unit we continued our discussion on chemical kinetics and took up the determination of order of reaction, temperature dependence of reaction rate and theories of reaction rate. We began by discussing different methods of the determination of order of reaction and hence the rate law for a chemical reaction. In the initial rate method, the initial rate of the reaction is determined with a given set of concentrations of the reactants. The experiment is repeated with a different concentration of one of the components, while that of the other remains the same. Comparison of these two rates gives the order of the reaction with respect to the species for which the concentration has been changed. Similarly, the order with respect to the other species is determined.

We explained clock reactions as a means for determining the initial rates. In the graphical or trial and error method the experimental data is plotted in terms of expected straight line plots for different orders. The one giving a straight line establishes the order. Similarly, the data can be used to calculate the rate constant as per the integrated rate equations for different orders. The one

giving a constant value gives the order. In half-life method, the half-lives for a reaction are determined using different initial concentrations of the reactant. Then the nature of dependence of half-life on the initial concentration establishes the order of the reaction. In the ratio variation method, the concentrations of all the reactants but one are made large, and the order is determined for which the concentration is small. Similarly, the order is determined for all the reactants one by one.

Having discussed different methods for the determination of order we discussed the effect of temperature on reaction rate in terms of Arrhenius equation. We demonstrated the uses of Arrhenius equation with the help of examples. Thereafter, we explained the collision theory of reaction rate and derived an expression for the rate constant. The comparison of this expression with Arrhenius equation was used to give the significance of the Arrhenius factor. In the end we discussed another theory of reaction rate i.e., the activated complex theory.

14.6 TERMINAL QUESTIONS

1. The reaction, $2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$ was studied at 298 K by measuring the initial rate as

$$\text{rate} = \frac{\Delta[S_2O_8^{2-}]}{\Delta t}$$

The following results were obtained where $[I^-]_0$ and $[S_2O_8^{2-}]_0$ denote the initial concentrations of the two species.

$10^2 \times [I^-]_0 / M$	$10^2 \times [S_2O_8^{2-}]_0 / M$	$10^6 \times \text{Initial rate} / Ms^{-1}$
8.0	4.0	12.50
4.0	4.0	6.25
4.0	2.0	3.12

Determine the rate law.

2. For the decomposition of N_2O at 773 K, $k = 1.00 \times 10^{-5}\ s^{-1}$ and $E_a = 250\ kJ\ mol^{-1}$. Calculate A using Arrhenius equation.

3. For the reaction,

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

The steric factor is 1.7×10^{-6} and mean collision cross-section $(\pi\sigma^2)$ is 0.46 nm^2 .Calculate A at 628 K. Use Eq. 14.57.

Given: i) $k_B = 1.381 \times 10^{-23}\ J\ K^{-1}$

ii) The relative molecular masses of ethylene and hydrogen are 28.05 and 2.016, respectively.

iii) $N_A = 6.022 \times 10^{23}\ mol^{-1}$

4. The following data was obtained for the decomposition of ethyl chloride at 500°C. Determine the order of reaction and calculate the rate constant at this temperature.

Initial concentration / mol dm^{-3}	Initial rate / mol $dm^{-3}h^{-1}$
0.010	0.00026
0.020	0.00052
0.040	0.00104

5. The rate constants for a certain reaction are found to be 5.25×10^{-3} and 11.1×10^{-3} at 303 K and 314 K respectively. Calculate the energy of activation of the reaction.

14.7 ANSWERS

Self Assessment Questions

1. Using Eq. 14.18, $n = 1 + \dfrac{\log(300/240)}{\log(5.00\times10^{-2}/4.00\times10^{-2})}$

$$n = t + \frac{0.0969}{0.0969} = 2$$

2. According to Arrhenius equation $k = A\, e^{-Ea/RT}$

Taking natural log we get : $\ln k = \ln A - Ea/RT$

Converting to log to the base 10

$2.303 \log k = 2.303 \log A - Ea/RT$

Dividing throughout by 2.303

$\text{Log } k = \log A - Ea / 2.303\, RT$

Substituting values and simplifying, we get

$\text{Log } k = -2.011$

$K = 9.74 \times 10^{-3}$

3. We are given the following data

$T_1 = 550 + 273 = 823$ K $\quad k_1$ (823 K) $= 1 \times 10\ M^{-1}s^{-1}$

$T_2 = 625 + 273 = 898$ K $\quad k_2$ (898 K) $= 6 \times 40 M^{-1}s^{-1}$

From Eq. (14.35),

$$E_a = 2.303 \frac{R(T_1T_2)}{(T_2 - T_1)} \log \frac{k_2}{k_1}$$

Substituting the values, we get

$$E_a = \left(\frac{2.303 \times 8.314 \times 823 \times 898}{75} \log \frac{1.10}{6.40} \right) \text{J mol}^{-1}$$

E_a = 144.24 *k*J mol^{-1}

Thus, the activation energy of the given reaction would be 144.24 kJ mol^{-1}.

4. Using Eq. 14.35,

$$E_a = \frac{2.303 RT_1 T_2}{(T_2 - T_1)} \log k_2/k_1$$

$$= \frac{2.303 \times 8.314 \times 298 \times 308}{10} \log \frac{28 \times 10^{-5}}{8.8 \times 10^{-5}}$$

= 88.3 kJ mol^{-1}

5. According to Eq. 14.76,

$$\Delta S^{\#} = (19.15 \log A/T^2 - 193.6) \text{J mol}^{-1} \text{K}^{-1}$$

$$= (19.15 \log \frac{9.4 \times 10^9}{298^2} - 193.6) \text{J mol}^{-1} \text{K}^{-1}$$

$$\Delta S^{\#} = -97.4 \text{J mol}^{-1} \text{K}^{-1}$$

Terminal Questions

1. Let us write the rate law as,

$$v = k\,[I^-]^p\,[S_2O_8^{2-}]^q$$

As in Example 11, $p = \dfrac{\log(12.50 \times 10^{-6} / 6.25 \times 10^{-6})}{\log (8.0 \times 10^{-2} / 4.0 \times 10^{-2})} = 1$

$$q = \frac{\log(6.25 \times 10^{-6} / 3.12 \times 10^{-6})}{\log (4.0 \times 10^{-2} / 2.0 \times 10^{-2})} = 1$$

The rate law is,

$$\text{rate} = k\,[I^-][S_2O_8^{2-}]$$

2. Using Eq. 14.29,

$\log A = E_a/2.303\,RT + \log k$

$$= (250 \times 10^3 / 2.303 \times 8.314 \times 773) + \log(1.00 \times 10^{-5})$$

i.e. $\log A = -5.00 + 16.89$

$A = 7.8 \times 10^{11} \text{s}^{-1}$

3. Mass of one molecule of substance= $\frac{\text{Molar mass}}{N_A}$

Mass of one molecule of ethylene= $\frac{28.05\times10^{-3}}{6.022\times10^{23}}$kg

Mass of one molecule of hydrogen= $\frac{2.016\times10^{-3}}{6.022\times10^{23}}$kg

Using eq. 14.41

$$\mu = \frac{28.05\times2.016}{30.07\times6.022\times10^{26}}\text{kg}$$

$$= 3.12\times10^{-27}\text{ kg}$$

$$\left(\frac{8k_BT}{\pi\mu}\right) = \left(\frac{8\times1.381\times10^{-23}\times628}{30.07\times6.022\times10^{-27}}\right)kg$$

$$= 2.66\times10^{3}\text{ m s}^{-1}$$

Using Eq. 14.57,

$$A = P\pi\sigma^2\left(\frac{8k_BT}{\pi\mu}\right)^{1/2}N_A$$

$$1.7\times10^{-6}\times0.46\times(10^{-9}\text{ m})^2\times2.66\times10^{3}\text{ m s}^{-1}\times6.022\times10^{23}\text{ mol}^{-1}$$

$$= 1.25\times10^{3}\text{ m}^3\text{mol}^{-1}\text{s}^{-1}$$

$$= [1.25\times10^{6}\text{dm}^3\text{mol}^{-1}\text{s}^{-1}](1\text{m}^3 = 10^3\text{dm}^3)$$

$$= 1.25\times10^{6}\text{ M}^{-1}\text{s}^{-1}$$

Let us write down the rate law as

rate = k [ethyl chloride]^m

From the first experiment rate,

R_1= 0.00026 =k [0.01]^m

From the second experiment rate,

R_2= 0.00052 =k [0.02]^m

Dividing R_2 by R_1

We get,

$$\frac{R_2}{R_1} = \frac{0.0052}{0.0026} = 2^m$$

➔ $2 = 2^m$ ➔ m =1

That is the order of the reaction is 1

Now, get the rate constant we can use the data from any of the experiments. Let us take experiment 3

$0.00104 = k\ [0.04]^1$

This gives, $k = 0.026\ h^{-1}$

4. We are given the following data

$T_1 = 303$ K $\qquad k_1\ (303\ K) = 5.25 \times 10^{-3}$

$T_1 = 314$ K $\qquad k_2\ (314\ K) = 11.10 \times 10^{-3}$

From Eq. (14.35),

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

Substituting the values, we get

$$E_a = \left(\frac{2.303 \times 8.314 \times 314 \times 303}{11} \log \frac{11.10 \times 10^{-3}}{5.25 \times 10^{-3}} \right) \text{Jmol}^{-1}$$

$E_a = 53.17\ k\text{J mol}^{-1}$

Thus, the activation energy of the given reaction would be 53.17 kJ mol^{-1}.