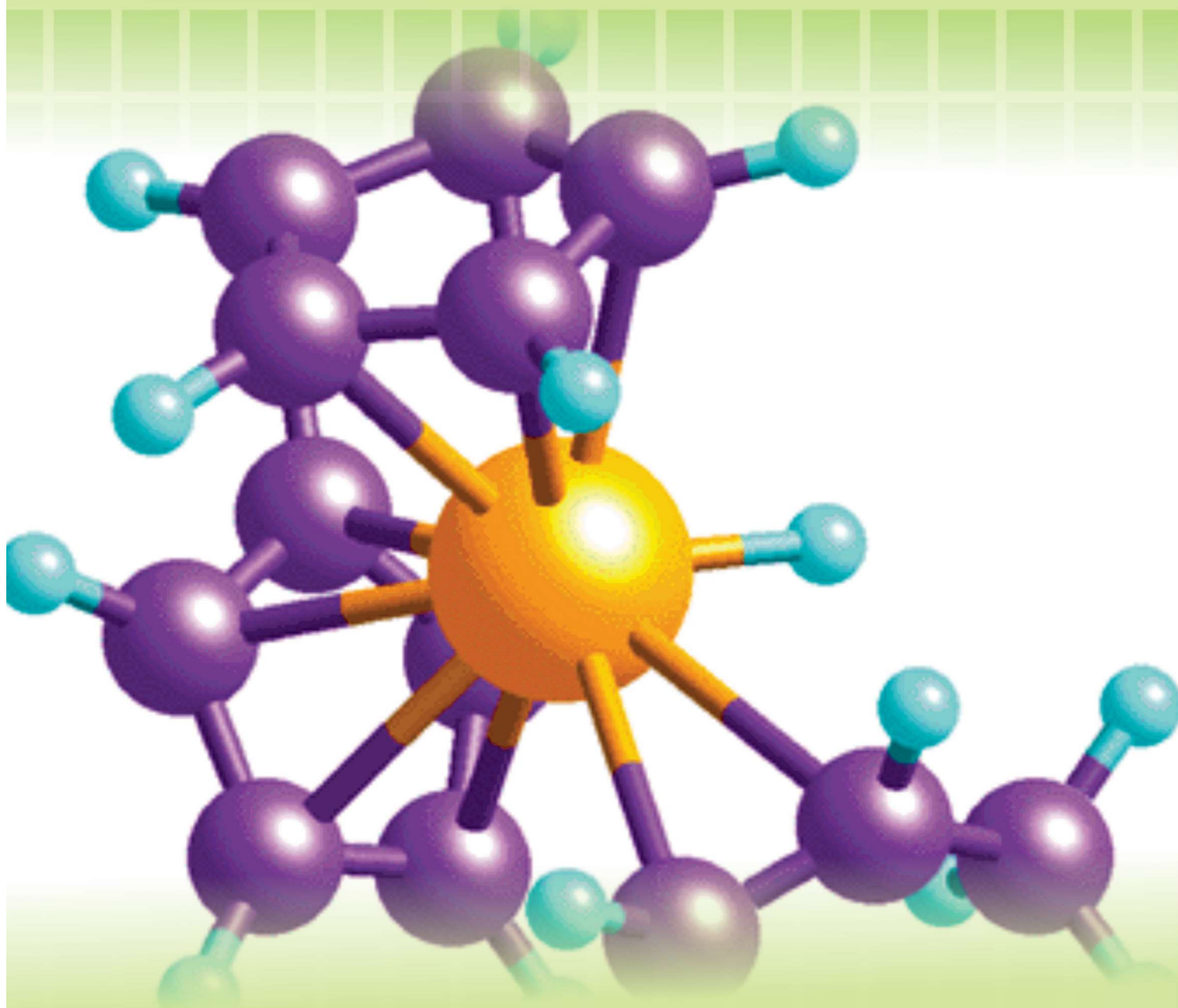


Physical Chemistry

CHM 111



CODeL

FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA
CENTRE FOR OPEN DISTANCE AND e-LEARNING

**FEDERAL UNIVERSITY OF TECHNOLOGY MINNA,
NIGER STATE, NIGERIA**



**CENTRE FOR OPEN DISTANCE AND
e-LEARNING (CODeL)**

**B.TECH. COMPUTER SCIENCE
PROGRAMME**

COURSE TITLE
PHYSICAL CHEMISTRY

COURSE CODE
CHM 111

Module 4

Chemical Equilibria Electrochemistry

- Unit 1: Chemical Equilibria
- Unit 2: Electrolytes
- Unit 3: Electrochemistry
- Unit 4: Chemical Kinetics

Unit 1

Chemical Equilibria

Content

- 1.0 Introduction
- 2.0 Learning Outcomes
- 3.0 Learning Content
 - 3.1 Reversible and Irreversible Reactions
 - 3.2 Chemical Equilibrium in Ideal Gas Mixtures
 - 3.3 Determination of Equilibrium Constants
 - 3.4 Application of Equilibrium Studies
 - 3.5 Effect of Temperature on Chemical Equilibrium
 - 3.6 Le Chatelier's Principle and Chemical Equilibria
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor-marked assignment
- 7.0 References/further reading

1.0 Introduction

Three important aspects of a chemical reaction must be studied for a complete understanding of the subject. These are: (i) whether a chemical reaction is feasible at all (ii) if the reaction is feasible, at what stage does it stop, and (iii) how fast or slow does the reaction occur. This last aspect we shall be studying under the heading of chemical kinetics in Unit 4.

The present unit describes the second aspect of a chemical reaction i.e, up to what stage does a reaction proceed. We have already defined, in general, the reversible and irreversible processes. However, for chemical reactions, the two processes can be defined as follows.

Irreversible reactions are said to go to completion, implying thereby that the reaction proceeds until at least one of the reactants is completely used up. On the other hand, all those reactions which appear not to proceed beyond a certain stage after sometime even when the reactants are still available, are reversible reactions.

They have only reached an equilibrium state. The present unit discusses the meaning of this state of equilibrium and how the equilibrium composition of the reactants and products are correlated with change in Gibb's free energy. It also explains the effects of different factors on chemical equilibrium.

2.0 Learning Outcomes

After studying this unit, you should be able to:

- i. describe chemical equilibrium
- ii. differentiate between reversible and irreversible reactions
- iii. derive an expression for equilibrium constant in terms of Gibb's free energy;
- iv. express the equilibrium constant in different ways and apply it to different systems, and
- v. predict the shift in equilibrium position with the changes in the concentration, temperature or pressure of the system.

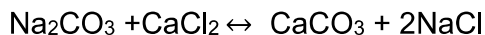
3.0 Learning Content

3.1 Reversible and Irreversible Reactions

In general, chemical reactions can be divided into two types - reversible and irreversible. The reversible reactions are those in which the products can combine back to form the reactants. However, in the irreversible reactions, the same reactants cannot be formed back from the products under normal set of experimental conditions. For the study of equilibrium, we are mainly concerned with reversible reactions.

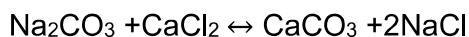
The idea of reversibility of chemical reactions was first realised by Berthollet in 1799. He was trying to explain the cause for substantial amount of deposits of sodium

carbonate around some salt lakes of Egypt. He proposed that these deposits are formed due to high concentration of sodium chloride in lake water which reacted with the carbonates present on the shores. Normally, in a laboratory experiment, we find that calcium carbonate is precipitated by the reaction of sodium carbonate with calcium chloride as represented by the equation:

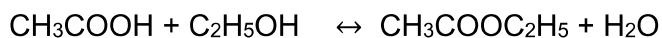


What Berthollet proposed was indeed a reverse reaction of the above and the cause for reversibility was in some way connected to the high concentration of dissolved sodium chloride.

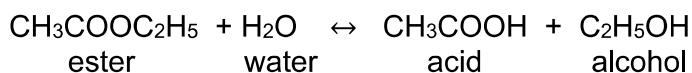
Thus, we realise that a chemical reaction such as given above .can proceed in both the directions-from left to right or vice-versa-depending on the experimental conditions. Each such reaction is usually written containing two half-arrows pointing in opposite directions (or a sign of equality between reactants and products) emphasising the fact that it is a reversible reaction:



Further, experimental studies by Gilles and coworkers on the reaction between acetic acid and ethyl alcohol giving ester and water, showed that the amount of ester formed varied with the initial concentrations of the reactants at a fixed temperature and pressure.



In 1864, Guldberg and Wagge showed experimentally that there exists an equilibrium between the reactants and products in a chemical reaction and that this equilibrium can be reached from either direction (starting either from reactants or the products). Furthermore, the relation between the concentrations of the reactants and the products can be expressed by a simple mathematical expression. Let us consider two reactions to clarify these points. van't Hoff, in 1877; studied the hydrolysis of ethyl acetate.



He observed that the ratio of the product of concentrations of the products to the product of concentrations of the reactants is always constant at equilibrium and is independent of the initial concentrations of the ester. Expressed mathematically,

$$K = \frac{[\text{C}_2\text{H}_5\text{OH}] \times [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COOC}_2\text{H}_5] \times [\text{H}_2\text{O}]}$$

Where [] represents molar concentration of a species.

The constant, *K*, in the above expression has a fixed value for a particular reaction at a constant temperature and pressure and is a measure of the extent of reaction. A large value of *K* means numerator, is greater than the denominator. This indicates the

presence of a larger concentration of products as compared to the concentration of reactants at equilibrium.

Consider another example of the reaction involving hydrogen, iodine and hydrogen iodide, all in the gaseous state. If hydrogen and iodine are kept together in a closed vessel at 723 K, they react chemically to give hydrogen iodide. However, if pure hydrogen iodide is taken in a closed vessel and heated to the same temperature of 713 K, it decomposes to give hydrogen and iodine. The true state of affairs is that, in both cases, after a sufficiently long time.

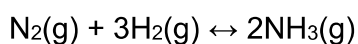
You would find all the three species, hydrogen, iodine and hydrogen iodide present in the container. At this stage, we say that an equilibrium has been reached between the reactants and the products as shown, by the equation, $H_2 + I_2 \leftrightarrow 2HI$. Furthermore, at equilibrium, there exists a definite relationship between the concentrations of hydrogen iodide, hydrogen and iodine. This state of chemical equilibrium can be viewed from a different point of view. The reaction between the two reactants, A and B, to give products, C and D, can be represented as follows:

Initially, there are only A and B present but as the reaction proceeds, some amount of C and D are formed. Once the products C and D are formed, they can also react to give A and B, if the reaction is reversible. Since, the concentration of C and D are small in the beginning, it seems logical that the rate of the reverse reaction, $C + D \rightarrow A + B$, should also be less than the rate of the forward reaction, $A + B \rightarrow C + D$. However, as the reaction proceeds, more and more of C and D are produced. Consequently, the rate of the reverse reaction would also increase.

Ultimately, a situation would be reached when the rate of the reverse reaction would be exactly equal to that of the forward reaction. Since, these are reactions in opposite directions, there is no change in composition with time and it seems as if the reaction has stopped. We then say that the reacting system is in the equilibrium state. Actually the reactions in both directions do take place but rates of forward and reverse reactions are equal. It is said that a state of dynamic equilibrium has been reached. At this stage, no further change in the concentrations of the products and reactants will take place.

Based on such observations, Guldberg and Wagge gave a quantitative formulation known as the law of mass action. This law gives the relationship between equilibrium concentrations of all the substances taking part in a chemical reaction at equilibrium. Instead of just stating this law, we shall derive this relationship with the help of basic principles of thermodynamics.

Equilibrium constant could also be expressed in terms of partial pressure. Consider the reaction



$$K_p = \frac{P_{NH_3}^2}{P_{N_2} \cdot P_{H_2}^3}$$

3.2 Determination of Equilibrium Constants

It is now clear from the above examples that if the initial concentrations and the extent of the reaction are known, equilibrium constants can be calculated. In fact, if we want to make use of any of the equations derived in the previous two sections, we must be sure that the equilibrium has indeed been reached. The following two criteria confirm the presence of equilibrium condition:

- 1) The value of equilibrium constant should be same' when the equilibrium is approached from either side.
- 2) The value of equilibrium constant should be same when the concentrations of the reacting substances are varied greatly.

Once it is established that an equilibrium has been reached, the next step is to find out the equilibrium concentration of at least one of the reactants or products in order to calculate the extent of the reaction. This can be achieved either by chemical analysis or by measurement of some physical property. The difficulty with the chemical analysis is that the concentration will change during the course of the analysis.

Hence, only when the reaction can be stopped at equilibrium by some means (like sudden cooling), can this method be used. Physical methods are more convenient since they do not require stopping of the reaction. The physical properties commonly used for this purpose are density, refractive index, electrical conductivity, light absorption etc.

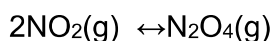
3.3 Applications of Equilibrium Studies

3.3.1 Homogeneous Systems

When all the reactants and products are present in the same phase (i.e., gaseous or liquid) we call it a homogeneous system. Let us consider a few examples:

Example 1

At 298 K. it was found that $K_p = 7.13$, for the reaction:



What is ΔG° for the reaction?

Solution

It is worth noting that K_p is given as a dimensionless quantity

$$\Delta G^\circ = -RT \ln K_p, = 2.303 RT \log K_p$$

Substituting the values of R , T and K_p in the above equation, we get,

$$\Delta G^\circ = (- 2.303 \times 8.314 \times 298 \log 7.13) \text{ J mol}^{-1} = - 4.868 \text{ kJmol}^{-1}$$

3.3.2 Heterogeneous Systems

Chemical reactions may also involve reactants or products in different phases, The most common examples are found where solids and gases are present together at equilibrium. Recall that at standard pressure of 1 bar, the activity of pure solid is unity. Hence, in writing the expression for equilibrium constant the activity or partial pressure terms for solids can be eliminated. Thus, for the reaction,



$$\begin{aligned} K_p &= \frac{P_{\text{CaO}} \cdot P_{\text{CO}_2}}{P_{\text{CaCO}_3}} \\ &= P_{\text{CO}_2} \quad [\text{since } P_{\text{CaO}} = P_{\text{CaCO}_3} = 1] \end{aligned}$$

Again for the reaction,

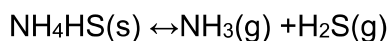


$$K_p = \frac{P_{\text{CO}} \cdot P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} \quad P_{\text{C}} = 1, \text{ carbon being in the solid form.}$$

Let us illustrate the heterogeneous systems with another example.

Example 2

$\text{NH}_4\text{HS}(\text{s})$ evaporates in an evacuated container at 298 K according to the equation.



Find the pressure of each gas at equilibrium if $K_p = 1.10 \times 10^9 \text{ Pa}^2$ at 298 K.

Solution

We can write for the above reaction, ..

$$K_p = P_{\text{NH}_3} \cdot P_{\text{H}_2\text{S}} \quad (\text{since } P_{\text{NH}_4\text{HS}} = 1)$$

Since the two gases produced in the reaction are in equimolar quantities,

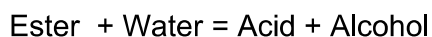
$$P_{\text{NH}_3} = P_{\text{H}_2\text{S}}$$

$$\text{or } K_p = P_{\text{NH}_3}^2 = 1.10 \times 10^9 \text{ Pa}^2$$

$$P_{\text{NH}_3} = P_{\text{H}_2\text{S}} = 3.32 \times 10^4 \text{ Pa}$$

3.3.3 Liquid Solutions

So far we have discussed the reactions which take place in gaseous state or those involving gaseous and solid phases. But the majority of reactions are carried out in liquid solutions. For example, you have already seen hydrolysis of an ester which can be written as:



Let us arrive at an expression useful in calculating the equilibrium constants of such reactions.

In an ideal solution, the concentration of each component can be conveniently expressed in terms of molarity. We can express K_c of a general reaction (given below) which takes place in a liquid solution; of course, the solution has to exhibit ideal behaviour.



In this reaction, A, B, ... etc., and P, Q, ... etc., are the reactants and products; a, b, \dots etc., and p, q, \dots etc., are the stoichiometric coefficients.

We can write K_c for the above reaction as,

$$K_c = C^p_P \cdot C^q_Q \dots$$

$$C^a_A \cdot C^b_B$$

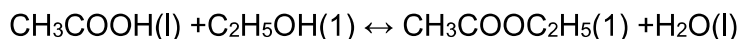
$$K_c = m^p_P \cdot m^q_Q = [P]^p [Q]^q$$

$$m^a_A \cdot m^b_B \quad [A]^a [B]^b$$

where m_p, m_q, \dots etc., are the molarities of substances. The square brackets denote the concentrations of the species within the brackets.

Example 3

Calculate the equilibrium constant for the reaction,



at 298 K if 1.00 mol of acetic acid and 1.00 mol of ethyl alcohol are mixed together. At the equilibrium point, the amount of water is 0.333 mol.

Solution

The concentration of substances are given below assuming the total volume to be V dm³:

	[CH ₃ COOC ₂ H ₅]	[H ₂ O]	[CH ₃ COOH]	[C ₂ H ₅ OH]	
Concentration at equilibrium	0.333/V	0.333/V	(1 - 0.333)/V	(1 - 0.333)/V	(1 - 0.333)/V
	(in mol dm ⁻³)				

$$K = \frac{(0.333/V)(0.333/V)}{(0.667/V)(0.667/V)} = 4.01$$

Note that K_c is a dimensionless quantity since $\sum \nu_i$ for this reaction is equal to zero. In cases such as this, volume need not be known as it cancels out in the final expression. If in any reaction $\sum \nu_i$ is not equal to zero, the final expression would contain volume term and K_c will have suitable dimensions.

3.4 Effect of Temperature on Chemical Equilibrium

The equilibrium constant, K , of a reversible chemical reaction is a constant at a given temperature; but it varies with temperature. Let us derive an expression useful in bringing out the relationship between the equilibrium constant and temperature.

$$\Delta G^\circ = -RT \ln K_p$$

$$\text{or } \ln K_p = -\Delta G^\circ/RT$$

Differentiating this expression with respect to temperature,

$$\frac{d \ln K_p}{dT} = -\frac{1}{R} \frac{d(\Delta G^\circ/T)}{dT}$$

$$\frac{d(\Delta G^\circ/T)}{dT} = -\frac{\Delta H^\circ}{RT^2}$$

This shows that equilibrium constant varies with temperature and depends on the standard enthalpy of the reaction.

Assuming that the standard enthalpy change (ΔH°) of the reaction remains constant over a small range of temperature; the above equation on integration between limits K_{p1} , K_{p2} , and T_1 , T_2 gives,

$$\int_{K_{p1}}^{K_{p2}} d \ln K_p = \int_{T_1}^{T_2} \frac{\Delta H^\circ}{RT^2} dT$$

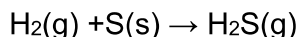
$$\text{or } \ln \frac{K_{p2}}{K_{p1}} = \frac{\Delta H^\circ}{R} (1/T_1 - 1/T_2)$$

$$\text{or } \log \frac{K_{p2}}{K_{p1}} = \frac{\Delta H^\circ}{2.303R} (1/T_1 - 1/T_2)$$
$$= \frac{\Delta H^\circ (T_2 - T_1)}{2.303RT_1 T_2}$$

This correlates the equilibrium constant values K_{p1} and K_{p2} (expressed in terms of partial pressures) at two different temperatures T_1 and T_2 to the standard enthalpy of reaction.

Example 4

The equilibrium constant for the reaction



is 18.5 at 925 K and 9.25 at 1000 K, respectively. Calculate the standard enthalpy of the reaction. Also calculate ΔG° and ΔS° at 925 K. .

Solution

$$\log \frac{K_{1000}}{K_{925}} = \frac{\Delta H^\circ (1/925 - 1/1000)}{(2.303 \times 8.314)}$$
$$\text{or } \log \frac{9.25}{18.5} = \frac{\Delta H^\circ (75)}{(2.303 \times 8.314)(925 \times 1000)}$$

$$\begin{aligned} \text{hence } \Delta H^\circ &= -71.1 \text{ kJ mol}^{-1} \\ \Delta G^\circ &= -2.303 \times 8.314 \times 925 \log 18.5 = -22.4 \text{ kJ mol}^{-1} \\ \Delta S^\circ &= \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{(-71100 + 22400) \text{ J}}{925 \text{ K}} \\ &= -52.6 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Self-Assessment Exercise 1

For the dissociation of mercuric oxide, K_p values are 0.0196 and 0.1794 at 693 K and 723 K, respectively. Calculate the standard enthalpy of the reaction. .

3.5 Le Chatelier's Principle and Chemical Equilibria

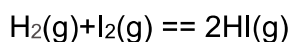
The equilibrium expressions derived earlier are very useful to perform numerical computations of various kinds as we have already seen with different examples given. However, often one is more interested in predicting qualitatively the results of a change brought about by external forces on the system under equilibrium: For instance, if pressure, temperature or volume is changed for a system under equilibrium what would be its effect, if any, on the equilibrium itself?

However, it is much more easily predicted with the help of Le Chatelier's principle. Le Chatelier's principle can be stated as follows: .

If a stress is applied to any system under equilibrium, the system would tend to shift in such a way so as to neutralise the effect of that stress (if possible). The stress for a chemical reaction could be in the form of a change in pressure, temperature or concentration at equilibrium. According to the above principle then, the equilibrium would shift in such a direction so that the effect of these changes is neutralised. We shall consider the effect of each one of these factors on equilibrium separately.

3.5.1 Effect of Change of Concentration

Let us consider the reaction,



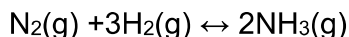
Which has attained equilibrium. Now, if we add some H_2 to the equilibrium mixture, it will obviously upset the equilibrium. According to Le Chatelier's principle, the equilibrium would shift in such a way so as to oppose the effect of this excess H_2 . It can do so by using up this excess H_2 to react with more I_2 to give more of HI .

We describe this process by saying that the final position of equilibrium has shifted to the right of the equation: In this final state of equilibrium, then, more amount of HI is formed as compared to earlier equilibrium state. Just the opposite would be the fate of the reaction if, instead of H_2 , some HI is added to the system under equilibrium: In short, by changing the concentration at equilibrium, the reaction will move forward or in the reverse direction so that the equilibrium constant has the same value.

3.5.2 Effect of Change of Pressure

If we consider the above reaction again and suppose that the pressure of the system is increased -perhaps by reducing the volume of the container-s-the system should react in such a way so as to reduce the effect of the increase in pressure. However. There is no way by which this can be achieved, The forward reaction or the reverse reaction will not be favoured by pressure change since the total number of moles of the reactants is the same as the total number of moles of the products.

However, the situation changes if we consider the synthesis of ammonia:



If the pressure of the system is increased at the equilibrium as was done in the previous example, the effect of this increase could be eliminated by the formation of more ammonia. This becomes obvious if you realise that the total number of moles of the reactants is four as compared to the moles of product which is two. Four moles will exert greater pressure than two moles; so, if the system wants to reduce the extra pressure, it can do so by moving in the forward direction. On the other hand, if we decrease the external pressure on the system, more of ammonia will decompose to give nitrogen and hydrogen.

Thus, if we want to produce ammonia industrially, it is preferable to carry out the reaction at high pressures. Comparing the two reactions given above, we can conclude that changes in pressure at equilibrium will affect the amounts of products formed for only those reactions where the total number of moles of reactants are different from the total number of moles of products.

3.5.3 Effect of Change of Temperature

Consider once again the synthesis of ammonia from nitrogen and hydrogen which is an exothermic reaction. If the temperature of the system is increased at equilibrium, Le Chatelier's principle tells us that the system should react in such a way so as to neutralize this effect. Let us see how this is possible. We know that the formation of ammonia is an exothermic reaction and, therefore, the reverse reaction of decomposition of ammonia will be endothermic.

Thus, the excess heat supplied by raising the temperature of the system can be absorbed by the system if the reaction goes more towards left. This will increase the amounts of N_2 and H_2 and decrease the amount of NH_3 at equilibrium. We can generalize this observation by saying that by raising the temperature of a system undergoing an exothermic reaction, we will decrease the amount of the products and increase the amount of the reactants.

Just the opposite will be true for all endothermic reactions. The effect of these factors gains special importance for the production of a substance on large scale. In any industrial production of a substance it is imperative to know the optimum conditions of temperature, pressure and concentrations in order to get the maximum yield at a

minimum cost. For instance, in the production of ammonia we know from Le Chatelier's principle that high pressure and high concentration of N_2 and H_2 will favour the reaction. Similarly, the above principle also predicts that the reaction would be more favourable at low temperatures since it is exothermic,

However, we cannot carry out the reaction at a very low temperature since another factor comes into the picture. That is, the rate of the reaction becomes too slow at lower temperatures. Hence, the reaction is performed at pressures of several megapascals and temperatures between 650 and 750 K.

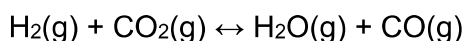
You should be able to do the following **SAEs** which are based on the above discussion.

Self-Assessment Exercises 2

1. Consider the reaction, $\text{PCl}_5(\text{g}) \leftrightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$. How would the equilibrium be affected by,

- i) the addition of Cl_2 and
- ii) decrease in the volume of the container?

2. If $\Delta H^\circ = 41 \text{ kJ mol}^{-1}$ for the reaction,



what will be the effect of increase of temperature on the equilibrium?

4.0 Conclusion

This describes an important aspect of a chemical reaction i.e, up to what stage does a reaction proceed or how far can a reaction go. We have also seen that, for chemical reactions, the two processes can be defined as follows. Irreversible reactions are said to go to completion, implying thereby that the reaction proceeds until at least one of the reactants is completely used up. On the other hand, all those reactions which appear not to proceed beyond a certain stage after sometime even when the reactants are still available, are reversible reactions. They have only reached an equilibrium state.

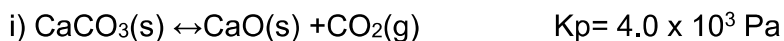
5.0 Summary

In this unit we have discussed the meaning of chemical equilibrium. A general expression for the equilibrium constant was derived from the basic principles of thermodynamics. Different forms of the general expression were then utilised in understanding the equilibria of homogeneous and heterogeneous systems. We then learnt Le Chatelier's principle and its use in predicting the shift in the position of equilibrium by the changes brought about in concentration, temperature and pressure of the system.

6.0 Tutor-Marked Assignments

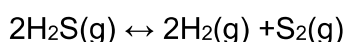
1) In a reaction $A + 2B \leftrightarrow 2C + D$, A and B are taken in a closed vessel at 300 K. The initial concentration of B is 1.5 times that of A. At equilibrium, the concentration of A and D are equal. Calculate the equilibrium constant at 300 K.

2) At 1000 K for the equilibria,



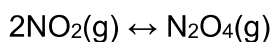
Solid C, CaO and CaCO_3 are mixed and allowed to attain equilibrium at 1000 K. What is the pressure of CO?

3) For the reaction,



Write an expression for the equilibrium constant, K_p ,

4. At a certain temperature, $K_c = 7.5 \text{ m}^3 \text{ mol}^{-1}$ for the reaction,



i) If 2.0 mol of NO_2 are placed in a 2.0 dm^3 container and allowed to react, what will be the concentrations of NO_2 and N_2O_4 at equilibrium?

ii) What will be the equilibrium concentration, if the volume of the container is doubled?

7.0 References/ Further Reading

Principles of Physical Chemistry, Samuel H. Maron and Carl F. Prutton, Oxford and IBH Publishing Co., New Delhi, 4th ed., 1985.

Physical Chemistry, Gilbert W. Castellan, Narosa Publishing House, Addison-Wesley/Narosa (Indian Student Edition), Delhi, 3rd ed., 1983.

Physical Chemistry, P.c. Rakshit, Sarat Book House, Calcutta, 5th ed., 1988.

Physical-Chemistry through Problems, S.K. Dogra and S. Dogra, Wiley Eastern Ltd., New Delhi, 1984.

Physical Chemistry-Principles and Problems, D.V.S. Jain and P. Jauhar, Tata McGraw-Hill Pub. Company Ltd., New Delhi. 1990.

Unit 2

Electrolytes

Content

- 1.0 Introduction
- 2.0 Learning Outcomes
- 3.0 Learning Content
 - 3.1 Interactions in Solutions
 - 3.2 Faraday's Laws of Electrolysis
 - 3.3 Electrolytic Conductance
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor-marked assignment
- 7.0 References/further reading

1.0 Introduction

An electrolyte on dissolution in water dissociates to give positive and negative ions which may carry single or multiple charges; For example, when sodium chloride is dissolved in water, the sodium ions, Na^+ , and chloride ions, are formed and get dispersed throughout the solution homogeneously, These ions are responsible for the passage of current through sodium chloride solution. In order to find the amount of current carried by these ions and the changes brought about by the passage of current through a solution, we should learn more about the nature and properties of the solvent.

For instance, depending on the nature of the solvent, there are many kinds of interactions possible in an electrolyte solution. Two of these are ion-dipole and ion-ion interactions. We shall study a few possible interactions which influence the passage of current through aqueous solution, since Water is a commonly used solvent. We shall then look into some of the useful applications of conductance. studies.

2.0 Learning Outcomes

After going through this unit, you should be able to:

- i. describe the nature of ions in solution and the possible interactions among them
- ii. state Faraday's law of electrolysis and apply the same to a few systems
- iii. define specific and molar conductance of a solution
- iv. describe the dependence of conductance on concentration
- v. state Kohlrausch's law of independent mobility of ions
- vi. state the applications of conductance measurements,

3.0 Learning Content

3.1 Interactions in Solutions

Since water is the most commonly used solvent, our studies are mainly confined to reactions in water. It is desirable that we refresh our memory about the nature and structure of water.

[Coulomb's law states that the force of attraction between two oppositely charged particles is directly proportional to the product of the charges and inversely proportional to the square of the distance between them. Mathematically it is expressed as:

$$F \propto \frac{q_1 \cdot q_2}{r^2}$$

where q_1 and q_2 are the charges on the two particles, r is the distance between them and F is the force of attraction].

Based on a number of physico-chemical studies, the water molecule may be represented as shown in Fig. 1.

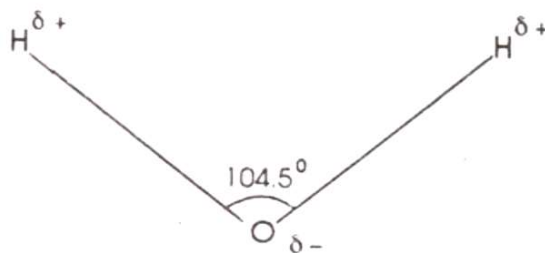


Fig. 1: Structure of water molecule

It is a bent molecule, H-O-H bond angle being approximately 104.5° . It shows polar character due to a large difference-in the electronegativities of oxygen and hydrogen atoms. It thus has a permanent dipole moment. We should, therefore, expect water molecules to interact with each other. This kind of interaction between permanent dipoles is called dipole-dipole interaction. Due to this interaction, there is net force of attraction between the molecules. In addition, there will be hydrogen bonds present between oxygen atom of one molecule and hydrogen atoms of other molecules.

When a salt is dissolved in water, it will produce ions in solution. As a result, there will be additional interactions between ions and water as well as between the ions themselves. We shall now consider such interactions in detail.

3.1.1 Ion-Solvent Interaction

An ion in solution will create an electrical field around it and solvent molecules with dipole moment will strongly interact with the field due to the ion. The water molecules will thus orient themselves in such a way that the dipoles lie along the field direction in order to minimise the energy of the system. The negative end of the water dipole will point towards the cation and the reverse will be true for the anion. Thus, each ion will be surrounded by a number of water molecules. Of course, generally, this number will depend on the size and charge of the ion and the nature of the solvent molecules.

These ions are then called 'solvated ions'; in case of water, they are known as hydrated ions. The ion-solvent interaction is strong enough to hold a certain fixed number of solvent molecules (called coordination number) around a particular ion; however, the interaction is not so strong as to always produce different chemical species in solution. Whenever the interaction is strong enough to give different product, we define it as solvolysis and, in case of water, it is called hydrolysis.

Solvent molecules so held by the central ion are known to form the first solvation shell. The first hydration shell for most of the cations usually contains either four or six molecules of water. For example, Cr^{3+} or Ni^{2+} is present as $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ or $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ in aqueous solution. The solvent structure far away from the ion differs little from the bulk structure of the solvent. In between these two extremes, there is a region of solvent structure where solvent molecules are under the influence of two forces, one

from the ions present in the solution and the other due to intermolecular forces of the solvent.

The solvent molecules in this region are consequently oriented randomly. To sum up, we can say that an electrolyte on dissolution in a solvent produces solvated ions. There is an inner or a primary solvent shell in which the solvent molecules are bound through the strong ion-dipole interaction. There is an outer or secondary solvent layer where molecules are not aligned in any particular fashion either by the field of the ion or by the forces that act in bulk solvent. The solvation number of an ion is defined as the mean number of solvent molecules in the primary solvation shell.

3.1.2 Ion-Ion Interactions

Any two ions present in a solution will interact with each other. Like charges will repel each other whereas unlike charges will attract each other. The electrostatic forces between any two ions is governed by Coulomb's law.

Thus a sodium ion in a solution of sodium chloride will be repelled by other sodium ions in its vicinity but it will be attracted by chloride ions. However in solutions, a well-ordered structure as found in the solids-where each ion is surrounded by a definite number of oppositely charged species at a fixed distance-is not possible. In solutions, the thermal motion will not leave the ions at fixed positions.

The net result is that at any given moment on an average, there will be an atmosphere of excess of negative ions around each positive ion and the reverse will be true for the negative ion as shown in Fig. 2

The measure of the electrostatic interaction is given by a term called, ionic strength, *I*. The ionic strength depends on the concentration of the ions present and the charge carried by the ions. It is given by the expression,

$$I = \frac{1}{2} \sum m_i z_i^2 \dots\dots\dots(1)$$

where m_i is the molal concentration of ion 'i' in solution and z_i is the charge associated with the same ion.

In the case of a dilute solution (of density, d), its molarity (C_i) is related to its molality (m_i) as per Eq. 2.

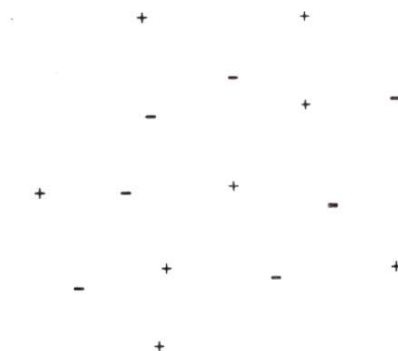


Fig. 2: Atmosphere of oppositely charged ions around each cation and anion.

$$C_i = m_i d \dots\dots\dots(2)$$

Substituting the value of m_i from Eq. 2 into Eq. 1 we get,

$$I \approx 1/2d \sum C_i z_i^2 \dots\dots\dots(3)$$

Eq. 3 indicates that the electrostatic interaction between any two ions in solution is directly proportional to concentration of the solution. This has been experimentally verified in terms of a quantity called ion-atmosphere radius. It is defined as the effective radius at which the atmosphere of opposite charges is situated around an ion. The radii of ion-atmosphere around sodium ion in 1.0×10^{-2} M, 10×10^{-4} M and 1.0×10^{-6} M sodium chloride solutions have been calculated to be in the ratio of 1:10:100. Thus, we see that ion-atmosphere radius increases with dilution.

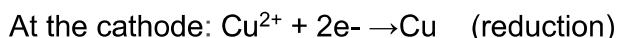
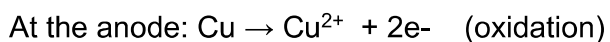
Hence, it can be concluded that at very low concentrations or at infinite dilution, an ion would be free from inter-ionic interactions. The concepts developed so far form the basis for the theory of ionic solutions as given by Debye and Huckel. However, our immediate concern is to study the effects of passage of current through an electrolyte solution but not the theory of electrolytic conductance. Next four sections are devoted to these studies only.

3.2 Faraday's Laws of Electrolysis

A process in which a chemical change is brought about by the passage of current through a solution is called electrolysis. The apparatus in which electrolysis is carried out is known as electrolytic cell. Consider a solution of an electrolyte into which two metal plates are dipped. The metal plates do not chemically react with the solution. On connecting the plates to the two terminals of a battery, a current starts flowing through the solution due to movement of ions in solution.

The negatively charged plate is called cathode and the positively charged plate is known as anode. The ions which move towards cathode and anode are known as cations and anions, respectively. The combined name for the two plates is electrodes. As the ions reach the two electrodes, a chemical reaction takes place at each electrode; oxidation at the anode and reduction at the cathode. Suppose that an electric current is passed through a solution of copper sulphate into which two copper electrodes are dipped.

Then the following reactions occur at the electrodes:



The battery pushes electrons to one electrode and takes away from the other. In other words, electrons are transferred between the electrodes and ions. The current in the solution is due to migration of ions. Suppose that a current (I) is passed through an electrolyte solution for a time t . Then the quantity of electric current (q) passed is given by the product of current and time.

$$q = I \cdot t \dots\dots\dots(4)$$

The units of quantity of electricity, current and time are coulomb (C), ampere (A) and second(s), respectively. Hence,

$$1C = 1 A s$$

An electrolytic cell designed to measure the quantity of electric current that has passed through the solution is called a coulometer (see Example 1). For example, a silver coulometer uses platinum electrodes and a solution of silver nitrate as an electrolyte. On electrolysis the following reaction occurs at the cathode and silver gets deposited.



By measuring the increase in mass of the cathode, one can calculate the quantity of electric current that has passed during electrolysis. To understand the calculations involving coulometer, we must study Faraday's laws of electrolysis. In 1813, Faraday made certain useful observations on the decomposition of electrolyte solutions by the passage of electric current. These are known as Faraday's laws of electrolysis and are stated below:

1) The mass (w) of a product formed at an electrode is directly proportional to the quantity

of electricity (q) passed i.e.

$$w \propto q \dots\dots\dots (6)$$

2) The masses of different products (say w₁ and w₂ for two substances 1 and 2) formed at the electrodes by the passage of the same quantity of electricity are directly proportional to their equivalent weights. Thus the quantity of electricity that has passed through the electrolytic cell can be measured by the extent of the chemical reaction which has taken place in a cell or vice-versa.

Before seeing the usefulness of these laws, let us explain the term faraday. The quantity of electricity carried by 1 mole of electrons is called faraday and given the symbol, F. The charge on one electron is 1.602×10^{-19} C. Hence, the charge on one mole of electrons' would be $1.602 \times 10^{-19} \times 6.022 \times 10^{23}$ C or 96489 C. It is usual to approximate one faraday as being equal to 96500 C. Consider an electrode reaction:



The quantity of electricity required for the deposition of 1 mole of X will be equal to nF, where n is the number of moles of electrons required for the reaction. Let M be the mass of 1mole atoms of an element X. Therefore, for the deposition of M kg (or 1 mole) of the element, we require nF or n x 96500 C of electricity. It can also be expressed as follows: n x 96500 C of electricity deposits M kg (or 1 mole) of an element. Hence, q coulomb of electricity deposits

$$\frac{M \times q}{n \times 96500} \quad \text{kg of the element.}$$

$$\text{or } w = \frac{M \times q}{n \times 96500} \quad \text{kg} \quad \dots\dots\dots (7)$$

where w = mass of an element deposited by the passage of q coulomb of current.
Substituting the value of q from Eq. 4 into Eq. 7 we get

$$w = \frac{M \times I \times t}{n \times 96500} \quad \dots\dots\dots (8)$$

This equation is useful in calculating the mass of all element deposited by the passage of known quantity of current. Let us make use of Eq, 8 in solving some problems.

Example 1

A current of 5.0×10^{-3} A is passed for 100 minutes through a silver coulometer. Calculate the mass of silver deposited on the cathode. Atomic mass of Ag = 107.9 (or $M = 0.1079$ kg/mol).

Solution

Substituting the given values in Eq. 8 we get,

$$w = \frac{0.1079 \text{ kg mol}^{-1} \times 5.0 \times 10^{-3} \text{ A} \times (100 \times 60) \text{ s}}{1 \times 96500 \text{ C mol}^{-1}}$$

($n = 1$, since 1 mole of Ag^+ ions needs 1 mole of electrons)

$$w = 3.4 \times 10^{-5} \text{ kg}$$

Example 2

Two electrolytic cells, one containing silver nitrate solution and the other copper sulphate solution as electrolytes were connected in series. A steady current of 1.50 A was passed through them until 0.00145 kg of silver was deposited at the cathode of the first cell. How long did the current flow? What mass of copper was deposited in the second cell?

Solution

Let t second be the time for which the current flowed through the cells.

For the deposition of Ag,

$$n = 1, \quad I = 1.50 \text{ A}, \quad w = 0.00145 \text{ kg}, \quad M = 0.1079 \text{ kg mol}^{-1}$$

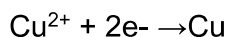
Rearranging Eq. 8 and substituting the given values we get,

$$t = \frac{w \times n \times 96500}{M \times I}$$

$$t = \frac{0.00145 \text{ kg} \times 1 \times 96500 \text{ A s mol}^{-1}}{0.1079 \text{ kg mol}^{-1} \times 1.50 \text{ A}}$$

Since the electrolytic cells containing AgNO_3 and CuSO_4 are connected in series, same quantity of current is passed through both the cells. Hence, for the deposition of

Cu, we have, $I = 1.50 \text{ A}$ and $t = 865 \text{ s}$. But $n = 2$ in the electrolysis of CuSO_4 solution, since



Further, mass of one mole atoms of Cu = 0.06354 kg.

Substituting these values in Eq. 8 we get,

$$\text{mass of copper deposited} = \frac{0.06354 \text{ kg mol}^{-1} \times 1.50 \text{ A} \times 865 \text{ s}}{2 \times 96500 \text{ C mol}^{-1}} = 4.27 \times 10^{-4} \text{ kg}$$

You should now be able to apply the laws of electrolysis in solving the following **SAEs**.

Self-Assessment Exercises 2

1. If a 5 A current is passed through an electrolytic cell containing molten magnesium chloride, 'how long would it take to prepare a mole of magnesium metal?
[Hint: $\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$]
2. 1 dm³ of a solution of 2.0 M CuSO_4 is electrolysed using platinum electrodes by passing 4.50 A current for 9000 s.
Calculate
 - i) the mass of Cu deposited, and
 - ii) the amount of Cu^{2+} in the solution at the end of the electrolysis

3.3 Electrolytic Conductance

We shall now consider a property of the electrolyte solution, called, conductivity. The electrical resistance (R) of a sample is directly proportional to its length (l) and inversely proportional to its cross-sectional area (A). It can be expressed as,

$$R \propto l/A$$

$$\text{or } R = \rho \cdot l/A \dots\dots\dots(9)$$

The proportionality constant, ρ , is known as its electrical resistivity. The unit of resistance is ohm (Ω) while the unit of resistivity is ohm metre ($\Omega \text{ m}$). The electrical conductance is defined as the inverse of electrical resistance. Similarly, conductivity or specific conductance (k) of a material is defined as the reciprocal of its electrical resistivity. Hence, Eq. 9 can be written as

$$R = 1/k \cdot l/A \dots\dots\dots(10)$$

$$\text{or } k = l/AR \dots\dots\dots(11)$$

Since the resistance is expressed in ohm, the reciprocal ohm (Ω^{-1}) was earlier used as the unit for conductance. However, in SI system; the unit for conductance is

'siemens' and, given the symbol 'S'. Hence, the unit for conductivity will be $S\ m^{-1}$. ($1\ S = 1\ \Omega^{-1}$).

For the measurement of electrical resistance (R_x) of a sample, we use a set-up known as Wheatstone bridge. It consists of two wires R_1 , R_2 , of known resistance values, and a third resistance, R_s the value of which can be adjusted. These are all connected to a battery source, E , as shown in Fig. 3. R_s is adjusted until points a and b are exactly at the same potential. This can be tested by momentarily connecting a sensitive ammeter (A) between a and b . If the two points are exactly at the same potential, there will be no deflection in the ammeter.

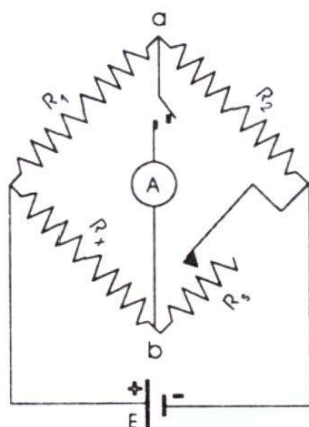


Fig. 3: Wheatstone bridge.

Under these conditions, the following relation holds:

$$R_1/R_2 = R_x/R_s$$

or $R_x = R_s \cdot R_1 / R_2$ (12)

For finding the resistance of a solution (R_{cell}), we make slight alterations in the Wheatstone bridge described above. Instead of a battery, we use an alternating current source to prevent electrolysis. The electrolysis that occurs when current passes in one direction is reversed when it passes in the other direction. The direction of current changes so rapidly that the build-up of charge at the electrode is not possible. Finally, instead of an ammeter, we use an alternating current detector as shown in Fig. 4.

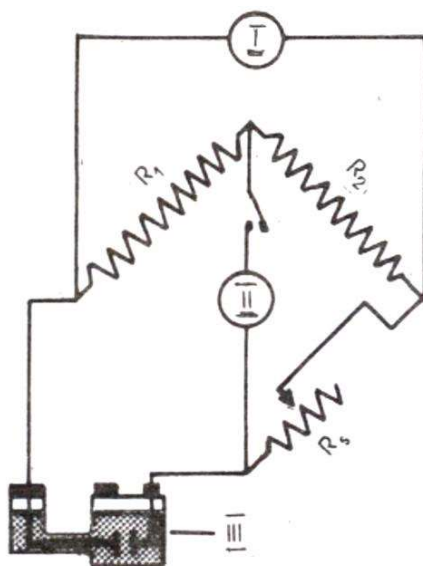


Fig. 4: Wheatstone bridge where electrolytic cell occupies one arm of the bridge :

- i) AC source of frequency
- ii) Alternating current detector
- iii) Test cell (R_{cell}) ,

At the balance point,

$$R_{\text{cell}} = R_3 \left(\frac{R_1}{R_2} \right) \dots \dots \dots (13)$$

The relationship between specific conductance and resistance is given by Eq. 11 as

$$k = \kappa \cdot l \cdot A \cdot 1/R$$

$$\text{or } k = k_{\text{cell}} \cdot 1/R \dots \dots \dots (14)$$

where k_{cell} is the cell constant representing $\kappa \cdot l \cdot A$ ratio; it is a constant as far the same cell is used for measurements. Since the conductivities of certain standard solutions have been carefully measured" we could use such a solution in a cell and measure its resistance. Thus knowing k and R , we can calculate the value of k_{cell} the cell constant. Once k_{cell} is determined, we can use the same cell for the measurement of conductivity of other electrolyte solutions. Using these ideas, work out the following **SAE**.

Self-Assessment Exercise 2

A conductance cell filled with 0.020 M KCl has a resistance of 195.96 Ω at 298 K. When filled with a 0.050 M AgNO_3 solution, it has a resistance of 94.2 Ω . The specific conductance of 0.020 M KCl is 0.2768 S m^{-1} . What is the specific conductance of 0.050 M AgNO_3 solution?

4.0 Conclusion

When an electrolyte dissolves in water, it dissociates to give positive and negative ions which may carry single or multiple charges. These ions are responsible for the passage of current through the solution. The nature and properties of the solvent determines the amount of current carried by these ions and the changes brought about by the passage of current through the solution. Faraday made certain useful observations on the decomposition of electrolyte solutions by the passage of electric current. These are known as Faraday's laws of electrolysis.

5.0 Summary

In the present unit, we have discussed the behaviour of electrolytes in solution under the influence of an electric field. Since the ions produced by the dissolution of an electrolyte are charged particles, these are bound to interact with each other. However, these interactions will not be as strong as in solid state due to the thermal motion of the ions. At the same time, the ions will interact with polar molecules of the solvent, water. After explaining the nature of these interactions, we then analysed in brief as to what happens to these solutions at the electrodes when we pass an electric current through them. This has been summed-up in the two laws of Faraday. Different ions, even when they carry same charge, will move at different rates under the influence of an electric potential.

6.0 Tutor-Marked Assignments

- 1) The specific conductance at 298 K of a saturated solution of BaSO_4 is $4.580 \times 10^{-4} \text{ S m}^{-1}$ and that of water is $5.50 \times 10^{-6} \text{ S m}^{-1}$. The molar conductance at infinite dilution of BaSO_4 is $2.86 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$. What is the solubility of BaSO_4 at 298 K?
- 2) 1000 C of electricity is passed through a NaOH solution in an electrolysis apparatus. Calculate the volume of hydrogen and oxygen liberated at S.T.P.
- 3) Calculate the time required to discharge all the Cr^{3+} ions from 500 cm^3 of 0.270 M $\text{Cr}_2(\text{SO}_4)_3$ by a current of 3.00 A.

7.0 References/Further Reading

- Principles of Physical Chemistry, Samuel H. Maron and Carl F. Prutton, Oxford and IBH Publishing Co., New Delhi, 4th ed., 1985.
- Physical Chemistry, Gilbert W. Castellan, Narosa Publishing House, Addison-Wesley/Narosa (Indian Student Edition), Delhi, 3rd ed., 1983.
- Physical Chemistry, P.c. Rakshit, Sarat Book House, Calcutta, 5th ed., 1988.
- Physical-Chemistry through Problems, S.K. Dogra and S. Dogra, Wiley Eastern Ltd., New Delhi, 1984.
- Physical Chemistry-Principles and Problems, D.V.S. Jain and P. Jauhar, Tata McGraw-Hill Pub. Company Ltd., New Delhi. 1990.

Unit 3

Electrochemistry

Content

- 1.0 Introduction
- 2.0 Learning Outcomes
- 3.0 Learning Content
 - 3.1 Galvanic or Voltaic Cells
 - 3.2 Experimental Measurement of emf
 - 3.3 Standard Electrode Potential
 - 3.4 Electrochemical Cell Representation and Cell Reaction
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor-marked assignment
- 7.0 References/further reading

1.0 Introduction

In an electrolytic cell, a chemical reaction takes place by passing electricity through an electrolyte in a fused state or in solution. On the other hand, when an electrochemical cell is used to generate electricity by the use of a chemical reaction, it is called a galvanic or voltaic cell. Also in this unit, we shall study different types of galvanic cells, the electrodes used and their effect on the voltage generated.

2.0 Learning Outcomes

After going through this unit, you should be able to:

- i. explain the terms used in electrochemistry such as anode, cathode, oxidation, reduction and emf
- ii. calculate the cell potential for a given cell
- iii. correlate the electrical energy generated by the cell with the free energy change for the cell reaction
- iv. correlate the dependence of the cell potential on the temperature and the concentration of the electrolytes
- v. describe the characteristics and the half-cell reactions of various kinds of electrodes used
- vi. differentiate between primary and secondary cells
- vii. list different types of dry cells in common use, and
- viii. describe the use of electrolytic cells.

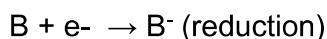
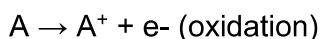
3.0 Learning Content

3.1 Galvanic or Voltaic Cells

Let us recapitulate the definitions of the terms, oxidation and reduction. Oxidation is the loss or release of electrons. Reduction is the gain or addition of electrons. These two processes are illustrated below:



Usually oxidation and reduction reactions take place together. Such reactions are also called redox reactions. Electrochemical cells make use of spontaneous oxidation-reduction reactions to produce electricity. These cells are known as galvanic or voltaic cells in recognition of the work by Italian scientists, Galvani and Volta. Let us explain the functioning of a voltaic cell. In any spontaneous redox reaction, the two processes,

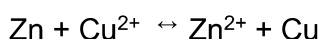


take place without doing any useful work, if we just mix them together. The energy released by such a reaction is in the form of heat. However, if we devise a means of performing oxidation and reduction in separate compartments rather than 'mixing the two together, we can force the electrons to flow from oxidation to reduction compartment through an external wire, thus producing current. Part of the energy of the reaction is thus converted into electrical work. Let us take the example of the most common and familiar galvanic cell, known as Daniell cell.

It consists of a container divided into two compartments by a porous plug. The function of the porous plug is not to allow the free mixing of the electrolyte solutions in the two compartments but to allow the flow of ions. In one compartment, a strip of zinc metal is immersed in a solution of zinc sulphate whereas, the other compartment holds a solution of copper sulphate with a copper strip immersed in the solution. The two metal strips henceforth called the electrodes, are connected to an ammeter through copper wires as shown in Fig. 1.

The moment the two electrodes are connected, a current starts flowing as shown by the deflection in the ammeter. As the current flows through the circuit, zinc strip dissolves while copper deposits at the other electrode.

The overall reaction in Daniell cell can be represented as



whereas the reactions taking place in the two compartments known as half-cell reactions can be written as:



There is always an equilibrium between the atoms in the electrode and the ions present in the solution as represented by the above equations. The electrode at which oxidation takes place is called anode; it is at a lower potential than the cathode at which reduction takes place. Zinc metal dissolves as Zn^{2+} ion leaving behind an excess of electrons at this electrode. Thus anode gets negatively charged and attains relatively lower potential.

On the other hand, ions in solution around the cathode withdraw electrons from it causing it to become positively charged and attain relatively higher potential. By convention, we regard the current through the connecting wire to flow from positive to negative, that is from cathode to anode in the present context. However, we should not forget that the flow of electrons in the wire is in the opposite direction, that is, from zinc to copper. However, in an electrolytic cell, the situation will be just the opposite. The anode would acquire a positive charge and the cathode, a negative charge.

In order to avoid any confusion, we shall always refer to an electrode, where oxidation takes place, as anode, and the electrode, where reduction takes place, as Cathode, irrespective of whether the cell is galvanic or electrolytic.

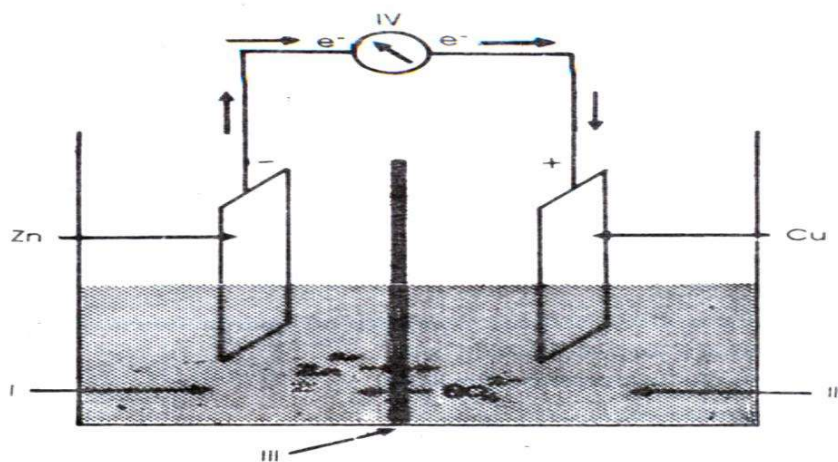


Fig. 1: Daniell Cell: I) ZnSO₄ solution; II) CuSO₄ solution; III) porous plug; IV) ammeter

Self-Assessment Exercise 1

1. How do we define anode and cathode? What sign - positive or negative - would you assign to anode and cathode in (a) a galvanic cell (b) an electrolytic cell?

3.2 Experimental Measurement of emf

The Capacity to do electrical work by a cell is called the cell potential. It is expressed in volt (V). We could use a voltmeter to measure the cell potential. However, this would not give us the Correct value of cell potential. The reason is that the cell potential is dependent upon the concentration of the electrolyte which would change if we allow the current to flow in the circuit through the voltmeter. Hence, we must measure the potential difference between the two half-cells when the cell is held at almost constant composition and no current is flowing.

The potential difference of a cell when no current is drawn out and when the cell is operating reversibly is called the emf (electromotive force) of the cell. The measurement of the emf can be done by using a potentiometer. More recently emf is found with the help of an electronic digital voltmeter which draws negligible current.

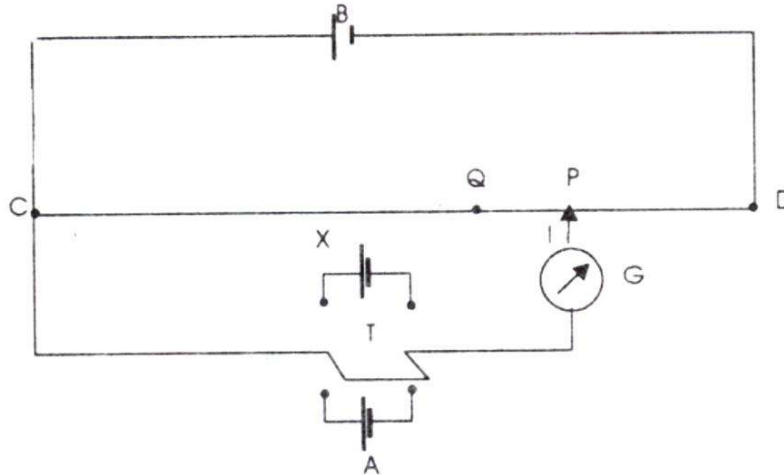


Fig. 2: Potentiometric measurement of emf of a cell

Fig. 2 shows a simple set-up to measure the emf of a cell. The potentiometer consists of a wire of uniform cross-section and high resistance. This wire is stretched between two terminals, C and D. It is connected to a storage battery, B. The terminal C is connected to a sliding point I which can be moved from C to D. In between C and D, there is a double throw-switch T and a galvanometer G. The function of the switch is to bring either a standard (Weston) cell, A, or the test cell X (for which emf is to be determined) in the circuit. First, we connect A in the circuit and move I to such a position P that there is no deflection in the galvanometer. The exact length of the wire from C to P is recorded. Let us suppose this length is l_1 . Next by means of the switch T, we remove A but bring cell X in the circuit. The emf of A and X may not be the same, hence on replacement of A by X, the galvanometer will show a deflection. We move the contact point to such a position Q that there is again no deflection in the galvanometer. Measure the length of the wire l_2 , from C to Q. Under the conditions of no deflection, the drop in potential of the battery B across the slide wire is balanced by the emf of the cell (A or X).

Hence, we can write, emf of X = Drop in potential from C to Q (E_2) = Resistance due to wire length CQ \times emf of A / Resistance due to wire length CP \times emf of A

$$\text{In general, } E_2 = E_1 l_1 / l_2$$

where E_2 and E_1 are the emf values of the test cell and the standard cell, respectively. We make use of a standard cell in the procedure described above for the standardisation of a potentiometer. We describe here, Weston cadmium cell, which is a commonly used standard cell.

Weston Cell

The most commonly used standard cell is called Weston cell. Its voltage remains constant for a long period of time and is reproducible. The change in voltage with

temperature is also small. Due to these advantages, Weston cell is widely used as a standard cell. The basic Cell reaction can be represented as



It is prepared in the form of a H-shaped container as shown in Fig. 11

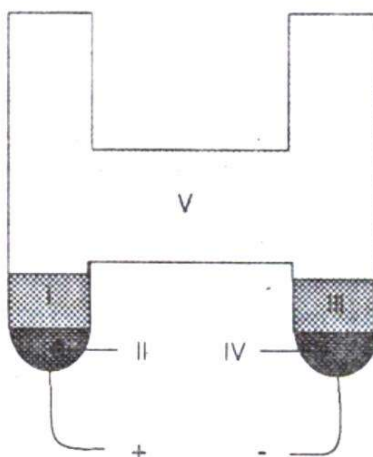


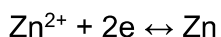
Fig. 3: Weston cell: I) Paste of Hg and HgSO₄ II) Mercury III) 3CdSO₄.8H₂O crystal IV) Cd(Hg) (V) Saturated CdSO₄ solution

In one arm of the container, mercurous sulphate - mercury paste is in contact with mercury. In the other arm, some crystals of cadmium sulphate are dropped over the surface of cadmium amalgam (12.5%). The container is then filled with a saturated solution of cadmium sulphate. The cell produces an emf of 1.01845 V at 293 K.

3.3 Standard Electrode Potential

Consider a strip of zinc metal immersed into an aqueous solution of zinc sulphate at constant temperature and pressure. Both metal and the solution, contain zinc ions which can be transferred between the two phases. If some zinc ions from the metal enter into the solution, there would be a net negative charge on the electrode due to the excess of electrons left behind. On the other hand, zinc ions already in solution attract electrons from the electrode and the resulting zinc atoms would stick to the surface of the electrode.

This process will leave a positive charge on the electrode, In a short time, however, the rate of escape and of return of zinc ions become equal and an equilibrium is established as expressed by



Depending upon whether the equilibrium lies towards left or right .the net-charge on the electrode will arise. Thus we see that there will be a potential difference developed at the junction of the metal and the solution. However, the potential difference between. the two phases cannot be readily measured. Therefore, instead of

measuring the electrode potentials, we usually measure the total cell potential. The cell potential can be written as the sum of the two electrode potentials neglecting other effects which contribute to the potential difference between the phases, Thus,

$$E_{\text{cell}} = E_{\text{cathode}} + E_{\text{anode}}$$

The total cell potential is a measure of the driving force of a chemical reaction whereas E_{cathode} and E_{anode} are representative of oxidising and reducing capabilities of the concerned reactants, respectively. Hence, in order to obtain a large cell potential, we must use a strong oxidizing agent along with a strong reducing agent. Now the question arises as to how do we decide which is a better oxidising agent and which is a better reducing agent.

To determine the comparative oxidising or reducing capacity of any substance, we must use some standard against which all other electrode potentials are measured. We shall now explain the necessity of having such a standard.

Let us consider an example, say Daniell cell, the standard cell potential of which is 1.1 V. It just tells us that zinc is a better reducing agent than copper since zinc gets oxidised to Zn^{2+} ion and it reduces Cu^{2+} ions to metallic copper. However, it will not tell us whether a third substance, say, Fe is a better reducing agent than zinc or copper. In order to get some idea regarding the relative oxidising and reducing abilities of different substances, we must measure the cell potentials keeping one-half-cell the same in every case.

This is necessary since we cannot measure directly the potential of a half-cell. It is like saying that for a reducing agent to give off its electrons, surely you must have an oxidising agent to accept that electron. It cannot function as an oxidising agent on its own without the presence of a reducing agent. Further, for comparing the reducing powers of different substances, we must use the same oxidising agent. The standard against which all other potentials are measured, is a hydrogen electrode. We now describe a standard hydrogen electrode. The chemical reaction taking place at the hydrogen electrode is given by the equation: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

The electrode potential for the standard hydrogen electrode is arbitrarily assigned a value of zero. Fig. 12 shows a standard hydrogen electrode where hydrogen gas is bubbled through a glass hood (B) over the surface of Pt electrode (A) at a pressure of 1 bar (≈ 1 atm). The electrode is immersed in an acid in which $[\text{H}_3\text{O}^+] = 1$ M. The whole set-up is kept at 298 K.

[Standard reduction potential indicates the willingness of a species to be reduced under standard conditions. Larger the reduction potential, greater is the ease with which a particular species can be reduced; in other words, it is a powerful oxidizing agent. This is so because, in an oxidation - reduction reaction, an oxidising agent gets reduced and a reducing agent gets oxidised].

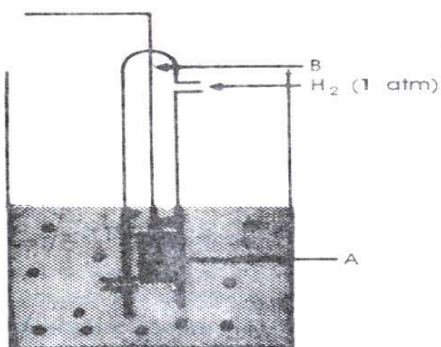


Fig. 4: Standard hydrogen electrode.

In view of the confusion that existed in literature regarding the sign convention in reporting the standard state half-cell potentials (E°), IUPAC has set down the following rules in this regard:

- 1) All electrode reactions are written as reduction reactions.
- 2) All reactions that produce better reducing agents than hydrogen are given a negative reduction potential value.
- 3) The most negative reduction potential values are written at the top of the table of standard reduction potentials (Table 1)

These E° values represent the driving force or spontaneity of the reactions under standard conditions. For example, the reaction, $F_2 + 2H^+ + 2e^- \rightarrow 2HF$

has a strong tendency to go in the forward direction since it has a high positive potential value, whereas, the reaction, $Li^+ + e^- \rightarrow Li$

has the least tendency to go in the forward direction; rather, it has strong tendency to go in the reverse direction. These observations are in accordance with our basic knowledge of chemistry. Fluorine shows a strong tendency to become fluoride ion; thus, fluorine should act as a powerful oxidising agent. The same reasoning tells us that lithium metal should act as a strong reducing agent. These conclusions are borne out by experimental results.

Table 1: The Standard Reduction Potentials (E°) for some Half-Cell Reactions

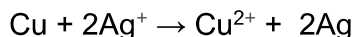
Half-cell reactions.	E°/V
$\text{Li}^+ + \text{e}^- \longrightarrow \text{Li}$	- 3.05
$\text{K}^+ + \text{e}^- \longrightarrow \text{K}$	- 2.93
$\text{Ca}^{2+} + 2\text{e}^- \longrightarrow \text{Ca}$	- 2.87
$\text{Mg}^{2+} + 2\text{e}^- \longrightarrow \text{Mg}$	- 2.36
$\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$	- 1.66
$\text{Zn}^{2+} + 2\text{e}^- \longrightarrow \text{Zn}$	- 0.76
$\text{Fe}^{2+} + 2\text{e}^- \longrightarrow \text{Fe}$	- 0.44
$\text{Sn}^{2+} + 2\text{e}^- \longrightarrow \text{Sn}$	- 0.14
$\text{Pb}^{2+} + 2\text{e}^- \longrightarrow \text{Pb}$	- 0.13
$\text{Fe}^{3+} + 3\text{e}^- \longrightarrow \text{Fe}$	- 0.04
$2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$	0.00
$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$	+ 0.34
$\text{Cu}^+ + \text{e}^- \longrightarrow \text{Cu}$	+ 0.52
$\text{I}_2 + 2\text{e}^- \longrightarrow 2\text{I}^-$	+ 0.54
$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \longrightarrow \text{MnO}_2 + 4\text{OH}^-$	+ 0.59
$\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$	+ 0.77
$\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$	+ 0.80
$\text{Br}_2 + 2\text{e}^- \longrightarrow 2\text{Br}^-$	+ 1.09
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+ 1.33
$\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$	+ 1.36
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+ 1.49
$\text{F}_2 + 2\text{H}^+ + 2\text{e}^- \longrightarrow 2\text{HF}$	+ 3.03

Now that we have a set of values for the standard half-cell potentials, we can use them to calculate the standard cell potential for any cell. There are, however, a few points to be kept in mind before we set out to calculate the standard cell potentials. Since the cell potentials are a measure of the tendency of a particular reaction to go in a particular direction, these potentials are cited in volt and not as volt per mole. The calculation of the standard cell potential from the standard potentials of the two half cells will not be affected by the stoichiometric coefficients used to balance the overall reaction.

You must remember that Table 1 gives the standard reduction potentials for some half cell reactions. But at the anode, a particular species gets oxidised. In order to get the standard potential for the oxidation reaction at the anode, the sign of the standard reduction potential for that reaction must be reversed.

i.e., $E_{\text{anode}} = -E^{\circ}$ as per Table 1.

For example, let us calculate the standard cell potential for the reaction:



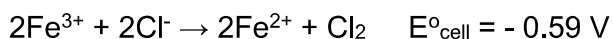
for which the half-cell reactions and corresponding potentials are given below: ..



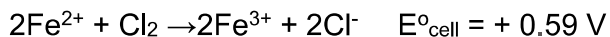
we shall not multiply the Ag^+/Ag cell potential by two which is a number used to balance the overall reaction. Secondly, we must keep in mind that in the overall reaction, copper metal is getting oxidised to Cu^{2+} ion. Hence, when we are adding the cathodic and anodic potentials to find the total cell potential, we must reverse the sign of the potential for Cu^{2+}/Cu couple. Thus the standard cell potential for the reaction would be

$$\begin{aligned} E_{\text{cell}} &= E^{\circ}_{\text{anode}} + E^{\circ}_{\text{cathode}} \\ &= -E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} + E^{\circ}_{\text{Ag}^+/\text{Ag}} \\ &= [(-0.34) + (0.80)] \text{ V} \\ &= 0.46 \text{ V.} \end{aligned}$$

A positive E_{cell} value indicates that the reaction is spontaneous under standard conditions. But, if any reaction is written in such a way that on calculation; the cell potential has a negative sign, it should be inferred that the reaction is non-spontaneous. For example, under standard conditions,



is not a spontaneous reaction. On the other hand, the following reaction is spontaneous:

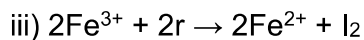
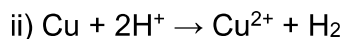
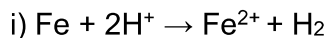


And the above is the cell reaction that takes place when a galvanic cell is designed using

Fe^{2+} , Fe^{3+} and Cl^- , Cl_2 , as reacting species,

Self-Assessment Exercise 2

Predict which of the following reactions will be spontaneous with the help of standard potential values:



3.4 Electrochemical Cell Representation and Cell Reaction

An abbreviated way of representing the Daniell cell is $\text{Zn} \mid \text{Zn}^{2+} (c_1) \parallel \text{Cu}^{2+} (c_2) \mid \text{Cu}$

The anodic reaction is always written on the left and, the cathodic reaction on the right. Also by convention, within the half-cell, the reactants are written before the products. A single vertical line is used to indicate a phase boundary and, a double vertical line represents the elimination of potential at the junction of two electrolyte solutions. Finally; the concentrations of aqueous solutions may be written in parenthesis after the symbol of the ions.

The line notation, therefore, corresponds to the direction of the flow of electrons. Many a times, instead of separating the two solutions by means of a porous plug, the two separate half-cells are connected by means of a salt-bridge. It consists of a U-tube filled with a saturated solution of a strong electrolyte such as KCl, NH_4NO_3 etc. The two ends of the U-tube are plugged by cotton-wool or the whole solution is set in agar-agar gel to prevent the free flow of KCl into the two cells (Fig. 5).

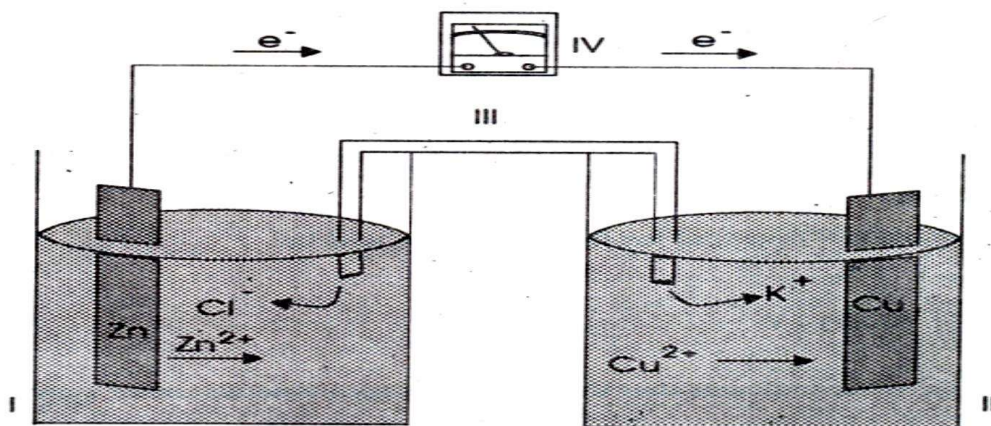


Fig. 5: Daniell Cell with salt bridge: I) anodic compartment II) cathodic compartment III) salt bridge IV) voltmeter

When we draw current from the cell, the negatively charged Cl^- ion will flow out from the salt-bridge to neutralise the excess of positive charge due to production of Zn^{2+} ion in the anode compartment. Similarly K^+ ion will flow into the other compartment to neutralise the excess of sulphate ions. Thus the electroneutrality of the solution in the two compartments is maintained.

Cell construction from cell reaction

Now we shall discuss the steps involved in constructing a cell from a given chemical reaction:

Step (i) : From the given chemical equation, write the balanced ionic equation.

Step (ii): Separate this ionic equation into two parts, one in which oxidation takes place and, another, in which reduction takes place. Balance each part using electrons.

Sometimes H^+ , OH or H_2O also may have to be added to either side of the equation for proper balancing.

Step (iii): The oxidation part must appear on the left side of the cell. The reduction part must appear on the right side of the cell. Usually electrons and H_2O are not indicated in the representation of the cell. Also stoichiometric numbers must not appear in the representation.

Step (iv): The electrodes are shown at the extreme left and right positions. These are shown distinctly separated from the corresponding electrolytes by means of single vertical lines. In case of gas electrodes and many redox systems, inert electrodes such as Pt wire or carbon rod are used for electrical contact.

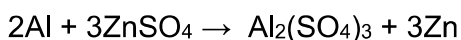
Step (v): A pair of vertical lines or a dotted line must be used to show the barrier between the left side and right side parts. Two vertical lines indicate the use of a salt bridge and a dotted line shows a porous barrier.

Step (vi): It is usual to represent the pressure of the gases, the concentration of the electrolytes and the physical state of the electrodes within parenthesis.

Using the principles explained above, answer the following **SAE**.

Self-Assessment Exercise 3

1. Draw a diagram of a Galvanic cell where the following reaction takes place:



4.0 Conclusion

An electrolytic cell is a set up in which a chemical reaction takes place by passing electricity through an electrolyte in a fused state or in solution. In an electrochemical cell is used to generate electricity by the use of a chemical reaction, it is called a galvanic or voltaic cell. There are different types of galvanic cells, the voltage generated depends on the reactions taking place and the electrodes used.

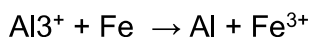
5.0 Summary

In this unit measurement of cell potential and its relation with the concentrations of the oxidised and the reduced species was developed in the form of Nernst equation. The different applications of Nernst equation were then discussed. Next we briefly looked at different kinds of galvanic cells and some of the commercial cells.

6.0 Tutor-Marked Assignments

- 1) With the help of standard reduction potential values, decide
 - a) which is a better oxidising agent- MnO_4^- or $Cr_2O_7^{2-}$ and
 - b) which is a better reducing agent- Cr or Br^- ?

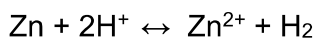
2) Calculate the cell potential at 298 K for the reaction



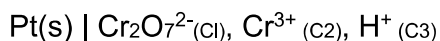
The concentrations of Al^{3+} and Fe^{3+} are 1.2 and 2.5 M.

3) Calculate E° for the cell

'Zn(s) | Zn²⁺ (1.0 M) || H⁺ (1.0 M) | H₂(g, 1atm) | Pt(s) and then calculate the equilibrium constant for the reaction,



4) Write an expression for the half-cell potential for the following redox system:



7.0 References/Further Reading

Principles of Physical Chemistry, Samuel H. Maron and Carl F. Prutton, Oxford and IBH Publishing Co., New Delhi, 4th ed., 1985.

Physical Chemistry, Gilbert W. Castellan, Narosa Publishing House, Addison-Wesley/Narosa (Indian Student Edition), Delhi, 3rd ed., 1983.

Physical Chemistry, P.c. Rakshit, Sarat Book House, Calcutta, 5th ed., 1988.

Physical-Chemistry through Problems, S.K. Dogra and S. Dogra, Wiley Eastern Ltd., New Delhi, 1984.

Physical Chemistry-Principles and Problems, D.V.S. Jain and P. Jauhar, Tata McGraw-Hill Pub. Company Ltd., New Delhi. 1990.

Unit 4

Chemical Kinetics

Content

- 1.0 Introduction
- 2.0 Learning Outcomes
- 3.0 Learning Content
 - 3.1 Some Fundamental Concepts
 - 3.2 Experimental Methods of Rate Studies
 - 3.3 First Order and Second Order Reactions
 - 3.4 Zeroth Order and Third Order Reactions
 - 3.5 Pseudo First Order Reactions
 - 3.6 Determining the Order of Reaction
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor-marked assignment
- 7.0 References/further reading

1.0 Introduction

Chemical kinetics is the study of rates and mechanisms of chemical reactions. The rate of a reaction depends on many factors such as the concentration of the reactants, temperature, catalyst, etc. Some of these factors shall be examined in this unit. We shall study thermal reactions in this unit. In thermal reactions, the reactants gain the energy required for the reaction through molecular collisions.

We shall start the unit explaining the dependence of rate of reaction on the concentrations of the reactants. In this process, we shall be defining the terms such as rate equation, rate law and order of a reaction. We shall then derive first order, second order and zeroth order equations. These equations will be used for calculating the rate constants of the reactions. We shall then explain the methods of determining the order of reaction.

2.0 Learning Outcomes

After studying this unit, you should be able to:

- i. define rate law, rate constant and order of reaction
- ii. differentiate between order of reaction and stoichiometry
- iii. state the experimental methods for studying the reaction rates
- iv. derive integrated rate laws for first order, second order and zeroth order reactions and use them for calculating rate constants
- v. state the methods for determining the order of reaction,

3.1 Some Fundamental Concepts

In this section, we shall define some terms such as rate of reaction, rate law, rate constant, order of a reaction and stoichiometry;

3.1.1 Rate of Reaction

The rate of reaction or the velocity of reaction at a specified time is defined as the decrease in the concentration of a reactant or the increase in the concentration of a product per. unit time. The rate of reaction at a specified time is also known as instantaneous rate of reaction; it can be generally defined as the rate of change of concentration of a specified species at a particular instant. While specifying the reaction rate, we must mention the component with respect to which it is stated. Let us consider a simple reaction,

$$A \rightarrow B$$

As per the reaction stoichiometry, one molecule of B is formed for every molecule of A consumed, The reaction rate can be specified in the following ways:

- i. We can measure the concentration of the reactant A at various time intervals. From these values, we can specify the decrease in concentration of A with respect to time at any particular instant. The reaction rate thus obtained is the rate of consumption of A

Rate of consumption of A = Decrease in the concentration of A

$$= \frac{\text{Decrease in the concentration of A}}{\text{Change in time}} = \frac{-\Delta[A]}{\Delta t}$$

- ii. $\Delta[A]$ means change in the concentration of A and $-[A]$ means the decrease in the concentration of A. While writing a rate expression with respect to a reactant, there is a preceding negative sign (since it is customary to express the rate of a reaction as a positive quantity).
- iii. We can measure the concentration of the product B at various time intervals. From these values, we can arrive at the rate of formation of B at any particular instant

$$\begin{aligned} \text{Rate of formation of B} &= \frac{\text{Increase in the concentration of B}}{\text{Change in time}} \\ &= \frac{\Delta[B]}{\Delta t} \end{aligned}$$

The rates of consumption of reactants and the rates of formation of products are related through their stoichiometric coefficients. For example, consider the decomposition of NO_2 , $2 \text{NO}_2 (\text{g}) \rightarrow 2 \text{NO} (\text{g}) + \text{O}_2 (\text{g})$

We can write the relationship between the rates of consumption of NO_2 and the rates of formation of NO and O_2 as follows:

$$\begin{aligned} \frac{1}{2} (\text{Rate of consumption of } \text{NO}_2) &= (\text{Rate of formation of } \text{NO}) \dots\dots\dots(1) \\ &= \text{Rate of formation of } \text{O}_2 \end{aligned}$$

$$\text{Reaction rate} = \frac{1}{2} \frac{-d[\text{NO}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}]}{dt} = \frac{d[\text{O}_2]}{dt}$$

You can understand the above relationship if you bear mind that if two molecules of NO_2 are consumed, two molecules of NO and one molecule of O_2 are formed. In other words, the reaction rate is equal to:

- (i) half the rate of consumption of NO_2
- (ii) half the rate of formation of NO , and
- (iii) the rate of formation of O_2

Throughout this unit, the phrase rate of reaction means instantaneous reaction rate. We shall shortly study the method of arriving at the reaction rates from the values of concentrations of a component at different time intervals. The symbol ' Δ ' is to be read as delta. It denotes change in a property. In order to obtain a single value for the reaction rate, it is necessary to divide the rate of consumption' of a reactant or the rate of formation of a product by, the stoichiometric coefficient of the respective species.

To illustrate this, let us consider the reaction: $aA + bB \rightarrow cC + dD$. In this reaction, A and B are reactants, and C and D are products; a, b, c and d are the stoichiometric coefficients. The reaction rate is related to the rates of consumption of the reactants and the rates of formation of the products as follows:

$$= \frac{1}{a} \left(\frac{-d[A]}{dt} \right) = \frac{1}{b} \left(\frac{-d[B]}{dt} \right) = \frac{1}{c} \left(\frac{d[C]}{dt} \right) = \frac{1}{d} \left(\frac{d[D]}{dt} \right) \dots\dots\dots(2)$$

The number preceding the formula of a substance in the balanced equation is its stoichiometric coefficient.

3.1.2 Calculation of Reaction Rate

You may be curious to know as to how the reaction rates are calculated. Take for instance the following reaction:



In Figs. 1 a, b and c, you can see concentration (c) against time. (t) plots for NO₂, NO and O₂ as per the values given in Table 1. In these figures; the graphical method of calculation of the reaction rates for the consumption of NO₂ and for the formation of NO and O₂ are illustrated. The reaction rate at any particular instant is obtained by calculating the slope of a line tangent to the curve at that point.

Table 1: Concentrations of NO₂, NO and O₂ at Different Time Intervals at 673K.

Time/s	[NO ₂]/M	[NO]/M	[O ₂]/M
0	0.0100	0	0
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

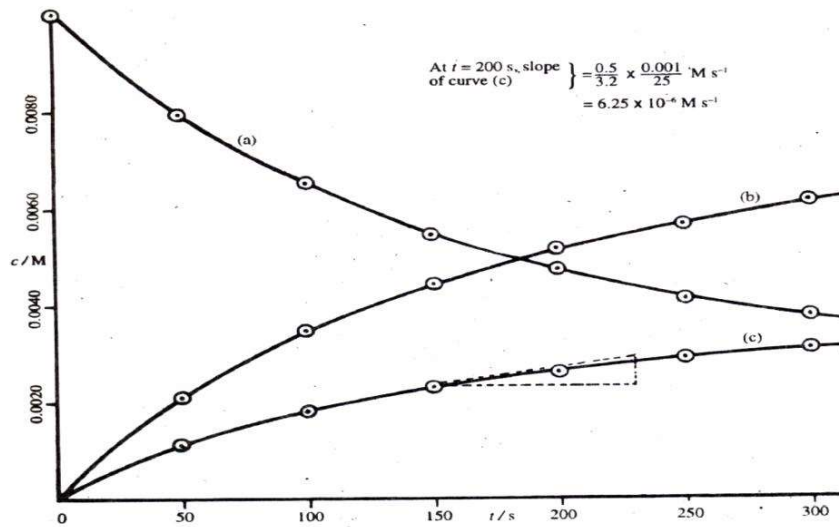


Fig. 1: Concentration against time plot

a) concentration against time plot for NO_2 ;

Rate of consumption of NO_2 at $t = 200$ s

= - Slope of the tangent line at $t = 200$ s

$$= - (-1.31 \times 10^{-5}) \text{ M s}^{-1}$$

$$= 1.31 \times 10^{-5} \text{ M s}^{-1}$$

$$\text{Reaction rate} = \frac{1}{2}(\text{Rate of the formation of NO}_2) = \frac{1}{2} \times 1.31 \times 10^{-5} \text{ Ms}^{-1}$$

$$= 6.55 \times 10^{-6} \text{ M s}^{-1}$$

b) concentration against time plot for NO ;

Rate of formation of NO = Slope of the tangent line at $t = 200$ s

at $t = 200$ s

$$= 1.30 \times 10^{-5} \text{ Ms}^{-1}$$

$$\text{Reaction rate} = \frac{1}{2}(\text{Rate of formation of NO})$$

$$= \frac{1}{2} \times 1.30 \times 10^{-5} \text{ M s}^{-1}$$

$$= 6.50 \times 10^{-6} \text{ M s}^{-1}$$

c) concentration against time plot for O_2 ;

Rate of formation of O_2 = Slope of the tangent line at $t = 200$ s

at $t = 200$ s,

$$= 6.25 \times 10^{-6} \text{ M s}^{-1}$$

Reaction rate = Rate of formation O_2

$$= 6.25 \times 10^{-6} \text{ Ms}^{-1}$$

For the curves (a) and (b), the tangents are not indicated.

From the slope values at $t = 200 \text{ s}$, you can see that the following relationship is nearly correct.

$$\text{Reaction rate} = \frac{1}{2}(\text{Rate of consumption of NO}_2) = \frac{1}{2}(\text{Rate of formation of NO})$$

$$= \text{Rate of formation of O}_2$$

In our discussion, we are mainly interested in the concentration against time plots for the reactants. In other words, we want to 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 up to 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 up to a particular time. Afterwards, enough nitric oxide and oxygen are formed and the reverse reaction also could take place leading to the formation of NO_2 . In order to simplify the situation, it is better to study the reaction rates before significant amounts of products are formed. 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. We shall be mostly concerned with this class of reactions.

3.1.3 Decomposition of N_2O_5

The decomposition N_2O_5 of in the gas phase was studied at 323 K.



The instantaneous rates of this reaction calculated from $[\text{N}_2\text{O}_5]$ against time plot (similar to

Fig. 1) are given in Table 2 .

Table 2: Rates Corthe Decomposition of N_2O_2 at 323 K

$[\text{N}_2\text{O}_5]/\text{M}$	Rate/ M s^{-1}	$\frac{\text{Rate}}{[\text{N}_2\text{O}_5]}$, s
(i)	(ii)	(iii)
0.300	2.73×10^{-4}	9.1×10^{-4}
0.150	1.37×10^{-4}	9.1×10^{-4}
0.100	9.10×10^{-5}	9.1×10^{-4}

From columns (i) and (ii), you can see that the rate for the decomposition of N_2O_5 decreases with the decrease in the concentration of N_2O_5 . Further, column (iii) gives the ratio of the rate to the concentration of N_2O_5 . In all the three cases, it is a constant. This shows that the rate is directly proportional to the concentration of N_2O_5

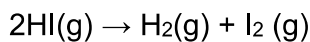
i.e., $\frac{\text{Rate}}{[\text{N}_2\text{O}_5]} = k$ (3)

Hence, $\text{rate} = k [\text{N}_2\text{O}_5]$ (4)

where k is proportionality constant

3.1.4 Decomposition of Hydrogen Iodide

The decomposition of hydrogen iodide was followed at a constant temperature:



The instantaneous rates of this reaction were calculated using the $[\text{HI}]$ against time plot like that of Fig. 1. These values are given in Table 3.

Table 3: Rates for the Decomposition of HI

$[\text{HI}]/\text{M}$ (i)	$\text{Rate}/\text{M s}^{-1}$ (ii)	$\frac{\text{Rate}}{[\text{HI}]}$ · s (iii)	$\frac{\text{Rate}}{[\text{HI}]^2}$ · M s (iv)
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 3, you can see that the rate of decomposition of HI decreases with decrease in the concentration of HI; as in the case of the decomposition of N_2O_5 . Further, it is evident from column (iii) that $\text{rate}/[\text{HI}]$ is not a constant. But, as per column (iv), $\text{rate}/[\text{HI}]^2$ is a constant.

From Table 15.3, it is evident that

$\text{Rate} / [\text{HI}]^2 = k$ (5)

Hence, $\text{rate} = k [\text{HI}]^2$ (6)

where k is a proportionality constant.

For many chemical reactions, the relationship between the reaction rate and the concentration can be expressed in a simple way as in Eq.4 or 6. We shall first consider these simple cases. Later we shall discuss those reactions for which the rate concentration relationship is more complex.

3.1.5 Rate Law and Rate Constant

The relationship expressed as in Eq. 4 or Eq.6 is called the rate law. A rate law is an equation expressing the relationship between the instantaneous reaction rate and the concentrations of the reactants in a reaction.

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

Reaction rate = $k [\text{Reactant}]$ (7)

where k is called the rate constant or rate coefficient or the specific rate 'of the reaction. Thus by definition, the rate constant is independent of concentration, but it may depend on other factors. In this equation, n refers to the order of the reaction; The order with respect to a component is the power to which the concentration of that component is raised in the rate law. Comparing Eq. 7 with Eqs. 4 and 6, we conclude that

i) $n = 1$ in Eq. 4; 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 .

$$\text{Rate} = k [\text{Reactant}] \dots\dots\dots (8)$$

where k is the first order rate constant.

From Eq. 7. it can be seen that if $[\text{reactant}] = 1$. then $k = \text{rate}$. For this reason. k is called the specific rate.

ii) $n = 2$ 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.

$$\text{i.e., Rate} = k [\text{HI}]^2 \dots\dots\dots (9)$$

where k is the second order rate constant.

3.1.6 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 1

The gas-phase decomposition of N_2O_5 yields NO_2 and O_2 at a particular temperature. The experimentally observed rate law for the reaction rate. Comment on the order and the stoichiometry of the reaction.

Solution

It can be seen that the stoichiometric coefficient of N_2O_5 is 2 whereas the order of reaction is 1.

Example 2

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



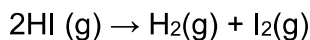
The rate law is,

$$\text{rate} = k [\text{N}_2\text{O}_5]$$

Comment on the order of the reaction and the stoichiometry.

Solution

Again the stoichiometric coefficient of N is 2 whereas the order of reaction is 1. In the above two 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:



$$\text{Rate} = k [\text{HI}]^2$$

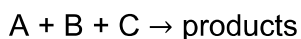
In the decomposition of HI, the order of reaction is two. The stoichiometric coefficient of HI is also 2. From the above examples, you can see that the stoichiometric coefficient and the order of

the reaction need not be the same. You must bear in mind the following points while arriving at a rate law.

- i) 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 since the rate measurements are done under the conditions where the reverse reaction rate is negligibly low.
- ii) The order of the reaction must be determined experimentally; the experimental methods will be discussed in the next section.
- iii) The order of a reaction need not be identical with the stoichiometric coefficient of the reactant.

So far we 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 such cases, we can calculate the order of the reaction with respect to the individual reactant and also the overall order. The overall order is the sum of the powers to which the individual concentrations are raised in the rate law.

In general, for a reaction,

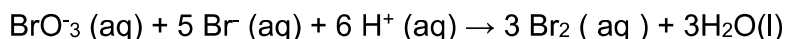


if the rate law is experimentally found to be,

$$\text{rate} = k [\text{A}]^m [\text{B}]^n [\text{C}]^p \dots\dots\dots(10)$$

then, the overall order of the reaction = $m + n + p$.

For example in the following reaction,



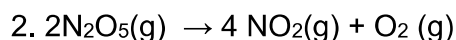
$$\text{Rate} = k [\text{BrO}_3^-] [\text{Br}^-] [\text{H}^+]^2 \dots\dots\dots(11)$$

The overall rate of the reaction is four, being first order in BrO_3^- , first order in Br^- and second order in H^+ . The rate laws discussed so far are called differential rate laws. Such rate laws describe the dependence of reaction rate on concentration. From these differential rate laws, we can obtain the integrated rate laws through integration. The integrated rate laws help us in relating the concentration of a substance to time. In other words, using the integrated rate laws, we can calculate the concentration of a substance at any specified time. In Sections. 1 and 2, we shall discuss the derivation of the integrated forms of rate laws. In the next section, we shall discuss some experimental methods of studying the reaction rates.

Self-Assessment Exercise 1

1. At 323 K, the rate of reaction for the decomposition of N_2O_5 at a particular instant is

$2.74 \times 10^{-4} \text{ M s}^{-1}$. Calculate the rate of formation of O_2 . The reaction is represented below:



In the decomposition of hydrogen iodide, what is the relationship between the rate of decomposition of HI and the rate of formation of H_2 ?

3.2 Experimental Methods of Rate Studies

Many physical and chemical methods are available for studying the reaction rates. Some of them are listed below:

i) Volume or Pressure Measurement

When one or more of the components are gases, the reaction rate can be followed by measuring the volume or pressure change. The partial pressures of the species are to be calculated using the reaction stoichiometry.

ii) Titrimetry

Using acid-base or oxidation-reduction titrations, the reaction course can be followed if at least one of the components in the reaction is an acid or a base or an oxidizing agent or a reducing agent.

iii) Conductometry or Potentiometry

If one or more of the ions are present or produced in the reaction, suitable methods can be designed based on conductivity or potentiometric measurements.

iv) Spectrophotometry

When a component of the reaction has a strong absorption band at a particular wavelength region, spectrophotometers could be used for measuring the reaction rate. Photoelectric colorimeters are cheaper instruments and are mainly useful for reaction rate studies in visible region.

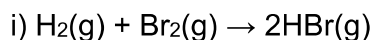
v) Polarimetry

When at least one of the components of a reaction is optically active, the reaction rate can be studied from the measurements of optical rotation.

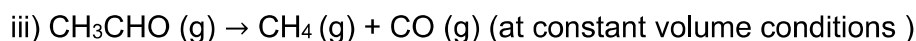
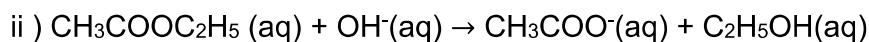
Depending on the reaction under study, the concentration of a reactant or a product is followed at various time intervals using any of the methods mentioned above. These values are then used for calculating the rate constant. Examples are worked out in the next section to illustrate the rate constant calculation. Before studying these examples, we shall discuss the method of arriving at the integrated forms of rate laws.

Self-Assessment Exercise 2

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



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



3.3 First Order and Second Order Reactions

In this section, we shall derive integrated rate laws for first and second order reactions.

3.3.1 Integrated Rate Law for First Order Reactions

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



Applying Eq.7, we can write

$$\text{Rate} = \frac{-d[\text{A}]}{dt} = k [\text{A}]^1 \text{ (13)}$$

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 = $[\text{A}]^0$

At time = t , the concentration of A = $[\text{A}]$,

Using these limits of concentration and time, we can integrate Eq. 13 after rearranging it as follows:

$$\int_{[\text{A}]^0}^{[\text{A}]^t} -\frac{d[\text{A}]}{[\text{A}]} = \int_0^t k dt \text{(14)}$$

$$\text{i.e.} - \{\ln [A]\} \frac{[A]_t}{[A]_0} = k [t]_0 \dots\dots\dots(15)$$

$$- \{\ln [A]_t - \ln [A]_0\} = k (t-0) \dots\dots\dots(16)$$

$$\ln [A]_0 - \ln [A]_t = kt \dots\dots\dots(17)$$

$$\text{Hence, } \ln \frac{[A]_0}{[A]_t} = kt \dots\dots\dots(18)$$

Eq. 18 can be written in the exponential form as follows:

$$[A]_t = [A]_0 e^{-kt} \dots\dots\dots (19)$$

Corresponding to Eq. 19, we can draw the concentration vs. time plot for a first order reaction. This curve is of the type shown in Fig. 2. 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 slow, 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.

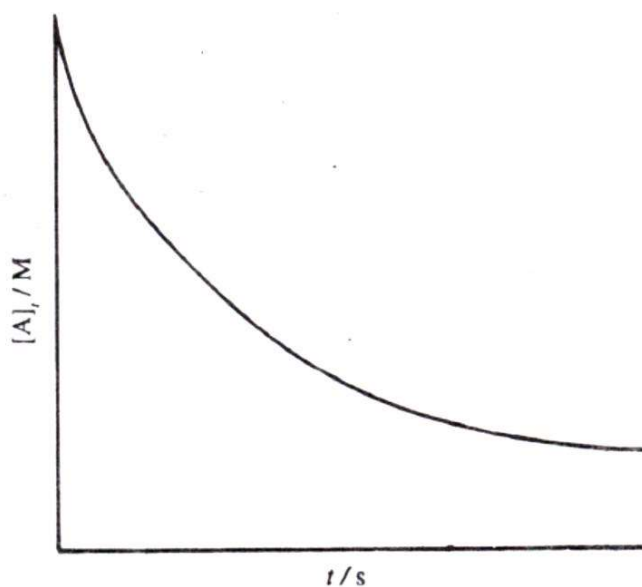


Fig. 2: Exponential decay of A.

Radioactive decay is a good example of first order reaction.

Let us come back to Eq. 18. It is more convenient to work with logarithms to the base 10 (known as common logarithms). Hence we can rewrite Eq.18 as follows:

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

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t} \dots\dots\dots(20)$$

Eq. 19 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 $[A]_0$, $[A]$, and t are known. Using the graphical method, we can test whether a reaction follows first order or not.

3.3.2 Graphical Method of Calculating First Order Rate Constant

In order to facilitate graphical representation, Eq. 20 is modified as follows:

From Eq. 20, we can derive Eq. 22 by substituting the concentrations of A at time intervals

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

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

Using this limit of concentration and time, we can integrate Eq.13 after rearranging it as follow:

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

$$\text{Hence } \log [A]_0 - \log [A]_t = \frac{kt}{2.303}$$

$$\text{i.e., } -\log [A]_t = \frac{kt}{2.303} - \log [A]_0$$

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

By comparing Eq. 24 with the equation for a straight line, $y = mx+c$, we can infer that by plotting $\log [A]_t$ against time, a straight line must be obtained for a first order reaction. Such plots are shown in Figs. 3 - 5. The rate constant can be calculated from the slope as follows:

$$k = -2.303 \times \text{slope} \dots\dots\dots(21)$$

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 Eq. 22.

$$\log \frac{[A]_1}{[A]_2} = \frac{K}{2.303} (t_2 - t_1) \dots\dots\dots (22)$$

The following hints may be useful while calculating the rate constants using the integrated rate law: .

i) If the concentrations of the reactant are given at various time intervals, the concentration at

$t = 0$ is equal to $[A]_0$ and the concentration at any given time is $[A]_t$; $\log [A]_t$ against t plot is made as described earlier. This principle is followed in Example 3.

ii) Instead of giving the concentrations of a reactant at various time intervals, parameters such as partial pressures, absorbances, volumes, titre values etc. which

are proportional to the concentration of the reactant may be given. In these cases, the measurements made at zero time and at any given time t may be used instead of $[A]_0$ and $[A]_t$. For example, we can substitute the partial pressure of the reactant instead of its concentration in Eq. 21 and obtain Eq. 28.

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

where $(pA)_0$ and $(pA)_t$ are the partial pressures of the reactant at the start and, after a time, t .

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. 21 could be written as,

$$\log \frac{[A]_0}{[A]_0 - x} = \frac{kt}{2.303} \dots\dots\dots(23)$$

Calculation of this type is illustrated in Example 5.

Let us work out some examples to illustrate the calculation of k by graphical method.

Example 3

On heating cyclopropane to 770k, 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.

Solution

Using the data, $\log [\text{cyclopropane}]/\text{M}$ values are calculated and tabulated along with t values.

$\log [\text{cyclopropane}]/\text{M}$	iv. 2.82	v. 2.91	vi. 3.00	vii. 3.08
t/s	0	300	600	900

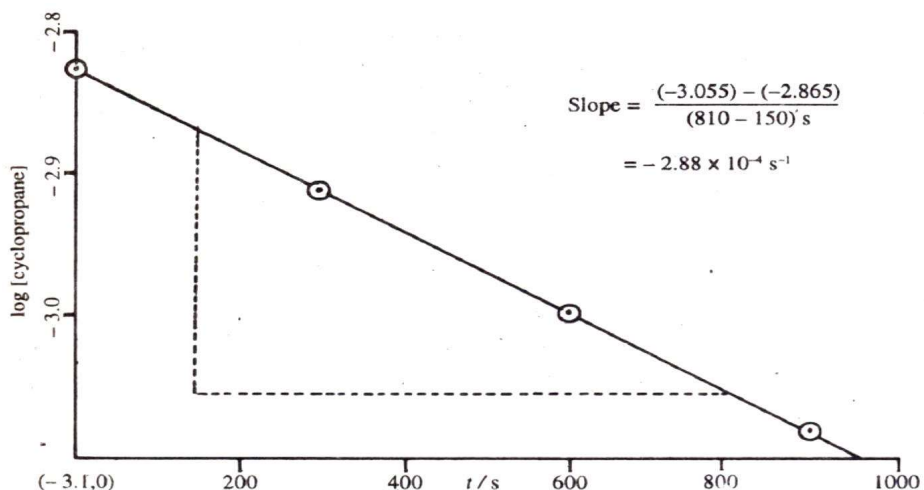


Fig. 3: log [cyclopropane] against t plot.
log [cyclopropane] vs. t plot is shown in Fig. 3.

The graph is a straight line, confirming that the reaction is first order.

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

$$= 6.63 \times 10^{-4} \text{ s}^{-1}$$

3.3.3 Half-Life of First Order Reactions

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 in calculating the half-life of a substance undergoing first order reaction using Eq. 24.

$$\log \frac{[A]_0}{[A]_t} = \frac{kt}{2.303} \dots\dots\dots (24)$$

We must bear in mind that when

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

Using these relationships in Eq. 18.21, we get,

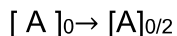
$$\log \frac{[A]_0}{[A]_0/2} = \frac{kt_{1/2}}{2.303} \dots\dots\dots (25)$$

i.e., $\log_2 = \frac{kt_{1/2}}{2.303}$

or $t_{1/2} = \frac{2.303 \log 2}{k} = \frac{0.693}{k}$

From Eq.25, we understand 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 leads to an interesting result that the time taken for the changes in the concentrations of the reactant such as,

or



is the same. The half-life periods required to bring about decrease in concentration of a reactant up to 12.5% of its initial concentration can be represented as in Fig. 6.

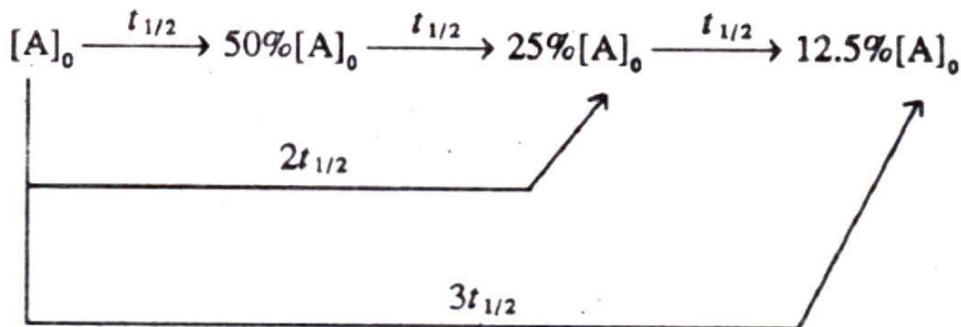


Fig. 6: Change in % $[A]_0$ over the first three half-life Periods of a first order reaction; $t_{1/2}$ is the half-life period for the conversion, $[A]_0 \rightarrow 50\% [A]_0$.

Example 4

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

Solution

a) Using $t_{1/2} = \frac{0.693}{5.20 \times 10^{-3} \text{ s}^{-1}}$
 $= 133 \text{ s}$

Hence, time taken for the concentration of N_2O_5 to decrease by 50% is 133 s.

b) The time required for the decrease in the concentration N_2O_5 to 25% of its initial value is 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 reactant, let us derive similar equations for second order reactions.

3.3.4 Integrated Rate Laws for Second order Reactions

There are two types of second order reactions.

i) A single reactant could give rise to products through a second order reaction

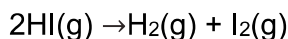
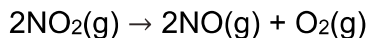


The rate equation is

$$\text{rate} = \frac{d[A]}{dt} = k [A]^2 \dots\dots\dots (27)$$

where k is the second order rate constant.

Two examples of this type are given below:



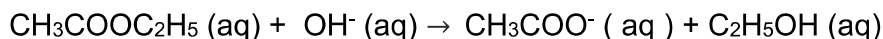
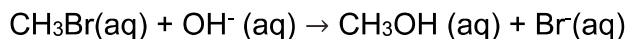
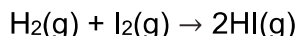
ii) Two different reactant molecules could react to give products through a second order reaction.



The rate equation is,

$$\text{reaction rate} = k [A] [B] \dots\dots\dots (29)$$

Examples of this type are given below. Note that the stoichiometric ratio of the reactants is 1:1.



Again the study of these reactions' could be simplified if the initial concentrations of both the reactants ([A]o and [B]o) are the same. i.e.,

$$[A]_o = [B]_o \text{ and so } [A] = [B]$$

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

Then Eq. 35 takes the same form as Eq. 30.

$$\begin{aligned} \text{Rate, } &= \frac{-d[A]}{dt} = k [A] [B] = k [A][A] \\ &= k [A]^2 \cdot \dots\dots\dots (30) \end{aligned}$$

Thus, we could see that the rate equation takes the same form for a second order reaction, 'if 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.

We use Eq.18.36 as the rate law for both these two types. We derive the integrated rate law for these two under case (i).

Case (i): Integrated Rate Law for a Reaction that Follows Differential Rate Law as per Eq. 36'

We start with the differential rate law,

$$\therefore \frac{d[A]}{dt} = k [A]^2 \dots\dots\dots (31)$$

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. 34, we get,

$$-\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = \int_0^t k dt \dots\dots\dots (32)$$

$$\text{i.e., } -\left[\frac{1}{[A]}\right]_{[A]_0}^{[A]_t} = k(t-0) \dots\dots\dots (33)$$

$$-\left[\frac{-1}{[A]_t} + \frac{1}{[A]_0}\right] = kt. \dots\dots\dots (34)$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \dots\dots\dots (35)$$

$$\text{or } \frac{1}{[A]_t} = \frac{1}{[A]_0} + kt. \dots\dots\dots (36)$$

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

$$k = \text{Slope}$$

We shall later illustrate this method in Example 8.

3.3.5 Half-Life of a Second Order Reaction

For reactions following second order rate as per Eq. 32, an equation could be derived which is useful in calculating the half-life period.

At the half-life period (t = t_{1/2}), [A]_t = [A]₀^{1/2}. Using this in Eq. 40,

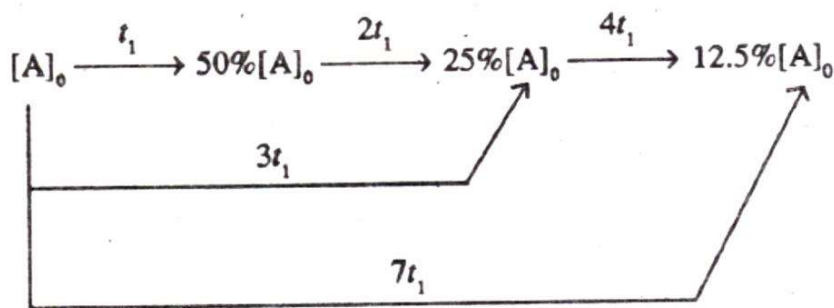


Fig. 7: Change in % [A]₀ over three successive half-lives in a second order reaction; t₁ refers to half-life for the change in concentration from [A]₀ to 50% [A]₀

$$t_{1/2} = \frac{1}{k[A]_0} \dots\dots\dots (37)$$

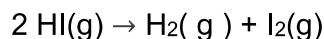
From Eq. 42, we understand that t_{1/2} is inversely proportional to initial concentration for a second order reaction. As initial concentration of the reactant decreases, t_{1/2}

increases. If for the decrease in concentration of A to 50% of its initial value, time required is 100s, then for the change from 50% A to 25% A, it will require 200 s.

Three successive half-lives for a second order reaction can be represented by Fig. 7.

Example 7

At 700 K, the second order rate constant for the reaction,



is $1.83 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. Calculate the time taken for $1.00 \times 10^{-2} \text{ M}$ HI to fall to (a) one-half and (b) one-eighth of its initial concentration.

Solution

$$\begin{aligned} \text{a) Using Eq. 42, } t_{1/2} &= \frac{1}{k[A]_0} = \frac{1}{1.83 \times 10^{-3} \times 1.00 \times 10^{-2}} \\ &= 5.46 \times 10^2 \text{ s} \end{aligned}$$

Time needed for the decrease in concentration of HI to one-eighth of its initial value is seven times the value calculated above as shown in Fig. 7; i.e., time needed is $3.82 \times 10^5 \text{ s}$.

Now we derive the integrated rate law for a reaction that is second order overall and is first order in each of the two reactants having different initial concentrations.

Case (ii): Integrated Rate Law for a Reaction that Follows Rate Law as per Eq.14

Let us start the reaction between A and B with different initial concentrations, $[A]_0$ and $[B]_0$.

Let these two react to give products as per the rate law given in Eq. 34;



$$\text{Reaction rate} = k [A][B] \dots\dots\dots (35)$$

As per the reaction stoichiometry, A and B react in the ratio 1:1. After t seconds, let the concentrations of A and B be $[A]_0 - x$ and $[B]_0 - x$.

$$\text{Hence, the reaction rate} = \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = k [A][B],'$$

$$\text{i.e. } \frac{-d\{[A]_0 - x\}}{dt} = k\{[A]_0 - x\}\{[B]_0 - x\}$$

$$\text{i.e., } \frac{-d[A]_0 - x}{dt} + \frac{dx}{dt} = k \{[A]_0 - x\}\{[B]_0 - x\}$$

$$\text{So, } \frac{dx}{dt} = k\{[A]_0 - x\}\{[B]_0 - x\} \dots\dots\dots(36)$$

$$\frac{d[A]_0}{dt} = kdt.$$

In order to get integrate form, we have to transform Eq. 43 as shown below

$$\frac{dx}{\{[A]_0-x\}\{[B]_0-x\}} = \frac{p}{\{[A]_0-x\}} + \frac{q}{\{[B]_0-x\}} \dots\dots\dots(37)$$

Let us write the expression, $\frac{1}{\{[A]_0-x\}\{[B]_0-x\}}$ as follow

$$\frac{1}{\{[A]_0-x\}\{[B]_0-x\}} = \frac{p}{[A]_0-x} + \frac{q}{[B]_0-x} \dots\dots\dots(38)$$

i.e., $\frac{1}{\{[A]_0-x\}\{[B]_0-x\}} = \frac{P\{[B]_0-x\} + q\{[A]_0-x\}}{\{[A]_0-x\}\{[B]_0-x\}}$

In other words, $p\{[B]_0-x\} + q\{[A]_0-x\} = 1$

Put $x = [A]_0$, then $p\{[B]_0-[A]_0\} = 1 \dots\dots\dots(39)$

or $p = \frac{1}{[B]_0-[A]_0} \dots\dots\dots(40)$

Hence $p = -\frac{1}{[A]_0-[B]_0} \dots\dots\dots(41)$

Put $x = [B]_0$ in Eq.15.46

Hence $q\{[A]_0-[B]_0\} = 1$

or $q = \frac{1}{[A]_0-[B]_0} \dots\dots\dots(42)$

From Eqs. 45, 48 and 49

$$\frac{1}{\{[A]_0-x\}\{[B]_0-x\}} = -\frac{1}{\{[A]_0-[B]_0\}\{[A]_0-x\}} + \frac{1}{\{[A]_0-[B]_0\}\{[B]_0-x\}} \dots\dots\dots(43)$$

We have adopted the partial fraction procedure in the above steps

Using Eq. 50 in Eq. 44,

$$\frac{dx}{\{[A]_0-x\}\{[B]_0-x\}} + \frac{1}{\{[A]_0-[B]_0\}\{[A]_0-x\}} = kdt \dots\dots\dots(44)$$

You can see that the two terms in the L.H.S of Eq. 51 contain either $\{[A]_0-x\}$ or $\{[B]_0-x\}$ in the denominator.

At time = 0, $x = 0$ ("x" denotes the change in concentration of A or B due to reaction)

At time = t, $x = x_t$,

$$\int_0^{xt} \frac{dx}{\{[A]_0-[B]_0\}\{[B]_0-x\}} - \int_0^{xt} \frac{dx}{\{[A]_0-[B]_0\}\{[A]_0-x\}} = k \int_0^1 dt \dots\dots\dots(45)$$

$$\frac{1}{[A]_0-[B]_0} [-\ln([B]_0-x)]_0 - \frac{1}{[A]_0-[B]_0} [-\ln([A]_0-x)]_0 = kt \dots\dots\dots(46)$$

$$\frac{-1}{[A]_0-[B]_0} \{ \ln([B]_0-x) - \ln[B]_0 \} - \frac{1}{[A]_0-[B]_0} \{ \ln([A]_0-x) - \ln[A]_0 \} = kt \dots\dots(54)$$

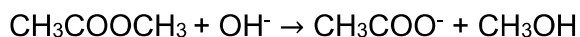
$$= \frac{1}{[A]_0-[B]_0} \ln \frac{([A]_0-x)_t [B]_0}{([B]_0-x)_t [A]_0} = kt \dots\dots\dots(47)$$

$$= \log \frac{([A]_0 - xt)[B]_0}{([B]_0 - xt)[A]_0} = \frac{k\{[A]_0 - [B]_0\}}{2.303} t \quad \dots\dots\dots(48)$$

By plotting $\log \frac{[A]_0 - xt}{[B]_0 - xt}$ against t , a straight line is obtained. The slope of the straight line is equal to $\frac{k([A]_0 - [B]_0)}{2.303}$

$$k = \frac{2.303 \times \text{slope}}{([A]_0 - [B]_0)} \quad \dots\dots\dots(49)$$

Let us discuss the saponification of ester as an example for the calculation of second order rate constant. The hydrolysis of ester by an alkali is called saponification. For example, the saponification of methyl acetate can be represented by the following equation:



The saponification rate is studied as follows. A reaction mixture is prepared with known concentrations of alkali and ester. At regular intervals, certain volume of the solution is withdrawn and titrated against standard HCl. From the titre values, the concentrations of the unreacted alkali and the unreacted ester could be determined at various time intervals. The rate constant can be determined using,

- i) Eqs. 40 and 41, if the initial concentrations of ester and alkali are same; .
- ii) Eqs. 56 and 57, if their initial concentrations are different. Now study the following example.

Example 8

The saponification of methyl acetate using sodium hydroxide was studied at 298 K. The initial concentrations of the alkali and ester in the reaction mixture were both $1.00 \times 10^{-2} \text{M}$. The reaction rate was followed by titration of a definite volume of the reaction mixture with standard HCl. The concentrations of unreacted alkali, $[A]$, at various time intervals are given below:

Time/s	240	550	720	1000	1550
$10^3 [A]_t/\text{M}$	6.85	4.81	4.17	3.38	2.49

Calculate the second order rate constant

Solution

Since the initial concentrations of the alkali and the ester are same, we can use Eqs. 40 and 41 for solving this problem. We tabulate $\frac{1}{[A]_t}$ values against various time intervals as follows:

$\frac{1}{[A]_t} \text{M}$	146	203	240	296	402
t/s	240	550	720	1000	1550

As suggested by Eq. 39, $1/[A]$, against t plot is a straight line (Fig.8) showing that the saponification of methyl acetate follows second order kinetics.

Having some experience with the differential and the integrated forms of rate laws for first order and second order reactions, we shall discuss zeroth order reactions in the next section. Also, we shall give some examples of third order reactions.

Self-Assessment Exercise 3

1. State the units of the rate constants for zeroth order, first order and second order reactions. The rate of reaction is measured in $M S^{-1}$ units .
2. The decomposition of HI is a second order reaction. At 700 K, the rate constant for the reaction is $1.83 \times 10^{-3} M^{-1} s^{-1}$. If the initial concentration of HI is $1.00 \times 10^{-2} M$, calculate its concentration after $1.68 \times 10^5 s$.

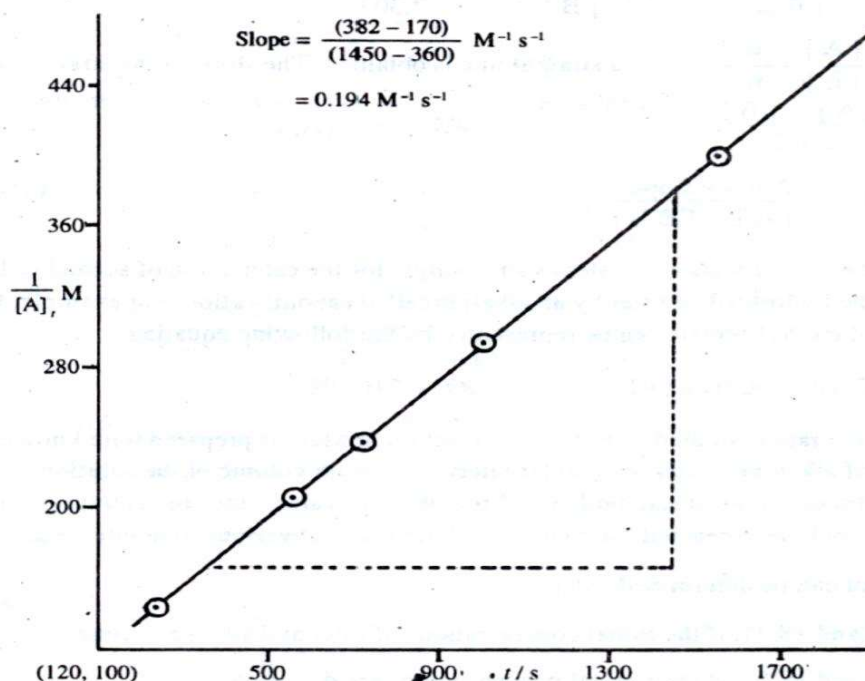


Fig. 8: $1/[A]$ against t plot for the saponification of methyl acetate.

3.4 Zeroth Order and Third Order Reactions

Let us study zeroth order reactions.

3.4.1 Zeroth Order Reactions

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

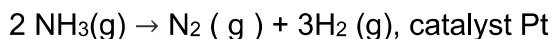
$$\frac{-d[A]}{dt} = k [A]^0 = k \dots\dots\dots(50)$$

Since $[A]_0 = 1$

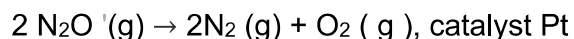
In a zeroth order reaction, the reaction rate is independent of the concentrations of the reactant

Some examples of zeroth order reactions are given below:

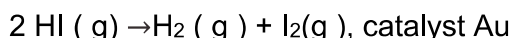
i) Decomposition of ammonia on a hot platinum surface.



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



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



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

3.4.2 Integrated Rate Law for Zeroth Order Reaction

Let us consider the zeroth order reaction:

$A \rightarrow \text{Products}$

Let the concentration of A at the start be $[A]_0$ and its concentration at the time t be $[A]_t$.

The integrated for in of Eq.15.58 can be derived as follows:

$$\int_{[A]_0}^{[A]_t} -d[A] = \int_0^t k dt \dots\dots\dots (51)$$

i.e., $-([A]_t - [A]_0) = k(t - 0)$
 $[A]_0 - [A]_t = kt \dots\dots\dots (52)$

$$[A]_t + [A]_0 = kt$$

or $[A]_t = [A]_0 - kt \dots\dots\dots(53)$

On plotting $[A]_t$ against t , a straight line is obtained for a zeroth order reaction. The slope is equal to $-k$.

$$k = -\text{Slope} \dots\dots\dots(54)$$

Example 9

The decomposition of hydrogen iodide on gold at 323 K is zeroth order reaction and the rate constant is $1.20 \times 10^{-4} \text{ M s}^{-1}$.

- a) If the initial concentration of hydrogen iodide is 0.500 M, calculate its concentration after $3.00 \times 10^3 \text{ s}$.
- b) How long will it take for all of the hydrogen iodide to decompose?

Solution

$$\begin{aligned} \text{(a) Using Eq.15.60, } [A]_t &= [A]_0 - kt \\ &= (0.500 - (1.20 \times 10^{-4} \times 3.00 \times 10^3) \text{ M}) \\ &= 0.140 \text{ M} \end{aligned}$$

(b), If hydrogen iodide completely decomposes, then $[A]_t = 0$

$$\begin{aligned} t &= \frac{[A]_0}{k} = \frac{0.500 \text{ M}}{1.20 \times 10^{-4} \text{ M s}^{-1}} \\ &= 4.17 \times 10^3 \text{ s} . \end{aligned}$$

Hence, the reaction will be complete after $4.17 \times 10^3 \text{ s}$.

3.4.3 Half-life of a Zeroth Order Reaction

As discussed for first and second order reactions,

$$[A]_0 = [A]_t/2 \text{ when } t = t_{1/2}$$

Hence, Eq. 60 becomes,

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

$$\text{.or } kt_{1/2} = [A]_0/2$$

$$t_{1/2} = \frac{[A]_0}{2K} \dots\dots\dots(55).$$

This means that the half-life of a zeroth order reaction is directly proportional to the initial concentration of the reactant.

Example 10

Calculate the half-life for the decomposition of hydrogen iodide on gold at 323 K. Use the data from Example 9.

Solution

Using the data from Example 9 in Eq. 54,

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

From Examples 9 and 10, you can understand that the zeroth order reaction is complete in two half-lives as shown in Fig. 9.

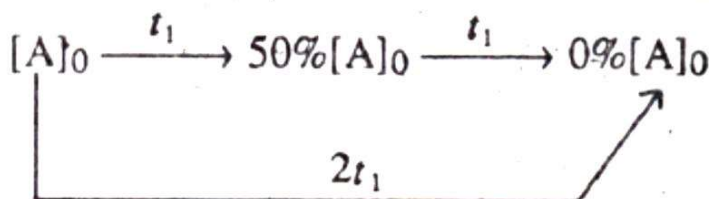
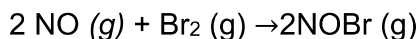
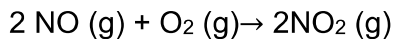


Fig. 9: Completion of a zeroth order reaction; t_1 is the time taken for both the conversions,

$[A]_0 \rightarrow 50\%[A]_0$ and $50\%[A]_0 \rightarrow 0\%[A]_0$.

3.4.4 Third Order Reactions

There are a few third order reactions. Two examples are given below:



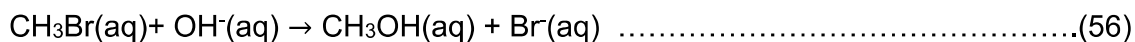
The methods of arriving at differential and integrated rate laws for third order reactions are similar to those of first and second order reactions. We are not going to discuss the same.

Self-Assessment Exercise 4

Using the data in Example 9, calculate the time required for the decomposition of HI on Gold at 323 K to proceed to 75%.

3.5 Pseudo-First Order Reactions

One of the ways of simplifying the study of reactions involving more than one reactant is to study under pseudo first order conditions. For example, consider the reaction:



$$\text{Reaction rate} = k [\text{CH}_3\text{Br}] [\text{OH}^-] \dots\dots\dots(57)$$

If the concentrations of CH_3Br and OH^- are comparable, then the reaction is second order, overall as indicated by Eq. 64. Suppose that the concentration of OH^- is much larger (say, 10 times or more) than the concentration of CH_3Br . In such cases the concentration of OH^- does not change much during the reaction and can be considered constant. Hence, the reaction rate depends on the concentration of CH_3Br only.

$$\text{Reaction rate} = k' [\text{CH}_3\text{Br}]$$

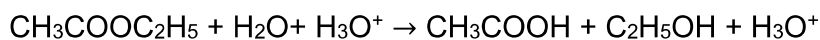
Where $k' = k [\text{OH}^-]$; k' is the pseudo first order rate constant. The reaction can be treated as first order for calculation purposes. Hence, the integrated rate law is similar to Eq.21.

$$\log \frac{[\text{CH}_3\text{Br}]_0}{[\text{CH}_3\text{Br}]_t} = \frac{k' t}{2.303}$$

In general, the reactions like the above which are effectively first order due to large excess of one of the reactants are called pseudo first order reactions. Let us discuss the following two reactions which are studied under pseudo first order conditions.

i) Acid Hydrolysis of Ester

The hydrolysis, of ethyl acetate in presence of a mineral acid (say, HCl) can be represented by the following equation:



The reaction rate depends on [ester], [water] and $[\text{H}_3\text{O}^+]$. Here H_3O^+ ion is a catalyst. Since the concentration of the catalyst does not change during the reaction, and water is present in large amount, the reaction becomes pseudo first order in ester.

$$\text{Rate} = k' [\text{ester}]$$

where k' includes concentrations of water and H_3O^+ . If the reaction is carried out in a solvent other than water, the first order dependence on [water] also could be seen. The pseudo first order rate constant is determined by titrating a definite volume of the reaction mixture containing ester and to HCl with standard alkali. Let V_0 , V_t and V_∞ be the volumes of standard alkali at the start" after a time t and after the completion of the reaction.

V_∞ = Volume of alkali equivalent to

- (i) acetic acid liberated after the completion of the reaction and
- (ii) HCl present.

V_t = Volume of alkali equivalent to

- (i) acetic acid produced at the time t and
- (ii) HCl present.

V_0 = Volume of alkali equivalent to HCl only.

Since the concentration of HCl is constant throughout the experiments,

$$[\text{A}]_0 \quad (\text{i.e. , initial concentration of ester}) \quad \propto (V_\infty - V_0)$$

$$\text{and } [\text{A}]_t \quad (\text{i.e. , concentration of ester remaining unreacted at } t) \quad \propto (V_\infty - V_t)$$

We can calculate pseudo first order-rate constant for the acid hydrolysis of ethyl acetate by

using the following modified form of Eq. 41.

$$\frac{k't}{2.303} = \log \frac{[\text{A}]_0}{[\text{A}]_t} = \log \frac{V_\infty - V_0}{V_\infty - V_t} \dots\dots\dots(58)$$

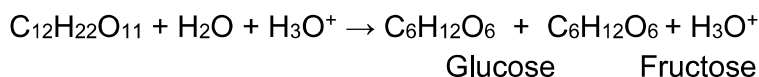
where k' is the pseudo first order rate constant.

Extrapolation is the process of extending a curve upto a desired x or y coordinate to obtain the correspondingly or value. Initial reaction rate, could be graphically arrived at by plotting the concentration of a reactant against time. The tangent to the concentration curve is drawn at the very start of the reaction and its slope is calculated. The negative of the slope value is the initial rate.

ii) Inversion of Sucrose

The hydrolysis of sucrose to form glucose and fructose in presence of mineral acid is similar to the

acid hydrolysis of ester as far as the reaction kinetics is concerned.



Sucrose turns the plane-polarised light to the right, (i.e., it is dextro rotatory). Glucose also turns the plane-polarised light to the right, while fructose turns it to the left (i.e., it is laevo rotatory). On completion of the reaction, the reaction mixture is laevo rotatory, since the angle of rotation is more for fructose than for glucose.

To start with, the reaction mixture is dextrorotatory due, to sucrose. Thus, the completion of reaction (infinite reading) is marked by the change in the sign of rotation. Due to this reason, the reaction is called inversion of sucrose. If r_0 , r_1 and r_∞ are the angles of rotation at the beginning, after time t and after completion of the reaction, then the pseudo first order rate constant (k') for the inversion of sucrose is given by,

$$k' = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_1 - r_\infty} \dots\dots\dots(59)$$

Eq. 66 is a modified form of Eq. 21, where $[A]_0$ is proportional to $(r_0 - r_\infty)$ and $[A]_t$ and is proportional to $(r_1 - r_\infty)$.

Self-Assessment Exercise 5

Give the details of the graphical method of obtaining the pseudo first order rate constant for

- i) acid hydrolysis of ethyl acetate
- ii) inversion of sucrose.

3.6 Determining the Order of Reaction

In order to write the rate law, we must know the order of reaction with respect to each reactant. In this section, we discuss some methods for determining the order of reaction.

3.6.1 Method of Initial Rates

The instantaneous rate of reaction extrapolated to the instant when the reagents were just mixed is called the initial rate of the reaction. Let us consider the reaction,



Let the rate of reaction be represented as,

$$V = k[\text{A}]^m[\text{B}]^n$$

where the reaction is m^{th} order in A and n^{th} order in B. The rate constant for the reaction is k . We have to obtain the initial rates from at least two experiments in which the initial concentrations of A (a_1 and a_2) are different while the initial concentration of B (b_1) is constant

$$\text{Rate in Experiment I} = v_1 = k a_1^m b_1^n$$

Rate in Experiment II = $v_2 = k a_2^m b_1^n$

From the ratio $\frac{v_1}{v_2} = \frac{k a_1^m b_1^n}{k a_2^m b_1^n} = \left(\frac{a_1}{a_2}\right)^m$, we can calculate m , since a_1 and a_2 are known

Taking logarithms we can write,

$$\log \frac{v_1}{v_2} = m \log \frac{a_1}{a_2} \dots \dots \dots (60)$$

Similarly, the rate is measured for one more experiment in which the initial concentration of

A is a_2 and the initial concentration of B is b_2 .

So, rate in Experiment III = $v_3 = k a_2^m b_2^n$.

$$\frac{\text{Rate in Experiment I}}{\text{Rate in Experiment II}} = \frac{v_2}{v_1} = \frac{k a_1^m b_1^n}{k a_2^m b_1^n} = \frac{b_1}{b_2} \dots \dots \dots (61)$$

$$\text{i.e. } \log \frac{v_2}{v_1} = n \log \frac{b_1}{b_2} \dots \dots \dots (62)$$

Since v_2 , v_3 , b_1 , and b_2 are known, n can be calculated. The overall reaction order = $m+n$.

You can understand this method from the following example.

Example 11

For the reaction, $\text{Cl}_2(\text{g}) + 2\text{NO}(\text{g}) \rightarrow 2\text{NOCl}(\text{g})$, the initial concentration, $[\text{Cl}_2]_0$ and $[\text{NO}]_0$ are given along with initial rates.

$[\text{Cl}_2]_0/\text{M}$	$[\text{NO}]_0/\text{M}$	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 the overall order;

(ii) what is the rate law? (iii) calculate the rate constant.

Solution

i) We can write the rate law as $k[\text{Cl}_2]^m[\text{NO}]^n$

Similar to Eqs. 68 and 70, we can write the logarithmic ratios and, calculate m and n as follows:

$$V_1 = k(0.10)^m (0.10)^n = 3.0 \times 10^{-3} \text{ M s}^{-1}$$

$$V_2 = k (0.20)^m (0.10)^n = 6.0 \times 10^{-3} \text{ M s}^{-1}$$

$$V_3 = k (0.20)^m (0.20)^n = 2.4 \times 10^{-2} \text{ M s}^{-1}$$

Using Eq. 62,

$$m = \frac{\log \frac{3.0 \times 10^{-3}}{6.0 \times 10^{-3}}}{\log \frac{0.10}{0.20}} = \frac{\log \frac{6.0}{3.0}}{\log \frac{0.20}{0.10}} = 1$$

Using Eq. 70,

$$n = \frac{\log \frac{6.0 \times 10^{-3}}{2.4 \times 10^{-2}}}{\log \frac{0.10}{0.20}} = \frac{\log \frac{2.4}{6.0}}{\log \frac{0.20}{0.10}} = 2$$

Hence, the reaction is second order in NO and first order in Cl₂. The overall order is 2 + 1 = 3.

ii) The rate law is given below:

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

iii) The rate constant can be calculated using any one of the three rates given above.

$$v_1 = 3.0 \times 10^{-3} \text{ M s}^{-1} = k(0.10 \text{ M})(0.10 \text{ M})^2$$

$$k = \frac{3.0 \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}}{(0.10)^3} = 3.0 \text{ M}^{-2} \text{ s}^{-1}$$

Care must be taken in applying the method of initial rates. For complex reactions like the formation of HBr (discussed in the next section) the product also affects the rate. The method of initial rates is applicable to simple reactions only.

1. Clock Reactions

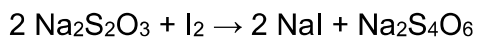
In the case of some reactions, the time taken for the colour change of the reaction mixture can be used for measuring the initial rate. Such self-indicating reactions are known as clock reactions. For example, the kinetics of the reaction,



Potassium perdisulphate

can be monitored as a clock reaction. A reaction mixture is prepared using potassium perdisulphate and potassium iodide in a higher concentration and sodium thiosulphate in much lower concentration. A drop of starch is also present in the reaction mixture.

The reaction mixture is colourless in the beginning and it turns blue after some time. The time, Δt , between the mixing of the reactants and the appearance of blue colour is noted. The blue colour develops due to the liberation of free iodine, after sodium thiosulphate (present in less concentration) is consumed completely as per the reaction:



Sodium tetrathionate

The order of the reaction with respect to KI (m) and the order of the reaction with respect to $\text{K}_2\text{S}_2\text{O}_8$ can be calculated by using the following formula:

$$\log (1/\Delta t) = m \log [\text{KI}] + n \log [\text{K}_2\text{S}_2\text{O}_8] + \text{constant}$$

A plot of $\log (1/\Delta t)$ against $\log [\text{KI}]$ is made using Δt values obtained by varying $[\text{KI}]$ and keeping $[\text{K}_2\text{S}_2\text{O}_8]$ constant, The slope of the straight line gives m . Similarly n is obtained from the slope of the straight line got by plotting $\log (1/\Delta t)$ against $\log [\text{K}_2\text{S}_2\text{O}_8]$. For the second plot, Δt is obtained by varying $[\text{K}_2\text{S}_2\text{O}_8]$ and keeping $[\text{KI}]$ constant.

Experimentally it has been found that $m = 1$ and $n = 1$.

$$\text{Hence, } -\frac{d[\text{K}_2\text{S}_2\text{O}_8]}{dt} = k [\text{KI}] [\text{K}_2\text{S}_2\text{O}_8]$$

For clock reactions, two more examples are given below:

- 1) Acid catalysed iodination of acetone
- 2) Saponification of ester (using phenolphthalein indicator).

2) Trial and Error Method '

We can determine the order of reaction

- i) by substitution of experimental data into Eqs. 21, 40 and 60, or
- ii) by graphical method using plots such as $\log [A]$ against t , $1/[A]$ against t and $[A]$ against t . The order of the reaction is one, two or zero depending on
 - i) which of the equations gives rise to a constant value, for k or
 - ii) which of the plots gives a straight line.

3) Half-Life 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

$$t_2/t_1 = ([A]_2/[A]_1)^{1-n} = ([A]_1/[A]_2)^{n-1}$$

$$n - 1 = \frac{\log t_2/t_1}{\log [A]_1/[A]_2}$$

or $n = 1 + \frac{\log t_2/t_1}{\log [A]_1/[A]_2} \dots(63)$

Example 12

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.

What is the order of the reaction?

Solution

Using Eq. 71,

$$n = 1 + \frac{\log 572/328}{\log 9.72 \times 10^{-3}/4.56 \times 10^{-3}}$$

$$= 1 + \frac{0.2415}{0.3287} = 1.735$$

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

4.0 Conclusion

The rate of a reaction depends on many factors such as the concentration of the reactants, temperature. The rate could be first order, second order and zeroth order equations, e.t.c. Many physical and chemical methods are available for studying reaction rates. Methods such as initial rates, trial and error and half-life could also be used to determine the order of reaction.

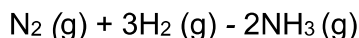
5.0 Summary

In this unit, we started with the definitions of the terms such as, rate of reaction, rate law, order of reaction and stoichiometry. We described experimental methods for rate studies. We derived the integrated forms of rate expressions for first order, second order and zeroth order reactions. We defined and illustrated the pseudo first order reactions.

We explained the methods of determination of order of reaction. We discussed the steps followed in arriving at the mechanisms of simple reactions. We described the theory of unimolecular reaction rates. Arrhenius equation, collision theory and the activated complex theory were discussed. Finally, we gave an outline of the methods of studying fast reactions.

6.0 Tutor-Marked Assignments

1) In the formation of ammonia,



the rate of consumption of hydrogen at a particular instant is $4.78 \times 10^{-4} \text{ M s}^{-1}$. What is the rate of formation of ammonia?

2) The rate constant for the decomposition of N_2O_5 at 340 K is $5.20 \times 10^{-3} \text{ s}^{-1}$. This reaction follows first order kinetics. If the initial rate of decomposition of N_2O_5 is $2.60 \times 10^{-4} \text{ M s}^{-1}$, 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 $k = 3.55 \times 10^{-4} \text{ s}^{-1}$?

5) The reaction,

$\text{I}^- (\text{aq}) + \text{S}_2\text{O}_8^{2-} (\text{aq}) \rightarrow \text{I}_2 (\text{aq}) + 2\text{SO}_4^{2-} (\text{aq})$ was studied at 298 K. The following results were obtained where

$$\text{rate} = - \frac{\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t}$$

$[\text{I}^-]_0$ and $[\text{S}_2\text{O}_8^{2-}]_0$ denote the initial concentrations of the two species.

$10^2 \times [\text{I}^-]_0/\text{M}$	$10^2 \times [\text{S}_2\text{O}_8^{2-}]_0/\text{M}$	$10^6 \times \text{Initial rate} / \text{M s}^{-1}$
8.0	4.0	12.50
4.0	4.0	6.25
4.0	2.0	3.12

Determine the rate law.

7.0 References/Further Readings

Principles of Physical Chemistry, Samuel H. Maron and Carl F. Prutton, Oxford and IBH Publishing Co., New Delhi, 4th ed., 1985.

Physical Chemistry, Gilbert W. Castellan, Narosa Publishing House, Addison-Wesley/Narosa (Indian Student Edition), Delhi, 3rd ed., 1983.

Physical Chemistry, P.c. Rakshit, Sarat Book House, Calcutta, 5th ed., 1988.

Physical-Chemistry through Problems, S.K. Dogra and S. Dogra, Wiley Eastern Ltd., New Delhi, 1984.

5) Physical Chemistry-Principles and Problems, D.V.S. Jain and P. Jauhar, Tata McGraw-Hill Pub. Company Ltd., New Delhi. 1990.

Answers to Self-Assessment Exercises

MODULE ONE: STATE OF MATTER

Unit 1: Units and Dimensions

SAEs 1

1. 7
2. Si stand for System Internationale.

SAEs 2

1. Fundamental Units
2. Energy, Electric Resistance, Frequency

SAE 3

1. No, only possible if mathematical relationship is available

SAE 4

Provide the Answer

SAE 5

Provide the answer

SAE 6

1. No

SAE 7

Provide the Answer

Unit 2: Kinetic Theory of Gases

SAE 1

The SI Unit of Pressure is Pa while that of Temperature is Kelvin.

SAE 2

1. Temperature

SAE 3

1. Pressure

SAE 4

Provide Answer

SAEs 5

Provide Answer

SAE 6

Provide Answer

SAE 7

Provide Answer

SAE 8

Provide Answer

Unit Three: Real Gases and Their Liquefaction

SAE 1

1. No, Just Hypothetical

SAE 2

Provide Answer

SAE 3

Using p_c , V_c and T_c values of methane from Table 1, calculate the value of z_c . Does methane obey van der Waals equation at the critical point?

SAE 4

Provide Answer

SAE 5

Provide Answer

SAE 6

The main intermolecular interactions in Cl_2 , Br_2 and I_2 are London forces. Since the polarisability and hence, London forces increases with relative molecular mass, the melting points are in that order.

Unit Four: Liquids

SAE 1

1. By heating liquid and by cooling gas under certain conditions

SAE 2

The amount of heat required at constant pressure to convert one mole of a solid into liquid at its melting point is called molar enthalpy of fusion ($\Delta H^\circ_{\text{fus}}$).

SAE 3

Provide Answer

SAEs 4

1. The cohesive forces between the molecules of water are stronger than the adhesive forces between water molecules and the hydrocarbon molecules in wax. Hence water does not "wet" the surface of wax.

2. Decane is expected to have the highest viscosity due to increased London forces with chain length.

SAE 5

Vaporization is the escape of molecules from liquid surface.

SAE 6

Boiling point is the temperature at which liquid vapour pressure equals the external pressure.

SAE 7

$$\Delta H_{\text{vap}} = 29.75 \text{ kJ mol}^{-1}$$

SAE 8

In an isotropic substance, the molecular arrangement is disorderly; the value for any physical property is same, irrespective of direction. In an anisotropic substance, the molecular arrangement is orderly and the values of some physical properties depend on the direction.

Unit 5: Solid State

SAE 1

1. A unit cell is the smallest unit chosen which repeats itself in three dimensions.

SAE 2

Simple cubic- lattice points at the eight corners only;

bcc- lattice points at the eight corners and the body-centre;

fcc- lattice points at the eight corners and the six face-centres.

3) $d_{123} = 2.132 \times 10^{-10} \text{ m}$.

SAE 3

Provide Answer

SAE 4

$$d_{123} = 2.132 \times 10^{-10} \text{ m}$$

SAE 5

11°

SAE 6

Using Eq. 14, density of tungsten = $1.936 \times 10^4 \text{ kg m}^{-3}$

SAE 7

Let us find out the number of formula units of KBr present in a unit cell using Eq. 17.

$$w = \text{Molar mass of KBr} = 0.119 \text{ kg mol}^{-1}$$

$$n = \frac{\rho a^3 N_A}{w} = \frac{2.826 \times 10^3 \text{ kg m}^{-3} \times (6.54 \times 10^{-10} \text{ m})^3 \times 6.022 \times 10^{23} \text{ mol}^{-1}}{0.119 \text{ kg mol}^{-1}} = 4$$

Since it has four formula units per unit cell, it has NaCl structure and not CsCl structure.

MODULE TWO: CHEMICAL THERMODYNAMICS

Unit 1: The First Law of Thermodynamics

SAE 1

- i) closed system
- ii) isolated system
- iii) open system

SAE 2

An extensive property of a homogeneous system is one which is dependent on the amount of a phase in the system.

SAE 3

- i. extensive
- ii. intensive (note that volume is an extensive property but volume per unit mass is an intensive property) .
- iii. intensive

SAE 4

1. **In an isothermal process**, the temperature of the system remains constant. When a system undergoes an isothermal process, it is in thermal contact with a large constant temperature bath, known as thermostat. The system maintains its temperature by exchange of heat with the thermostat .
2. **In an adiabatic process**, no heat is allowed to enter or leave the system. Systems in which such processes occur are thermally insulated from the surroundings. An adiabatic process may involve increase or decrease in the temperature of the system.
3. In an isochoric process, the volume of the system remains constant. Thus, a chemical reaction in a sealed flask of constant volume is an isochoric process.
4. **A process is cyclic** if the system (after any number of intermediate changes) returns to its original state. The initial and final values of each thermodynamic variable is identical after the completion of a cyclic process.

SAE 5

Work (W) is defined as the product of the force applied (F) and the distance (X) moved along the direction of the force.

SAE 6

$$C_p = 52.6 \text{ J mol}^{-1} \text{ K}^{-1}; n = 3.00 \text{ mol}$$

$$T_1 = 305 \text{ K}; T_2 = 405 \text{ K}$$

$$\begin{aligned} \text{Using Eq. 5, } q_p &= \int_{T_1}^{T_2} n C_p dT = \int_{305}^{405} 3.00 \times 52.6 dT \\ &= 3.00 \times 52.6 (405 - 305) \text{ J} \\ &= 15.8 \text{ kJ} \end{aligned}$$

SAE 7

In a system of constant mass, energy can neither be created nor be destroyed

SAE 8

Work done on the gas against vacuum is zero as per Eq. 13.

Unit 2: Thermochemistry**SAE 1**

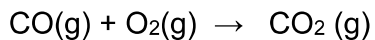
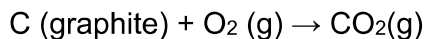
In a closed vessel and in a pressure regulated vessel.

SAE 2

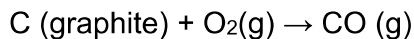
(i) 1 (ii) 0

SAE 3

$$\Delta H^\circ_f = 2 \Delta H^\circ_f(\text{CO}_2) + 3 \Delta H^\circ_f(\text{H}_2\text{O}) - \Delta H^\circ_f(\text{C}_2\text{H}_6) - 7/2 \Delta H^\circ_f(\text{O}_2)$$

SAE 4

Subtracting (2) from (1) and rearranging, we get



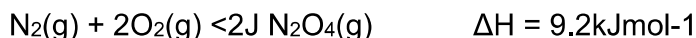
$$\Delta H = (-393.5 + 283.5) \text{ kJ}$$

$$\Delta H = -110 \text{ kJ}$$

$$-393.5 \text{ kJ}$$

$$-283.5 \text{ kJ}$$

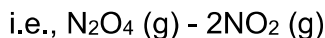
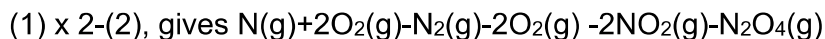
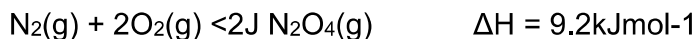
$$33.2 \text{ kJ mol}^{-1}$$



SAE 5

This is defined as the enthalpy change when a solution containing one mole of solute at concentration C_1 is diluted by the addition of solvent so that the final concentration is C_2 . It is obvious that the enthalpy of dilution depends on both C_1 and C_2 .

SAE 6



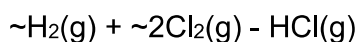
$$\text{and } \Delta H = (2 \times 33.2) - 9.2 \text{ kJ} = 57.2 \text{ kJ}$$

SAE 7

$$\Delta C_p = C_p(\text{CO}) + C_p(\text{H}_2) - C_p(\text{graphite}) - C_p(\text{H}_2\text{O})$$

$$= (9.58 - 9.60 \times 10^{-3}T + 23.09 \times 10^{-7}T^2) \text{ J K}^{-1}$$

SAE 8



$$L_{\text{rff}}(\text{HCl}) = \sim B(\text{H-H}) + B(\text{Cl-Cl}) - B(\text{H-Cl})$$

$$G(436) + (242) - 431 \text{ kJ mol}^{-1} = -92 \text{ kJ mol}^{-1}$$

Unit 3: The Second Law of Thermodynamics

SAE 1

- Using Eq. 22; work done by the engine = Efficiency of the engine \times heat absorbed from the source = $(0.250 \times 8.00 \times 10^2) \text{ J}$

$$= 2.00 \times 10^2 \text{ J}$$

Heat rejected to the sink ($-q_c$) can be calculated using Eq. 25.

$$\eta = 0.250 = 1 + q_c/q_H$$

$$\therefore q_c/q_H = -0.75$$

$$q_c = -0.75q_H = -0.75 \times 8.00 \times 10^2 \text{ J}$$

$$= -6.00 \times 10^2 \text{ J}$$

Heat rejected to the sink = $-q_c = 6.00 \times 10^2 \text{ J}$

SAE 2

Using Eq. 42 entropy change = Heat transferred reversibly

Temperature

$$= \frac{2.40 \times 10^4 \text{ J}}{3.00 \times 10^2 \text{ K}} = 80 \text{ J K}^{-1}$$

$$3.00 \times 10^2 \text{ K}$$

$$\eta = 0.250 = 1 + q_c/q_H$$

$$\therefore q_c/q_H = -0.75$$

$$q_c = -0.75q_H = -0.75 \times 8.00 \times 10^2 \text{ J} \\ = -6.00 \times 10^2 \text{ J}$$

Heat rejected to the sink = $-q_c = 6.00 \times 10^2 \text{ J}$

SAE 3

Using Eq. 42 entropy change = $\frac{\text{Heat transferred reversibly}}{\text{Temperature}}$

$$= \frac{2.40 \times 10^4 \text{ J}}{3.00 \times 10^2 \text{ K}} = 80 \text{ J K}^{-1}$$

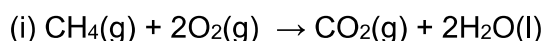
$$\eta = 0.250 = 1 + q_c/q_H$$

$$\therefore q_c/q_H = -0.75$$

$$q_c = -0.75q_H = -0.75 \times 8.00 \times 10^2 \text{ J} \\ = -6.00 \times 10^2 \text{ J}$$

Heat rejected to the sink = $-q_c = 6.00 \times 10^2 \text{ J}$

SAE 4



Standard entropy change for the combustion of methane

$$= S^\circ(\text{CO}_2) + 2S^\circ(\text{H}_2\text{O}) - (S^\circ(\text{CH}_4) + 2S^\circ(\text{O}_2)) \\ = [213.7 + (2 \times 69.9) - (186.3 + (2 \times 205.1))] \text{ J K}^{-1} \\ = -243 \text{ J K}^{-1}$$

Hence, entropy change of the system

$$= \Delta S^\circ \text{ for the combustion of methane} \\ = -243 \text{ J K}^{-1}$$

(ii) Entropy change of the surroundings:

$$= \frac{q_{\text{surr}}}{T_{\text{surr}}}$$

But $q_{\text{surr}} = -(\Delta H \text{ for the combustion of one mole of methane}) = 8.90 \times 10^5 \text{ J}$

Hence, ΔS for the surroundings = $\frac{q_{\text{surr}}}{T_{\text{surr}}}$

$$= \frac{8.90 \times 10^5 \text{ J}}{298.15 \text{ K}} \\ = 2990 \text{ J K}^{-1}$$

MODULE THREE: SOLUTIONS AND PHASE RULE

Unit 1: Solution

SAE 1

- i) Solid in solid
- ii) Liquid in solid
- iii) Gas in liquid

SAE 2

The masses of ethanol and water are 0.100 kg each.

$$\text{No. of mol of ethanol} = \frac{0.100 \text{ kg}}{0.046 \text{ kg mol}^{-1}} = 2.17 \text{ mol}$$

$$\text{No. of mol of water} = \frac{0.100 \text{ kg}}{0.018 \text{ kg mol}^{-1}} = 5.56 \text{ mol}$$

Mole fraction of ethanol in the solution

$$= \frac{2.17 \text{ mol}}{(2.17 \text{ mol} + 5.56 \text{ mol})}$$

$$= \frac{2.17 \text{ mol}}{7.73 \text{ mol}} = 0.28$$

Mole fraction of water in the solution = $(1 - 0.28) = 0.72$.

SAE 3

The solubility of oxygen is less in warm water and hence the amount of oxygen is not enough for the fish to survive.

SAE 4

Mole fraction of acetone (x_A) = 0.500

Mole fraction of chloroform (x_C) = 0.500

$$\begin{aligned} \text{Partial Vapor Pressure of Acetone (P}_A\text{)} &= 0.500 \times 4.60 \times 10^4 \text{ Pa} \\ &= 2.30 \times 10^4 \text{ Pa} \end{aligned}$$

$$\begin{aligned} \text{Partial Vapour Pressure Chloroform (P}_C\text{)} &= 0.500 \times 3.92 \times 10^4 \text{ Pa} \\ &= 1.96 \times 10^4 \text{ Pa} \end{aligned}$$

If this solution were to behave ideally, the total vapour pressure should be $(2.30 \times 10^4 \text{ Pa}) + (1.96 \times 10^4 \text{ Pa}) = 4.26 \times 10^4 \text{ Pa}$. The observed value ($3.47 \times 10^4 \text{ Pa}$) is less than the value from an ideal solution. That is, acetone-chloroform mixture exhibits negative deviation from Raoult's Law.

Unit 2: Colligative Properties

SAE 1

i) True ii) False iii) False.

SAE 2

Provide the Answer

SAE 3

i. True ii. False iii. False

Unit 3: Phase Equilibria

SAE 1

1) a) 3 (two due to toluene and water liquids which are immiscible and, one due to their vapours).

b) 2 (since acetone and water are miscible).

2) a) $C = 1$ as per Eq. 1, since $S = 3$ and $R = 2$.

b) $C = 2$, since $S = 3$ and $R = 1$.

SAE 2

The four phases of sulphur cannot coexist since then $F = -1$.

SAE 3

$(\partial\mu/\partial T)_p = -S$ for a closed system, hence the slope of Fig. 1a or b gives the partial molar entropy of a substance with the sign inverted.

MODULE FOUR: CHEMICAL EQUILIBRIA ELECTROCHEMISTRY

Unit 1: Chemical Equilibria

SAE 1

308 kJ mol⁻¹

SAE 2

1. The equilibrium expression for the reaction,



can be written as,

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

When,

i) Cl_2 is added, $[\text{PCl}_5]$ must increase in order to keep the K_c value constant; i.e.; some Cl_2 will combine with PCl_3 to give more of PCl_5 . Hence, the equilibrium will shift towards left.

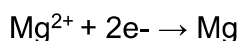
ii) volume of the container is decreased, the pressure will increase. According to Le Chatelier's principle, the equilibrium would shift in such a direction so as to neutralise or reduce this increase. Since the total number of moles on the L.H.S. is less than in R.H.S., the equilibrium has to shift towards left in order to bring about pressure decrease.

2. For endothermic reactions, the increase in temperature will move the equilibrium in the forward direction according to Le Chatelier's principle

Unit 2: Electrolytes

SAEs 1

1) To reduce each Mg^{2+} ion to magnesium metal, two electrons are required,



Hence $n = 2$

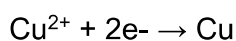
Rearranging Eq. 8, we get, $t = \frac{96500 n w}{I M}$

Since 1 mole of magnesium is to be prepared, $w/M = 1 \text{ mol}$.

Also, $I = 5 \text{ A}$

Hence $t = \frac{96500 \times 2 \times 1}{5} \text{ s} = 38600 \text{ s}$

2) i) To reduce each Cu^{2+} ion to copper metal, two electrons are required.



Hence $n = 2$

According to Eq. 8, $w = \frac{MIT}{96500 n}$

Substituting for M , I , t and n we get,

$$w = \frac{0.06354 \times 4.50 \times 9000 \text{ kg}}{96500 \times 2} \quad [\text{smce } M = 0.06354 \text{ kgmol}^{-1}]$$

$$w = 1.33 \times 10^{-2} \text{ kg.}$$

ii) Amount of Cu deposited = $w/M = 0.21 \text{ mol}$

Amount of Cu initially present = 2.0 mol

(since 1 dm^3 of 2.0 M solution contains 2.0 mol of copper)

Amount of Cu at the end of the electrolysis = $(2.0 - 0.21) \text{ mol} = 1.79 \text{ mol}$

This must also be equal to the amount of Cu^{2+} ions present in the solution at the end of electrolysis.

SAE 2

Substituting the given values for 0.020M KCl in Eq. 14, we get,

$$k = k_{\text{cell}} \times 1/R$$

$$0.2768 \text{ S m}^{-1} = \frac{k_{\text{cell}} \times 1}{195.96 \Omega}$$

$$k_{\text{cell}} = 0.2768 \times 195.96 \text{ m}^{-1}$$

Using this value of k_{cell} for 0.050 M AgNO_3 solution in Eq. 14 we get

$$k(\text{AgNO}_3) = 0.2768 \times 195.96 \text{ m}^{-1} \times \frac{1}{94.2 \Omega}$$

$$= 0.576 \text{ S m}^{-1}$$

Unit 3: Electrochemistry

SAE 1

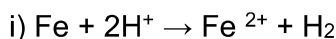
The electrode, at which oxidation occurs, is called anode, whereas the electrode where reduction takes place, is called cathode.

a) In galvanic cell, the cathode is given a positive sign and the anode, a negative sign.

b) In electrolytic cell, the two signs are reversed. The anode is given a positive sign and the cathode is given a negative sign.

SAE 2

If any reaction leads to negative cell potential, that particular reaction will be non-spontaneous. Hence, we have to calculate the cell potentials in each case to know whether a particular reaction is spontaneous or not.

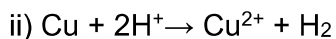


$$E_{\text{cell}} = E_{\text{anode}} + E_{\text{cathode}}$$

$$= [- (-0.44) + 0] \text{ V (since standard potential for } \text{Fe}^{2+}/\text{Fe} \text{ is } -0.44 \text{ V)}$$

$$= 0.44 \text{ V.}$$

This reaction is spontaneous.

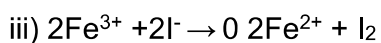


$$E_{\text{cell}} = E_{\text{anode}} + E_{\text{cathode}}$$

$$= [- (0.34) + 0] \text{ V (since for } \text{Cu}^{2+}/\text{Cu}, E^{\circ} = +0.34 \text{ V)}$$

$$= -0.34 \text{ V.}$$

. This reaction is non-spontaneous.



$$= [- (0.54) + 0.77] \text{ V}$$

= 0.23 V. This reaction is spontaneous

SAE 3

Provide the Answer

Unit 4: Chemical Kinetics

SAE 1

1. Using Eq. 2, $\frac{d[\text{O}_2]}{dt} = \text{Rate}$

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

2. $\frac{1}{2}(-d[\text{HI}]/dt) = d[\text{H}_2]/dt$

SAE 2

i) Spectrophotometry

ii) pH measurement, conductance or titration

iii) pressure measurement

SAE 3

Units of k

Zero order = M s^{-1}

First order = s^{-1}

Second order = $\text{M}^{-1} \text{ s}^{-1}$

5) Substituting in Eq. 40,

$$\frac{1}{[\text{A}]_t} = \frac{1}{[1.00 \times 10^{-2}]} + 1.83 \times 10^{-3} \times 1.68 \times 10^5 \text{ M}^{-1}$$

$$[\text{A}]_t = 2.45 \times 10^{-3} \text{ M}$$

SAE 4

Using Eq. 53,

$$[\text{A}]_t = \frac{25}{100} \times 0.500 \text{ M} = 0.125 \text{ M}$$

100

$$t = \frac{(0.500 - 0.125) \text{ s}}{1.20 \times 10^{-4}}$$

$$= 3.13 \times 10^3 \text{ s}$$

SAE 5

i) After obtaining V_0 , V_t and V^∞ $\log (V^\infty - V_t)$ is plotted against t .

$$k' = -2.303 \times \text{slope}$$

where k' is the pseudo first order rate constant for the acid hydrolysis of ester.

ii) Using r_0 , r_t , and r^∞ values, $\log (r_t - r^\infty)$ is plotted against t .

$$k' = -2.303 \times \text{slope}$$

$$t = \frac{(0.500 - 0.125) \text{ s}}{1.20 \times 10^{-4}}$$

$$= 3.13 \times 10^3 \text{ s}$$

