UGCHE-L4

BLOCK-1

Uttar Pradesh
Rajarshi Tandon Open University

UGCHE-L4

Chemistry Lab–IV

Block

1

LABORATORY SKILLS AND TECHNIQUES

UNIT 1

Basic Laboratory Skills 5

UNIT 2

Handling of Data 30

UNIT 3

Low-Cost Instruments 63

COURSE INTRODUCTION

It is advisable to complete CHE–03 (L) and CHE–04 courses before taking up chemistry Lab–IV course. This course deals with experiments in Physical Chemistry. This 4–credit course consists of four blocks. In Block 1, we shall have a discussion on the laboratory skills and techniques. Data handling will also be discussed. The use of low-cost instruments will be explained. In Block 2, the theoretical basis and experimental details for some of the experiments concerning properties of liquids and thermochemistry will be discussed.

In Block 3, we shall see experiments pertaining to the study of one of the colligative properties, ionic equilibria, adsorption and phase equilibria. In Block 4, we shall discuss the experiments in chemical kinetics.

After studying the materials in this course and performing the experiments discussed in it, you should be able to:

- explain the basic concepts pertaining to surface tension, viscosity and thermochemistry,
- state the principles involved in the measurement of pH and determination of solubility product,
- draw phase diagrams of eutectic system and partially miscible system which has upper critical solution temperature, and
- explain the basic concepts pertaining to chemical kinetics.

Study Guide

There are around twenty one experiments in this course apart from three demonstration experiments. These experiments are to be performed in about two weeks. The demonstration experiments will be performed by your counsellor. The demonstration experiments are aimed at acquainting you with the low-cost instruments.

The general pattern of discussion of experiments in this course is similar to that of CHE–03 (L) course. In this course, the performance of the experiments, recording the data, calculations and expression of result are to be done as in CHE–03 (L) course. As an additional feature, there is a discussion on significant figures in Unit 2. It is advisable that you maintain significant figures in your calculations. The maintenance of laboratory note book may be done as per guidelines given in U[illegible] of this course. Remember that each experiment is going to be evaluated. He[illegible]as. This read the blocks before going to the laboratory for performing the experi[illegible] will help you in doing the experiments in a proper way.

BLOCK INTRODUCTION

In Block 1, we shall discuss the basic ideas related to laboratory techniques, methods of using the experimental data for arriving at the desired result and the method of operation of low-cost instruments.

In Unit 1, we shall discuss some of the aspects regarding laboratory safety and first aid. We shall discuss how to weigh a sample, prepare a standard solution and, carry out a titration. Heating methods will also be discussed.

In Unit 2, features regarding data handling will be explained. We shall first discuss SI units of basic and derived physical quantities. The concept of significant figures will be explained. Examples will be stated for maintaining significant figures during addition, subtraction, multiplication and division. Maintenance of laboratory record also will be discussed. Tabulation of data and plotting of graphs will be explained.

In Unit, 3 the principles of colorimetry, conductometry and potentiometry will be discussed. The use of low-cost instruments such as colorimeter, conductometer and mV/pH meter will be illustrated through three demonstration experiments.

Objectives

After studying this block, you should be able to:

- explain the method of weighing a sample and preparing a standard solution,
- explain the principles of titrimetric analysis,
- discuss the various heating methods,
- explain the SI units of basic and derived physical quantities,
- explain the concept of significant figures,
- maintain significant figures during calculations, and
- state the principles of colorimetry, conductometry and potentiometry.

UNIT 1 BASIC LABORATORY SKILLS

Structure

1.1 Introduction
  Objectives
1.2 Laboratory Safety and First Aid
1.3 Titrimetric Analysis
  Types of Titrations
  Apparatus for Titrimetric Analysis
  Carrying out a Titration
1.4 Weighing a Substance
1.5 Expression of Concentration
1.6 Preparation of Standard Solution
1.7 Titrimetric Calculations
1.8 Heating Methods
1.9 Use of Thermometers
1.10 Filtration
1.11 Summary
1.12 Answers

1.1 INTRODUCTION

In this introductory unit, we shall describe some of the experimental techniques. You are going to use these techniques during this laboratory course. Therefore, you must understand the principles behind these techniques. In some cases, the required apparatus for an experimental technique will also be discussed.

We shall start with a discussion on laboratory safety and first aid. We shall explain the main features of titrimetric analysis. We shall then state the method of finding the mass of a substance using an analytical balance; this discussion will help you in understanding the method of preparation of standard solution. The use of thermometers will be illustrated with reference to the determination of melting point of a substance. Finally the method of filtration will be explained.

Objectives

After studying this unit, you should be able to:

- state the measures to be taken under laboratory safety and first aid,
- explain the types of titrations and the principle of titrimetric analysis,
- discuss the method of using an analytical balance for weighing a substance,
- state the different ways of expressing the concentration,
- explain the method of preparation of a standard solution
- carry out titrimetric calculation using the given data,

- state the method of determination of melting point of a substance, and
- explain the technique of filtration.

1.2 LABORATORY SAFETY AND FIRST AID

Laboratory is a place for learning the experimental skills. You are strongly advised to be careful at all times. It is recommended not to perform unauthorised experiments. This will ensure your safety as well as the safety of your fellow-students. Even a small accident involving minor injury must be reported to the counsellor. The following instructions should be observed during the laboratory work.

i) You must wear a laboratory coat or apron over your clothes while working in the chemistry laboratory. This will save you from injury and protect your clothes from damage.

ii) Handle the hot glass carefully; it cools very slowly and may be very hot without appearing so.

iii) Protect your eyes from any spurting of acid or a corrosive chemical. In case of such spurting into the eyes, immediately wash with lot of water and go to a doctor.

iv) You must not reach across lighted burners as it may result in an accident.

v) Wash your apparatus thoroughly with a washing powder.

vi) While heating substances, do not point the tube towards your neighbour or to yourself. A suddenly formed bubble may eject the contents violently and dangerously.

vii) When diluting sulphuric acid, pour the acid slowly and carefully into the water with constant stirring. Never add water to the acid as it may result in the liberation of a lot of heat.

viii) Read the label on the bottle carefully before using the required chemical. Never pour back the unused reagent into the bottle.

ix) Never touch or taste a chemical or solution as most of chemicals are either corrosive or poisonous.

x) Always bring your container to the reagent shelf and do not take the bottles to your desk.

xi) Do not insert the pipette or dropper into the reagent bottles; this helps in avoiding any possible contamination.

xii) Graduated cylinders and bottles are not to be heated because these break very easily and their volume also changes.

xiii) At the end of the experiment, clean and dry the glass apparatus and wipe off the top of the working table. Ensure that the gas and water taps are closed before you leave the laboratory.

Laboratory First-Aid

If a corrosive substance falls on your skin, immediately wash the spot with large quantities of water, followed by remedial action indicated below:

Acid spill : Treat with sodium bicarbonate or ammonium carbonate (2M) solution; then apply vaseline or a soothing cream.

Base spill : Treat with acetic acid (1 M) followed by vaseline or a soothing cream.

'M' is a unit for concentration. You will understand this unit in Sec. 1.5 of this unit.

Bromine : Treat with 2 M ammonia; keep the affected part dipped in dilute sodium isulphite solution till bromine is washed off. Finally apply vaseline.

henol : Wash with ethanol and then take hospital treatment.

The most common accidents in the chemistry laboratory involve cuts, burns or fire. The first-aid to be given in each case is below :

uts : If you have a cut, wash the wound well with cold water immediately. If leeding is severe, apply pressure directly on to the wound to stop the bleeding. hen an antiseptic cream can be applied to the wound; it should be followed by roper dressing of the wound.

urns : Wash the burnt part with cold water for sometime and then apply Burnol it.

ire : A small fire in a beaker, caused by the vapours of an imflammable liquid can extinguished by covering it with a watch glass. If the clothes catch fire, one iould lie on the floor and, fire can be put off by wrapping a thick blanket around ie body.

3 TITRIMETRIC ANALYSIS

uring this laboratory course, you will be often doing **titrimetric analysis.** trimetric analysis generally consists in determining the volume of a solution of curately known concentration which is required to react completely with a known lume of the solution of a substance being estimated. The solution of accurately iown concentration is called the **standard solution**. The standard solution ntains a definite amount of the solute per litre (dm^3) of the solution. The term, lumetric analysis, is also used in the place of the term, titrimetric analysis.

tration is the process of adding a standard solution to a test solution (or vice rsa) until the reaction is just complete. The point at which the completion of iction occurs is called the **equivalence point** or the **end point**. Let us explain se two terms. The stage at which the reacting solutions are used up in their ichiometric proportions is called the **equivalence point**. The detection of uivalence point is often done using instrumental measurements at various stages titration. Conductometer and mV/pH meter are two such instruments used for determination of equivalence point. In experiments 2 and 3 of CHE–03 (L) irse, their usage in titrimetric analysis has been illustrated.

t us now explain the term, the end point. Sometimes it is possible to use a istance to indicate the completion of titration. Such a substance is called an icator and the equivalence point determined using an indicator is called the **end** nt. An indicator indicates the completion of reaction by a change in physical iperty such as colour. The basic requirement for an indicator is that its colour iuld be quite different before and after the end point. Ideally, end point should close to the equivalence point. But the colour change occurs only after the iivalence point; hence the end point differs at least slightly from the equivalence nt. A well known example of indicator is phenolphthalein used in acid-base ation. It is pink in basic solution and colourless in acidic solution. In experiments 1, 4, 9, 10 and 11 of CHE–03 (L) course, the use of indicators for titrimetric analysis has been explained.

For carrying out the titrimetric analysis of any given substance, a reaction must satisfy following conditions:

a) The substance to be estimated must react completely with another of known strength in stoichiometric proportions.

b) There must be a simple and instantaneous reaction.

c) An indicator may be used for identifying the completion of titration by the change in colour of the solution. In the absence of indicators, instrumental method should be available to conduct a titration.

Next let us discuss the types of titrations.

1.3.1 Types of Titrations

There are four main types of titrations as given below.

a) Neutralisation titration or acid-base titration

Neutralisation titration involves the titration of a base with an acid. The reaction essentially involves the combination of hydroxyl ions with the hydrogen ions to form water. A typical example is the titration of sodium hydroxide against hydrochloric acid.

b) Precipitation titration

Precipitation titration results in the formation of a precipitate. An example for this type is the titration of silver nitrate against sodium chloride.

c) Oxidation–reduction titration

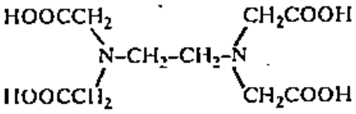
Oxidation–reduction titration involves the change in the oxidation number or transfer of electrons among the reacting substances. The principal oxidising agents are potassium permanganate, potassium dichromate, iodine and potassium iodate. The reducing agents are ferrous and stannous compounds , oxalic acid and sodium thiosulphate.

A typical example of this type is the titration of potassium permanganate against ferrous ammonium sulphate.

d) Complexometric titration

In complexometric titration, a complexing reagent forms complex ions with metal ions like Ca^{2+} and Mg^{2+}. Sodium salt of EDTA(ethylenediamine tetraacetic acid) is often used as a complexing reagent in titrations.

The complexing reagent is also called a ligand. A complex ion is a metal ion with one or more ligands bonded to it.



$$(HOOCCH_2)_2N-CH_2-CH_2-N(CH_2COOH)_2$$

EDTA

Before trying to know how titrations are carried out, let us know some of the apparatus used during titrations.

1.3.2 Apparatus for Titrimetric Analysis

The apparatus for titrimetric analysis is of three principal kinds:

(i) Volumetric flasks (ii) pipettes and (iii) burettes.

Let us discuss each of them.

i) Volumetric Flasks

Volumetric flasks are used for the preparation of standard solutions and for diluting the sample to known volumes. The volumetric flasks have a flat bottom, pear shaped body and long narrow neck. These have a ring engraved around their neck. When filled up to this ring, the volumetric flask contains the volume of the liquid marked on it. The volumetric flasks are of varying capacities such as 100 cm^3, 200 cm^3, 250 cm^3, etc. As an example, 100 cm^3 flask is illustrated in Fig. 1.1.

Fig. 1.1 : 100 cm^3 volumetric flask.

In Sec. 1.6, we shall see the use of volumetric flasks in preparing a standard solution.

ii) Pipettes

Pipettes are used to transfer known volume of a liquid from one container to another. A pipette usually consists of a narrow tube with a bulb in the middle. The ring mark engraved on the stem indicates the length to which the liquid level must be drawn to get exactly the volume of the liquid marked on the bulb. Some pipettes, known as graduated pipettes, are calibrated so that any volume upto its maximum capacity can be transferred. The pipettes of volume 1 cm^3, 2 cm^3, 5 cm^3, 10 cm^3, 20 cm^3 and 25 cm^3 are used commonly. As an example, 20 cm^3 pipette is indicated in Fig. 1.2 (a).

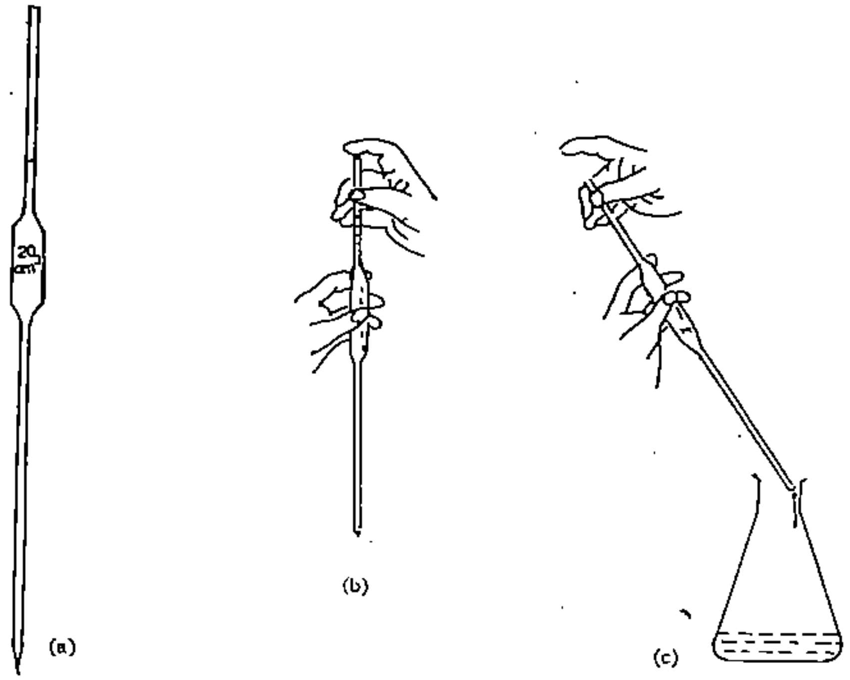
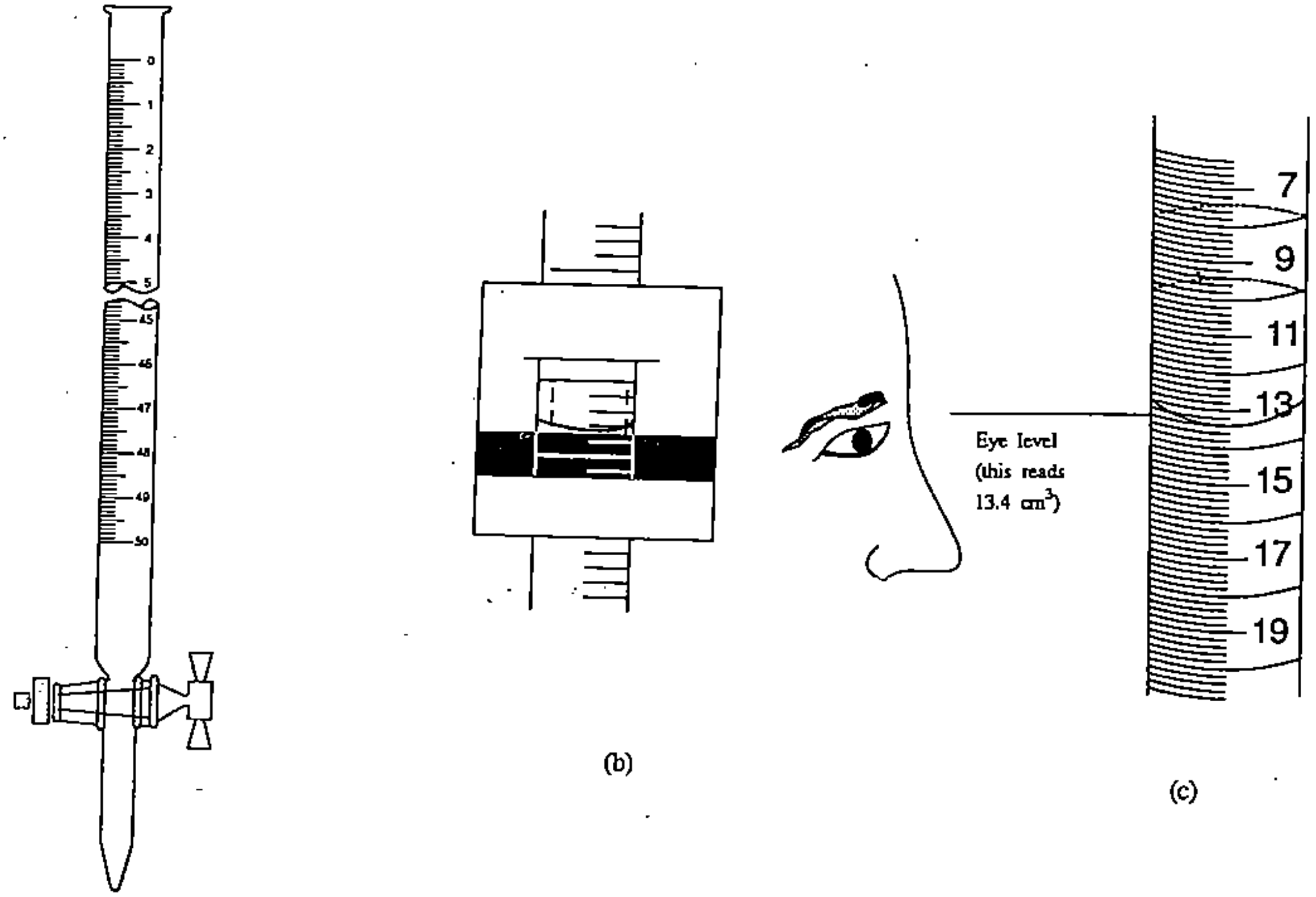


Fig. 1.2 : a) pipette; b) handling a pipette
c) draining out the pipetted solution.

Before using a pipette for transferring a liquid for estimation, it has to be thoroughly washed with a good quality detergent, followed by plenty of water and finally with distilled water. It is then to be rinsed with a solution which is to be pipetted. For rinsing, the solution is taken in a clean dry beaker. The pipette is dipped into the solution and the solution is sucked into the pipette to fill it about half its volume. The upper tip of the pipette (the suction end) is closed by the finger tip. The pipette is then taken out ad held horizontal between the two hands and rolled gently. This ensures the wetting of the walls of the pipette. Make sure that the solution in the pipette does not reach the suction end. The solution is then drained into the sink and the process is repeated. This completes the rinsing process. Now we can use the pipette for transferring the solution for estimation. The solution is drawn through the pipette past the ring mark. The suction end is closed by the tip of the index finger (Fig. 1.2 (b)). By rolling the finger-tip slightly, excess liquid is allowed to drain out until the meniscus descends to the ring mark. Now the liquid in the pipette is allowed to drain out into the receiving vessel (Fig. 1.2 (c)). By touching the walls of the receiving vessel with the tip of the pipette, the last drop is also transferred. **Do not blow out the last drop.**

iii) Burettes

Burette is a common device for measuring precisely the volume of a liquid used during titration. There are two well-known types of burettes. The first type consists of a calibrated tube with a narrow end to which a glass tubing is attached by means of a rubber tubing. To the rubber tubing, a spring-clip is attached. When you press the clip, the liquid flows out of the burette. In another type of burette, a stopcock is used instead of spring-clip. The burette is graduated, the zero being at the top. Mostly we use 50 cm^3 burette. For some titrations, we use 5 cm^3 burette. A 50 cm^3 burette is shown in Fig. 1.3 (a).



(a)

(b)

(c)

Fig. 1.3 : a) Burette (with a stopcock) b) using a parallax card c) eye level for burette reading.

Before filling the burette with a liquid, it has to be washed, first with a detergent, followed by plenty of water and distilled water. It is then rinsed with the liquid which is to be taken in it. For rinsing it, fill the burette to half its volume with the liquid, rotate it repeatedly keeping it horizontal between the two hands; then drain out the liquid. The burette is then vertically mounted on the stand and is filled with the liquid through a funnel. After taking out the funnel, the meniscus is adjusted to any definite graduation mark in the burette by drawing out the necessary volume of the liquid through the stopcock (or spring clip). It is not necessary for the meniscus to be at zero mark, since the volume delivered from a burette can be obtained simply by noting the difference between the initial and final readings.

To avoid error in burette reading, you may make use of a parallax card. Parallax card is a small piece of cardboard covered with white paper in which the lower half is blackened with ink. While reading a burette, adjust the dividing line at the same level as the meniscus as shown in Fig. 1.3 (b).

In order to avoid the parallax, view the position of the burette such that the front and rear levels of the liquid coincide, Fig. 1.3 (c). For accurate titration results, the volume of liquid used for titration should neither be too large nor too small. Titre value is obtained by noting the difference between the intial burette reading and final burette reading (after titration).

1.3.3 Carrying out a Titration

In general, during titration, a standard solution taken in the burette, is added dropwise to a test solution in the conical flask (Fig. 1.4).

A solution for which the concentration is known accurately is called a standard solution.

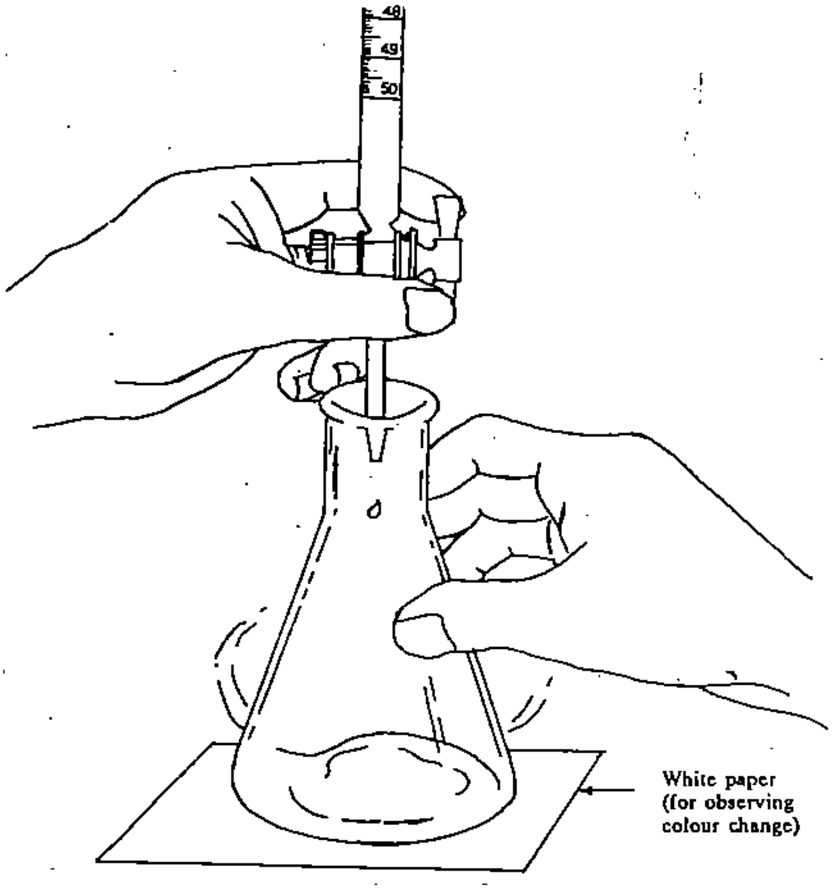


Fig. 1.4 : Delivery of a liquid from a burette.

The purpose of the titration is to find the concentration of the test solution. The equivalence point (or the end point) is determined. The volume of the standard solution delivered through the burette for attaining the equivalence point is known as the titre value. From the titre value, the concentration of the standard solution and the volume of the test solution, it is possible to calculate the concentration of the test solution. The calculation part will be discussed in Sec. 1.7. In the next section, we shall discuss weighing of a substance. This will help us in understanding Sec. 1.6 in which the preparation of standard solution is going to be discussed.

SAQ 1

Define the term, titrimetric analysis.

....

....

....

....

SAQ 2

You are given a solution of sodium hydroxide of known concentration and you are asked to find out the concentration of given hydrochloric acid solution. Indicate a method based on each of the following :

i) determination of end point

ii) determination of equivalence point

....

....

....

....

In the next unit, we shall discuss SI units for various physical quantities.

Mass is the quantity of matter of which the object is composed. Mass of an object is same, irrespective of the location where it is weighed.

Throughout this laboratory course, we use an analytical balance to find the mass of an object.

Weight of an object is the force exerted on it by gravitational attraction. The gravitational force and the weight differ at different locations on the earth. A spring balance is used to find the weight of an object.

1.4 WEIGHING A SUBSTANCE

The internationally accepted unit (SI unit) of mass is kilogram. One gram is one-thousandth part of one kilogram whereas one milligram is one-thousandth part of one gram. In this laboratory course, you would be measuring mass from a few milligrams to grams. You would be using analytical balance for weighing.

An analytical balance (Fig. 1.5) can be used for finding masses to a precision limit of 0.2 mg. As we proceed with the study of this laboratory course, you will notice that many experiments involve at least one measurement of mass. Hence the accuracy of your experiment will depend largely on your skill of using the analytical balance. The analytical balance actually compares the unknown mass of a sample with a standardised mass.

In an analytical balance, (Fig. 1.5), two pans are suspended from the ends of the balance beam. A pointer is attached to the center of the balance beam and it projects down to a scale at the base. The upper edge of the balance beam is

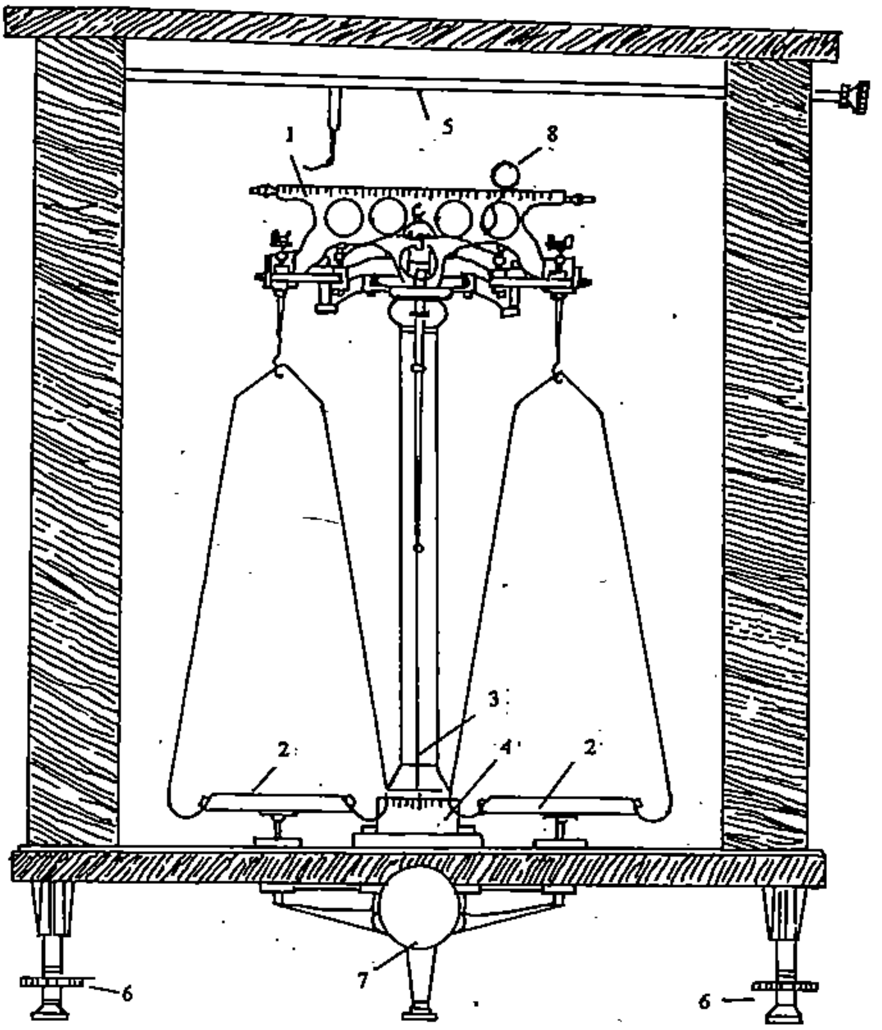


Fig. 1.5 : Analytical balance;

(1) beam (2) pans (3) pointer (4) scale (5) rider-carrier (6) levelling screws (7) arrest-knob (8) rider.

graduated, with the zero of the scale at the center of the beam, with major divisions reading 1 mg and the subdivisions reading 0.2 mg. Both ends of the beam are thus graduated. So an analytical balance can weigh only up to an accuracy of 0.2 mg (or 0.0002 g). The balance is fixed inside a glass case. A rider-carrier is attached to the case which is parallel to the balance beam and is slightly above it. An arrest-knob for the beam-control is on the outside of the balance case. The balance case is supported on levelling screws. You will be provided with a set of weight box and fractional weights (Figs. 1.6 (a) and (b)) for use on analytical balance.

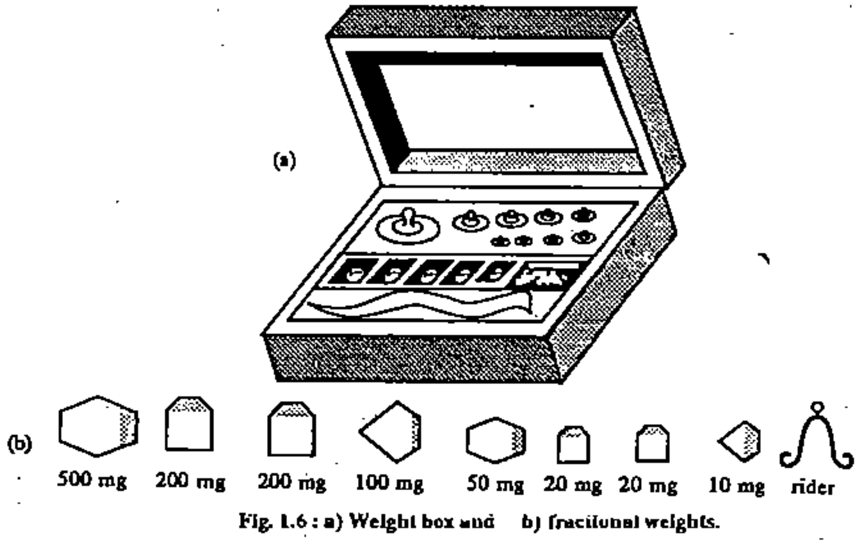


Fig. 1.6 : a) Weight box and b) fractional weights.

Using an Analytical Balance for Weighing

Before using a balance for weighing, we have to examine whether the balance functions properly. For this, first the side doors of the balance are to be closed. The arrest-knob is to be slowly and carefully turned counter-clockwise. When the arrest-knob is turned fully to the left, the pointer starts swinging around the centre of the scale. The first two swings are ignored. Then, starting with the third swing, the extreme positions of the swing are noted for at least two more swings. The readings of the swings to the left and to the right must be equal or can differ by one unit only during each swing. If the readings to the left and right are much different, the balance must be adjusted by means of the screws, for which you may request your counsellor.

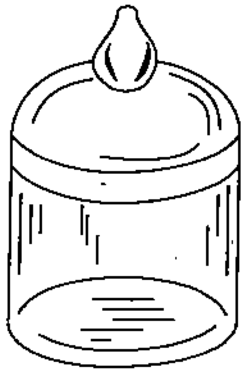


Fig. 1.7 : Weighing bottle.

After adjusting the balance (if necessary), we come to actual weighing. For this purpose, we use a glass or a plastic weighing bottle, Fig. 1.7. First of all, the weighing bottle is weighed on a rough balance to find its approximate mass to the nearest gram. Then the left side door of the analytical balance is opened and the weighing bottle is kept on the left side pan and the door is closed. Through right side door, weights equal to the approximate mass of the weighing bottle are transferred to the right side pan from a weight box with the help of forceps and, the right side door is closed.

Always use forceps to transfer the weights. Refrain from using your hands.

The arrest knob is once again turned to the left and the movement of the pointer is seen. If it moves more to the left, then the weights transferred are in excess of the mass of the bottle. In that case, some weights have to be removed . On the other hand, if the pointer moves more to the right, then the added weights are not sufficient and, we need to add more weights. Arrest the movement of the beam by turning the arrest-knob fully towards the right and, open the right side door to add or remove some weight(s), as the case may be. Recheck the movement of the pointer by using the arrest-knob. Continue this process till the addition of 1 gram weight makes the right hand pan heavier while its removal makes it lighter, e.g., if the weight is say 15.5 g, then 15g weight would be lighter and 16 g weight would be heavier. After this, the fractional weights marked in mg, have to be added in decreasing order till the two sides are balanced. Do not use fractional weights less than 10 mg; you should use a rider in such cases. A rider (Fig. 1.6 (b)) is a thin metallic wire suitably bent to be seated on the beam of the balance. It is normally put on the right hand side of the beam with the help of the rider carrier. By varying the position of the rider on the beam, the two pans are balanced.

A rider is used for mass adjustments below 10 mg (0.01 g).

$$\begin{aligned}\text{Mass of the object} = &(\text{Weights added in grams})\\ &+(\text{fractional weights added} \times 0.001)\text{ g}\\ &+(\text{main division of the rider position} \times 0.001)\text{ g}\\ &+(\text{subdivision of the rider position} \times 0.0002)\text{g}\end{aligned}$$

Let us illustrate the use of this formula. Suppose that while weighing an object, the weights added to the right side pan are 15 g, 200 mg and 2 × 20 mg. Let the rider position be 2 on the main divisions and 3 on the subdivisions.

Then the mass of the object

$$\begin{aligned}&=15\text{ g} + (240 \times 0.001)\text{ g} + (2 \times 0.001)\text{ g} + (3 \times .0002)\text{ g}\\ &=15.2426\text{ g}\end{aligned}$$

You have, so far, seen how to weigh an object, such as a weighing bottle, accurately. If we want to weigh a substance in the weighing bottle, we make use of the method of weighing by difference. For this, the weighing bottle is first approximately weighed. The substance to be weighed is put into the bottle (a little more than required) and weighed accurately (x g). The substance is transferred into a volumetric flask and the bottle is again weighed accuracy (y g). The difference between the two masses, i.e., $(x-y)$ g is the exact mass of the substance transferred (m g).

Mass of the substance (m g)
= (Mass of the bottle with substance (x g))
− (mass of the bottle after transferring the substance (y g))
i.e., $m = (x-y)$ g

You will see the way of entering the data for weighing towards the end of Sec. 1.6.

You are advised to observe following precautions for getting accurate results during weighing :

a) Ensure that your balance is in good condition. In case there is any malfunctioning, it may be reported to the counsellor.

b) Clean the pans. Never release the beam arrest-knob abruptly as this may damage the balance and you may not get reliable results.

c) Arrest the beam before adding or removing either the sample or the weights.

d) Never place the hot objects for weighing on the balance. An object must be cooled to attain the room temperature before weighing.

e) Always shut the doors of the balance before raising the pans using the arrest-knob.

f) Handle the sample with a piece of paper. The weights must be picked with forceps only.

g) Avoid jerks to the balance.

Having learnt in general about some apparatus to be used in the experiments of this lab course, let us now understand the various terms and concepts used in many of the experiments. Before proceeding to the next section, try the following SAQ's.

SAQ 3

What is the precision limit of an analytical balance ?

....

....

....

SAQ 4

What is the mass of a substance if the following weights are needed to weigh it ?

g	mg	position of rider
10		
5	200	6.1
2	100	
1	50	

....

....

....

1.5 EXPRESSION OF CONCENTRATION

The term 'concentration' refers to the relative amounts of a solute and a solvent in a solution. **Solute** is the dissolved substance in a solution. **Solvent** is the substance in which the solute is dissolved. **Solution** is the homogeneous mixture of a solute and a solvent. Before we discuss the different ways of expressing the concentration of a solution, let us explain a few terms used in quantifying a substance.

The number of ^{12}C atoms in 0.012 kg (i.e., 12 g) of ^{12}C is equal to 6.022×10^{23}

Mole, denoted as mol, is the amount of a substance that contains as many elementary entities as in 0.012 kg of ^{12}C isotope of carbon. The mole may be of atoms, ions, molecules, electrons or any other entity. The number of elementary entities in a mole of any substance is fixed and is given by a constant called the Avagadro number, N_A, which equals 6.022×10^{23}.

Relative molecular mass is unitless, since it represents a ratio.

Relative molecular mass (molecular weight) denoted as M_r is the mass of one molecule in atomic mass unit (a.m.u.) relative to 1/12th the mass of pure ^{12}C isotope (12.000 a.m.u.). We find the relative molecular mass by multiplying the atomic mass of each element in the molecule by its subscript in the formula and then adding the total for each element to get the grand total, e.g., one molecule of CO_2 has relative molecular mass of 44, which is calculated as :

$$[(12 \times 1) + (16 \times 2)] = (12 + 32) = 44$$

Although SI unit of molar mass is kg mol^{-1}, it is more convenient to use g mol^{-1} for titrimetric calculations.

Molar Mass, denoted by symbol (M_m), is the mass of one mole of a given substance. It is numerically equal to the relative molecular mass but is expressed in g mol^{-1} units. The following illustration explains this point.

The relative molecular mass of oxalic acid dihydrate [$(COOH)_2 \cdot 2H_2O$] crystals is equal to 126. Hence, the molar mass of oxalic acid dihydrate crystals = 126 g mol^{-1}.

It is better to use the phrase 'amount of a substance' rather than 'number of moles of a substance'.

Amount of a substance is given by the ratio of the mass of the substance to its molar mass.

$$\text{Amount of a substance} = \frac{\text{Mass}}{\text{Molar mass}} \qquad \ldots (1.1)$$

Thus the amount of substance having mass equal to molar mass is called mole. Let us now see various methods of expressing the concentration of a solution.

Molarity

For titrimetric purposes, we express concentration in terms of molarity denoted by symbol M. Molarity is defined as the amount present in one dm^3 of the solution. It can be expressed as follows:

$$\text{Molarity} = \frac{\text{Amount of solute}}{\text{Volume of solution in } dm^3} \qquad \ldots (1.2)$$

Thus, if you dissolve 126 g of oxalic acid dihydrate (molar mass = 126 g mol^{-1}) in water and make up the volume to 1 dm^3, then the solution would be 1 M.

The molarity of a solution containing m g of the solute in V cm^3 of a solution can be calculated as follows :

Let the molar mass of the solute be M_m g mol^{-1}.

Using Eq. 1.1,

$$\text{amount of a solute} = \frac{\text{Mass}}{\text{Molar mass}} = \frac{m\ \text{g}}{M_\text{m}\ \text{g mol}^{-1}}$$

$$= \frac{m}{M_\text{m}}\ \text{mol} \qquad \ldots (1.3)$$

Volume of the solution = $V\ \text{cm}^3$

Since $1000\ \text{cm}^3 = 1\ \text{dm}^3$,

$$\text{Volume of the solution} = V\ \text{cm}^3 \times \frac{1\ \text{dm}^3}{1000\ \text{cm}^3}$$

$$= \frac{V}{1000}\ \text{dm}^3 \qquad \ldots (1.4)$$

Using Eqs. 1.1 to 1.4,

$$\text{molarity of solution} = \frac{\text{Amount of solute}}{\text{Volume of solution in dm}^3}$$

$$= \frac{m}{M_\text{m}}\ \text{mol} \times \frac{1}{\dfrac{V}{1000\ \text{dm}^3}}$$

$$\text{i.e., molarity} = \frac{1000\,m}{M_\text{m}\,V}\ \text{mol dm}^{-3} \qquad \ldots (1.5)$$

By substituting the volume of a solution in cm^3 unit in the above expression, molarity of a solution can be calculated.

Though molarity is accepted nowadays as the way of expressing concentrations, another related term, viz, normality is still in use. Here equivalent mass is used in place of relative molecular mass. **Normality** is defined as the number of gram equivalents of the solute per dm^3 of the solution. In other words,

$$\text{Normality} = \frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution (in dm}^3)} = \frac{\text{Mass}}{\text{Equivalent mass} \times \text{volume of solution (in dm}^3)}$$

We are not discussing the methods of arriving at the equivalent masses of substances, since we are not going to use normality in our calculations.

The molar mass of a substance is an inherent property. It is independent of the nature of the chemical reaction it may be undergoing. Hence, a given solution containing a known amount of the solute will have the same molarity independent of the type of chemical reaction. Normality, on the other hand, can change as the equivalent mass of a substance depends on the chemical reaction involved in the titration. For example, $KMnO_4$ can have equivalent mass of 158.04 g, 52.6 g or 31.6 g depending on the reaction conditions. In the light of the above, it is advisable to use molarity rather than normality. We would be using molarity in all the titrimetric experiments. However, percentage, formality and molality, are some other ways of expressing concentration. These are briefly explained here.

Percentage

The percentage of a solute in a given solution can be expressed in three different ways depending upon the nature of the solute and the solvent. Let us illustrate by taking some examples.

(a) If we take 10 g of, say, NaCl and dissolve it in water to make a solution of volume 100 cm^3, then we get a 10% mass by volume, i.e., 10% m/V solution of NaCl in water.

(b) If instead of preparing 100 cm^3 of solution, we add enough water (to 10 g of NaCl) to prepare 100 g of solution, then we get 10% mass by mass, i.e. 10% m/m solution of NaCl in water.

(c) In cases where the solute is also a liquid, it is possible to represent concentration as volume by volume. For example, if we mix 10 cm^3 of methanol (solute) with enough H_2O (solvent) to prepare 100 cm^3 of the solution, then we get 10% volume by volume, i.e. 10% V/V solution of methanol in water.

We shall use percentage units for denoting the concentration of solutions in Units 5, 12 and 13 of this course.

Formality

For certain ionic compounds, e.g., NaCl, which are completely dissociated in solution, it is less accurate to talk in terms of (molecules or) molar mass. Here, it is more appropriate to talk of formality than of normality or molarity. Formality is defined as the number of gram formula masses dissolved per dm^3 of the solution.

$$\text{Formality of a solution (F)} = \frac{\text{Mass of the substance in gram unit}}{\text{Gram formula mass}} \times \frac{1}{\text{Volume of the solution in } dm^3 \text{ units}} \quad \text{... (1.6)}$$

The gram formula mass of a substance is obtained by multiplying the atomic mass of each element by its subscript in the formula and then adding the total for each element to get the grand total. Thus, one gram formula mass of sodium chloride $= [(1 \times 23) + (1 \times 35.45)]\text{ g} = 58.45\text{ g}$

Molality

The molality of solution is the number of moles of the solute per kilogram of the solvent contained in a solution. It is given by the following expression :

$$\text{Molality} = \frac{m_1 \times 1000}{m_2 \times M_m} \quad \text{. . . (1.7)}$$

where,

m_1 = mass of the solute (in g)
m_2 = mass of the solvent (in g)
M_m = Molar mass of the solute (in g mol^{-1})

The molality scale is useful for experiments in which depression of freezing point, elevation of boiling point, and relative lowering of vapour pressure, are measured. For example, we shall see its use in Unit 8.

SAQ 5

Calculate the molarity of a sodium hydroxide solution, if 500 cm^3 of the solution contains 2 g of solute.

. . . .

. . . .

. . . .

1.6 PREPARATION OF STANDARD SOLUTION

You may recall that a standard solution is one for which the concentration is known accurately. A standard solution may be prepared by dissolving an accurately weighed, pure stable solid (solute) in an appropriate liquid solvent. Preparation of a standard solution is generally the first step in any quantitative experiment; hence it is important to know how to prepare a standard solution.

Primary and Secondary Standards

In titrimetry, certain chemicals are used frequently in known concentrations as reference materials. Such substances are classified as **primary standards** or **secondary standards.** A primary standard is a substance of sufficient purity. A standard solution can be prepared by weighing a quantity of the primary standard directly, followed by dissolution and dilution to give a definite volume of the solution. The following specifications have to be satisfied for a substance to qualify as a primary standard:

1) It must be easily available and easy to preserve.

2) It should not be **hygroscopic** nor should it be otherwise affected by air.

3) It should be readily soluble in the given solvent.

Hygroscopic substances are those which have a tendency to absorb moisture.

Some of the available primary standards for titrations are given below along with their relative molecular mass (M_r) values:

Potassium hydrogen phthalate (KHP), $C_8H_5O_4K$ (an acidic substance)	$M_r = 204.2$
Anhydrous sodium carbonate, Na_2CO_3 (a basic substance)	$M_r = 106$
Potassium dichromate, $K_2Cr_2O_7$ (an oxidising agent)	$M_r = 294.2$
Arsenic (III) oxide, As_2O_3 (a reducing agent)	$M_r = 197.6$
Potassium iodate, KIO_3 (an oxidising agent)	$M_r = 214.0$
Sodium oxalate, $Na_2C_2O_4$ (a reducing agent)	$M_r = 134.0$

Solutions prepared from the primary standards are called primary standard solutions.

Substances which do not satisfy all the above conditions, are known as secondary standards. In such cases, a direct preparation of a standard solution in not possible. Examples are alkalies and various inorganic acids. These substance cannot be obtained in pure form. Therefore, concentration of these substances is to be determined by titrating them against primary standard solutions. This process is called **standardisation** and, the solution so standardised is called a **secondary standard solution.** Now let us discuss the method of preparation of a standard solution.

Alkalies (sodium hydroxide and potassium hydroxide) are hygroscopic. Further, these absorb carbon dioxide from air and, some part of the alkalies get converted into carbonates. Hence, alkalies cannot be used as primary standards.

To prepare a standard solution of volume, V cm^3, of known molarity, M mol dm^{-3}, the mass of the solute required, m g, of molar mass M_m can be calculated by rearranging Eq. 1.5 as follows:

$$\text{Mass of the solute } (m) = \frac{\text{Molarity}\cdot M_m \cdot V\cdot}{1000} g \qquad \ldots (1.8)$$

The solute is weighed in an analytical balance as explained before (Sec. 1.4), transferred into a volumetric flask with the help of a funnel and dissolved in a small quantity of the solvent. The solution is then made up to the mark by carefully adding the solvent. This can be done using a wash bottle or with a pipette. It is then shaken thoroughly to get a homogeneous solution.

In preparing a standard solution of concentration, say, around 0.1 M, the mass of the substance weighed need not be exactly equal to the mass required for 0.1 M. It can be slightly less or more, but the weighing must be accurate. From the mass of the solute actually taken, molarity of the solution can be calculated using Eq. 1.5.

In the example given below, we show how to enter the data for

- weighing potassium hydrogen phthalate (for preparing a standard solution) and,
- calculation of molarity of the solution.

Preparation of 250 cm^3 of a standard solution of potassium hydrogen phthalate

Approximate mass of the weighing bottle = m_1 = ... g
Mass of the weighing bottle + potassium hydrogen phthalate = m_2 = ... g
Mass of the bottle after transferring the salt = m_3 = ... g
Mass of potassium hydrogen phthalate = $m_2 - m_3 = m$ = ... g
Molar mass (M_m) of potassium hydrogen phthalate = 204.2 g mol^{-1}
Volume of potassium hydrogen phthalate solution prepared = 250 cm^3
Molarity of potassium hydrogen phthalate (M_t) is calculated using Eq. 1.5 as,

$$M_t = \frac{m \times 1000}{M_m \times 250} = \frac{m \times 4}{204.2} = \text{.........} \text{ mol dm}^{-3}$$

SAQ 6

You are asked to standardise the solutions of following substances. Suggest a primary standard for each.

(i) hydrochloric acid

(ii) potassium permanganate (an oxidising agent)

....

....

....

1.7 TITRIMETRIC CALCULATIONS

You may be interested to know as to how titrimetric calculation is done. For this purpose, let us consider the general case of a reaction between two substances, A and B, yielding C and D, as per the stoichiometric equation:

$$pA + qB \longrightarrow rC + sD \qquad \ldots (1.9)$$

where p, q, r and s are the stoichiometric coefficients. As per Eq. 1.9, p moles of A are required for q moles of B for complete reaction. At any instant, the amount of A and B reacted are related as follows:

$$\frac{\text{Amount of A reacted}}{\text{Amount of B reacted}} = \frac{p}{q} \qquad \ldots (1.10)$$

Suppose that during titration, V_A cm^3 of A of molarity M_A has reacted with V_B cm^3 of B of molarity M_B.

p and *q* are known, once stoichiometric equation is written.

Amount of A reacted = Molarity of A × volume of A in dm^3
(using Eq.1.2)

$$= M_A \cdot V_A/1000 \qquad \ldots (1.11)$$

[since V_A is given in cm^3 units]

Similarly, amount of B reacted

$$= \text{Molarity of B} \times \text{volume of B in dm}^3$$

$$= M_B \cdot V_B/1000 \qquad \ldots (1.12)$$

Using Eqs. 1.10 to 1.12,

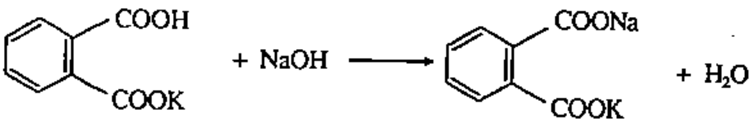
We get, $\dfrac{M_A V_A/1000}{M_B V_B/1000} = \dfrac{p}{q}$

or $$\frac{M_A V_A}{M_B V_B} = \frac{p}{q} \qquad \ldots (1.13)$$

Assume that a standard solution of A (M_A known) is available. The volume of A (V_A) required to react with a known volume of B (V_B) is found out by titration. Since *p* and *q* are known from the stoichiometric equation, the molarity of B (M_B) can be determined using Eq. 1.13. See the following examples.

(i) The reaction between sodium hydroxide and potassium hydrogen phthalate

Sodium hydroxide and potassium hydrogen phthalate (KHP) react according to the equation:



By comparison with Eq. 1.9,
p = Coefficient of KHP = 1
q = Coefficient of NaOH = 1

Let the molarities of potassium hydrogen phthalate and sodium hydroxide solutions be represented as M_1 and M_2. Let the volumes of these two solutions used during neutralisation be V_1 and V_2, respectively.

Using Eq. 1.13,

$$\frac{M_1 V_1}{M_2 V_2} = \frac{1}{1} = 1$$

or $$M_1 V_1 = M_2 V_2 \qquad \ldots (1.14)$$

The tabulation of titration data and calculation method for the standardisation of sodium hydroxide solution using standard potassium hydrogen phthalate are given below:

Indicator : Phenolphthalein

Colour change : Colourless to pink

Potassium hydrogen phthalate vs. sodium hydroxide solution

Sl. No.	(Volume of potassium hydrogen phthalate)/cm^3	Burette Reading		(Volume of NaOH) / cm^3
		Initial	Final	
1	20	...	...	...
2	20	...	...	...
3	20	...	...	...

Determination of molarity of sodium hydroxide solution

Molarity of potassium hydrogen phthalate = M_1 = ... mol dm^{-3}

Volume of potassium hydrogen phthalate solution = $V_1 = 20$ cm^3

Volume of NaOH solution used (from the above table) = V_2 = ... cm^3

Molarity of NaOH solution = M_2 = ?

Using Eq. 1.14,

$M_1 V_1 = M_2 V_2$

Molarity of NaOH solution $= M_2 = \frac{M_1 V_1}{V_2}$

= ..... mol dm^3

Since M_1, V_1 and V_2 are known, M_2 can be calculated.

ii) The reaction between oxalic acid and potassium permanganate in presence of dilute sulphuric acid

The stoichiometric equation for this reaction is given below :

$$5\,H_2C_2O_4 + 2\,KMnO_4 + 3\,H_2SO_4 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 10\,CO_2$$

Here again, p = Coefficient of $H_2C_2O_4$ = 5 and

q = Coefficient of $KMnO_4$ = 2

Using Eq. 1.13, $\frac{M_{H_2C_2O_4} V_{H_2C_2O_4}}{M_{KMnO_4} V_{KMnO_4}} = \frac{5}{2}$

or $$2\,M_{H_2C_2O_4}\,V_{H_2C_2O_4} = 5\,M_{KMnO_4}\,V_{KMnO_4} \quad \ldots (1.15)$$

For this case, we do not intend giving the tabulation of titration data. But we illustrate the use of Eq. 1.15 in the calculation of molarity of oxalic acid. Assume that 25 cm^3 of oxalic acid of unknown concentration requires 20 cm^3 of 0.02 M potassium permanganate for complete reaction.

Using Eq. 1.15, $M_{H_2C_2O_4} = \frac{5}{2}\,\frac{M_{KMnO_4} V_{KMnO_4}}{V_{H_2C_2O_4}}$

$$= \frac{5 \times 0.02\,M \times 20\,\text{cm}^3}{2 \times 25\,\text{cm}^3}$$

$$M_{H_2C_2O_4} = 0.04\ \text{M}$$

Thus the molarity of oxalic acid is 0.04 M.

Based on the study of Secs. 1.3-1.7, we can sum up the steps involved in the titrimetric estimation of a test solution using primary and secondary standards. To illustrate the steps, we consider the estimation of given ferrous sulphate solution. Assume that oxalic acid is used as a primary standard while potassium permanganate solution is used as a secondary standard.

Step	**Illustration**
1. Weigh the necessary amount of the primary standard.	1. Weigh the necessary amount of oxalic acid crystals.
2. Prepare the solution of primary standard from the amount weighed in step (i).	2. Dissolve the oxalic acid crystals in water and make up to known volume to prepare a standard solution.
3. Titrate the secondary standard against the primary standard using proper medium. From the titre value, calculate the concentration of secondary standard (using equation similar to Eq. 1.13).	3. Titrate potassium permanganate solution against standard oxalic acid solution in presence of dilute sulphuric acid. Calculate the concentration of potassium permanganate solution (using Eq. 1.15)
4. Titrate the secondary standard against the test solution using proper medium. Calculate the concentration of test solution (using equation similar to Eq. 1.13).	4. Titrate potassium permanganate solution against ferrous sulphate solution in presence of dilute sulphuric acid. Calculate the concentration of ferrous sulphate solution using the following equation. $\frac{M_{FeSO_4} V_{FeSO_4}}{M_{KMnO_4} V_{KMnO_4}} = \frac{10}{2} = 5$ (Write the balanced equation for $FeSO_4$–$KMnO_4$ reaction and verify this equation).

Based on the study of this section, answer the following SAQ.

SAQ 7

Write an equation similar to Eq. 1.14 for the reaction between sodium carbonate and hydrochloric acid.

....

....

....

1.8 HEATING METHODS

In this lab course, you will use the following heating devices:

i) burner

ii) water bath

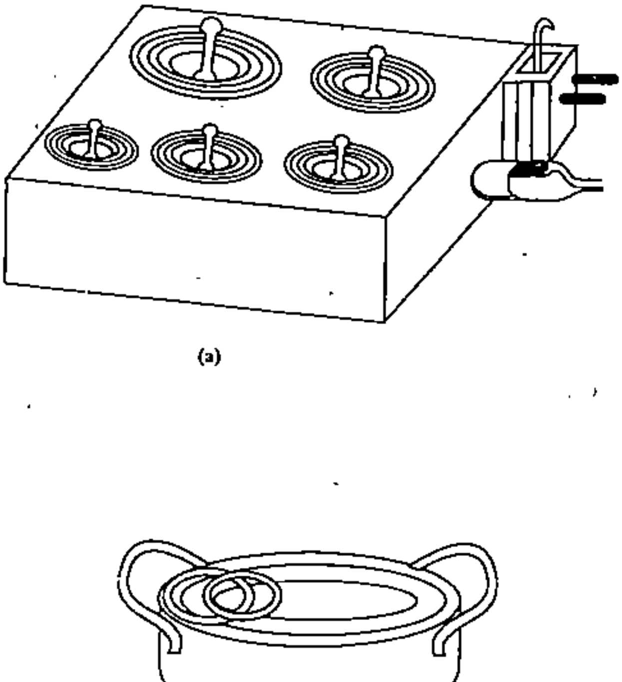
iii) oil bath

Since many of the substances get decomposed at high temperatures or are inflammable, care should be exercised in using the heating devices.

Direct heating on a burner flame should be avoided as far as possible. Heating on a burner should be done using a wire gauze. While using a burner, all inflammable and volatile materials should be removed away from the burner.

A water bath, an oil bath or a sand bath should be used to provide uniform heating. For temperatures upto 100°C, a water bath is generally employed. The simplest form of a water bath consists of a beaker containing water. Water is boiled in a beaker and, the vessel to be heated is kept on the rim of this beaker. If a test tube or a boiling tube is to be heated, it can be kept immersed in it as such or by clamping it using a stand. You may be using an electrically heated water bath or a copper water bath (which can be heated on a burner). These two water baths are shown in Figs. 1.8(a) and (b).

Each of these water baths is covered with rings, which can be adjusted according to the size of the vessel to be heated.



(b)

Fig. 1.8 a) : Electrically heated water bath b) copper water bath.

An oil bath or a sand bath is used when heating is carried out in the range 100–200°C. An oil bath can be made by filling a copper bowl with a liquid like paraffin oil. A sand bath is a shallow iron plate filled with sand. Both these baths are heated by means of a burner.

SAQ 8

It is proposed to study the miscibility of 10 cm^3 mixtures of phenol and water at different volume by volume percentage compositions in the temperature range 35°C and 75°C. Suggest a simple heating arrangement for this experiment.

....

....

....

1.9 USE OF THERMOMETERS

Temperature measures the degree of hotness of a body. Temperature scales such as celsius scale are, in general, empirical and arbitrary. The thermodynamic scale or the kelvin scale, is based on the second law of thermodynamics. It is independent of the properties of any particular substance. It is defined in terms of the efficiency of a thermodynamically reversible heat engine. The temperature in the kelvin scale (T K) and that in the celsius scale (t°C) are related as follows :

In Unit 8 (Block 2) of Physical chemistry course, thermodynamic scale of temperature has been explained.

$$T\,\text{K} = t\,°\text{C} + 273.15$$

The kelvin scale of temperature suffers from lack of convenient instruments for measurement. In this course, we shall use thermometers calibrated in celsius unit. Typical examples are mercury thermometers. We shall be using 0-360°C and 0-110°C thermometers. The former is sensitive to 1°C, whereas the latter is sensitive to 0.1°C. We shall be using thermometers for various purposes. Some of them are given below :

i) For determining the heat capacity and the enthalpy of neutralisation (Unit 7)

ii) For determining the melting point (for estimating the molar mass of a nonvolatile solute using Rast method) (Unit 8)

iii) For obtaining the phase diagram of a given system (Units 12 and 13)

iv) For studying the rate of a reaction (Units 15 and 16)

To illustrate one of the above mentioned uses of thermometers, we shall discuss the method of finding out the melting point of a substance.

Determination of Melting Point

The melting point of a solid is that temperature at which the solid changes into liquid at one atmosphere pressure. A pure solid has a sharp melting point. For a pure solid, the difference between the temperature at which the collapse of the crystal is first observed and the temperature at which the sample becomes completely a liquid, does not exceed by 0.5°-1.0°. But an impure solid melts over a range of temperatures, depending on the amount of the impurity. Let us now discuss the experimental details for determining the melting point of a substance.

The freezing point of a substance is that temperature at which a liquid changes into a solid at one atmosphere pressure. The freezing point of a substance in the liquid state is the same as its melting point in the solid state. This principle is made use of in Unit 8 of this course.

Melting points are usually determined in capillary tubes open to the air. A capillary tube is a thin glass tube about 1-2 mm in diameter. For melting point determination, a capillary tube of about 8-9 cm long is taken and sealed at one end by holding it horizontally into the edge of a small burner flame for a few seconds while rotating it. The molten glass would seal the capillary. Formation of large glass beads should be avoided. Let us now see how the capillary tube is filled.

Melting point can also be determined by keeping the liquid bath in

i) a long-necked flask, known as Kjeldahl flask, or
ii) a 100 cm^3 beaker.

About 25 mg of the dry substance is placed on a clean porcelain plate and finely powdered with a metal or glass spatula forming it into a small heap. The open end of the capillary tube is pushed into the powder, when a small amount of the powder gets into the capillary tube. The solid is shaken down the tube by tapping the closed end of the tube gently on the work-table. The process is repeated until the length of the tightly packed material is about 3-5 mm. The outside of the tube is then wiped clean.

The capillary tube can be heated in a liquid bath or on an electrically heated metal block. You may be using Thiele's melting point apparatus (Fig. 1.9), which is a tube with a closed bent side–arm. On heating the bent side–arm, the heated liquid circulates and rises the temperature of the sample. The tube is filled with the liquid to just above the bent side-arm. No stirring is required. The bath liquid generally used is liquid paraffin, which can be safely heated upto 220°C; above this temperature it starts fuming and gets discoloured. Silicone oils, though more stable, are expensive.

The attachment of the capillary tube to the thermometer through moistening is due to the phenomenon of surface tension. You will study the phenomenon of surface tension in Unit 4 of this course.

If the arrangement used in your laboratory for noting the melting point is different from the one explained here, you can get the details of using the same from your counsellor.

Into the melting point apparatus, the thermometer is fitted through a cork. A section of the cork is cut away, so that the thermometer scale is visible and the heated air could escape. The filled capillary tube is moistened with the bath liquid which helps in attaching the capillary tube to the thermometer. The filled capillary tube is attached to the lower end of the thermometer in such a way that the substance is at the level of the middle of the mercury bulb. The thermometer, with the capillary tube attached, is then inserted into the bath. Care is taken that the open end of the capillary tube is well above the level of the liquid.

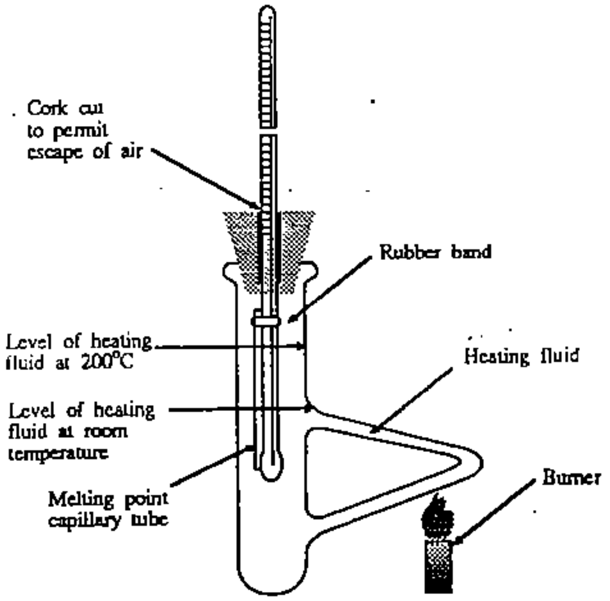


Fig. 1.9 : Thiele's melting point apparatus.

The melting poing apparatus is heated with a small flame comparatively rapidly till the temperature is about 15° below the melting point of the substance. Later it is heated slowly such that the rise of temperature is about 2° per minute. The temperature at which the substance starts to melt and the temperature at which it has completely liquified are noted. These two temperatures give the melting range. As said above, for a pure compound, the melting range should not exceed 0.5° – 1°. In case of an unknown compound, an approximate melting point may be taken first.

The following precautions must be observed while determining the melting point:

1. The capillary used must be of uniform bore.
2. The packing of the substance should be compact and uniform.
3. A sand bath must be placed below the melting point apparatus, in case the bath liquid is concentrated sulphuric acid.
4. A section of the cork must be cut away.
5. The heating of the flask must be slow.
6. The substance should be dry.

In the next section, we shall discuss filtration.

1.10 FILTRATION

Filtration is employed for separating a precipitate from a solution. For this, we make use of a funnel, a circular sheet of filter paper, a stand, a beaker, a glass rod and a wash bottle. A wash bottle is designed to deliver a fine stream of distilled water in a controlled way. A typical wash bottle is shown in Fig. 1.10.

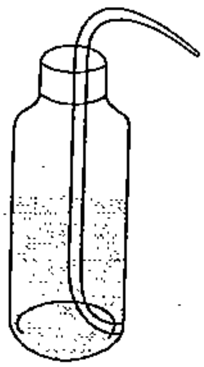


Fig. 1.10 : Wash bottle.

The first step in the filtration of a precipitate is to fold the filter paper properly into halves along any diameter as shown in Fig. 1.11(a). The side holding three quarters is opened to obtain a cone of the filter paper (Fig 1.11(b).

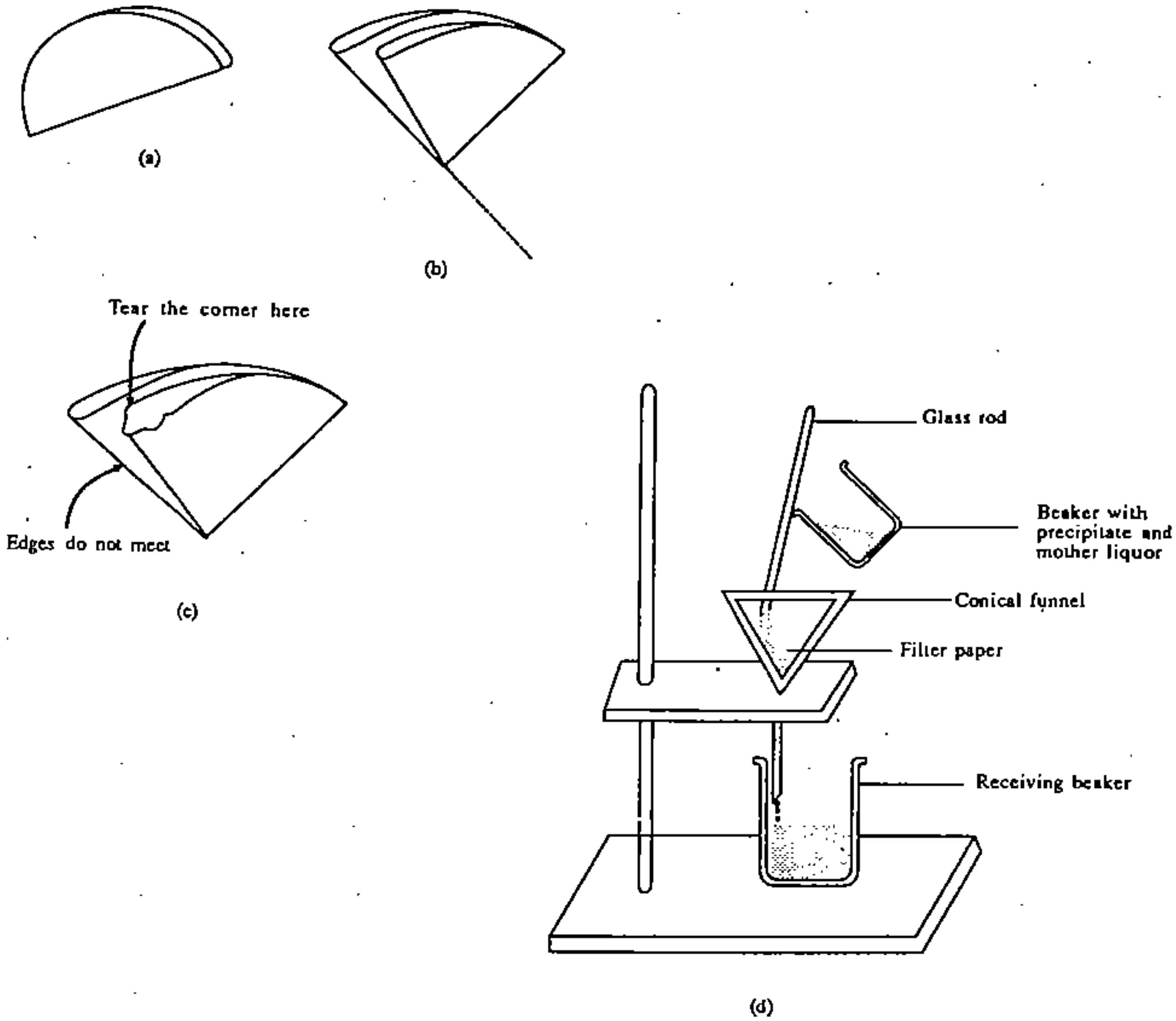


Fig. 1.11 : a) and b) Folding the filter paper c) tearing the corner d) filtration set-up

In order to get efficient filtration, tear off the upper tip of the filter paper cone (Fig.1.11(c)) so that the cone fits into the funnel. Also a long stem funnel should be used. The filter paper cone is fixed in the mouth of the funnel using a little water. Now the funnel is placed on a stand with its stem touching the side of the receiving vessel kept for collecting the filtrate. The mixture to be filtered is poured into the filter paper gently along a glass rod, the lower tip of which rests on three quarters of the filter paper cone (Fig.1.11(d)). The solid particles in the mixture will be collected on the filter paper, while the filtrate will be collected in the receiving vessel. At the beginning of filtration, the solid particles should be allowed to settle down and the liquid should be decanted into the funnel, leaving most of the precipitate in the vessel. The precipitate should be washed with the wash-liquid, the solid again allowed to settle down and the liquid transferred to the funnel. This process is repeated to free the precipitate of other ions. Finally the precipitate is completely transferred to the funnel using more of wash-liquid. Usually wash-liquid is water or a liquid in which the precipitate is insoluble. Wherever quantitative estimation is done, proper filter paper is to be used as per the advice of the counsellor.

1.11 SUMMARY

In this unit, we discussed the safety measures to be adopted while working in a chemistry laboratory. We explained some of the techniques which are useful in performing the experiments of this course. We also discussed the relevant calculations and the apparatus for these experiments.

1.12 ANSWERS

Self Assessment Questions

1) Titrimetric analysis consists in determining the volume of a standard solution which is required to react completely with a known volume of the solution of a substance being estimated.

2) i) Titration using phenolphthalein as an indicator

   ii) Titration using conductometer or mV/pH meter.

3) An analytical balance can be used for weighing masses to a precision limit of 0.2 mg.

4) 18.3562 g

5) As per Eq. 1.5, molarity

$$= \frac{1000\,m}{M_m V}$$

$$= \frac{1000 \times 2}{40 \times 500}\ \text{M}$$

$$= 0.1\ \text{M}$$

6) i) Sodium carbonate

   ii) sodium oxalate

7)

$$\underset{\text{(from Na}_2\text{CO}_3)}{CO_3^{2-}} + \underset{\text{(from HCl)}}{2H^+} \longrightarrow H_2CO_3$$

Let M_1 and M_2 stand for the molarities of sodium carbonate and hydrochloric acid, respectively while V_1 and V_2 refer to the equivalent volumes of sodium carbonate and hydrochloric acid, respectively. In comparison to Eq. 1.13.

$$\frac{M_1 V_1}{M_2 V_2} = \frac{1}{2}$$

or $$2 M_1 V_1 = M_2 V_2$$

8) Mixtures of different compositions of phenol and water are to be taken in different test tubes and heated in water bath to study the miscibility temperature in each case.

UNIT 2 HANDLING OF DATA

Structure

2.1 Introduction

2.2 SI Units
   - Basic Units
   - Derived Units
   - SI Prefixes
   - Grammatical Rules for Representing SI Units

2.3 Some Useful Mathematical Operations
   - Scientific Notation
   - Using the Table of Logarithms
   - Finding the Numbers from their Logarithms

2.4 Significant Figures
   - Calculation of Significant Figures in a Number
   - Addition and Subtraction Maintaining Significant Figures
   - Multiplication and Division Maintaining Significant Figures
   - Taking Logarithms and Antilogarithms Maintaining Significant Figures

2.5 Laboratory Note Book

2.6 Tabulation of Data and Plotting of Graphs

2.7 Summary

2.8 Answers

2.1 INTRODUCTION

In Unit 1, we studied some of the laboratory techniques which are to be used in this course. As part of this, we discussed the methods of expression of concentration and, titrimetric calculation. These two are, in fact, part of data handling techniques. Handling of data consists of processing the experimental data and expressing the values of the physical parameters with proper magnitude and units. Processing of data includes stepwise calculation to obtain the value of a parameter and representation of results using tables or graphs.

In this unit, we shall discuss the basic and derived SI units. We shall explain the principles to be followed in expressing a number in scientific notation. We shall define the term, significant figure. We shall explain how to maintain significant figures while doing calculations of various types such as addition, subtraction, multiplication, division, taking logarithms and antilogarithms etc. We shall finally discuss how to record the observations, tabulate the data and plot the graphs.

Objectives

After studying this unit, you should be able to

- state the SI units of basic and derived physical quantities,
- arrive at the SI units of a physical quantity,

- write numbers using scientific notation,
- calculate the significant figures in a number,
- carry out calculations maintaining significant figures,
- state the important features concerning the maintenance of laboratory note book, and
- explain the methods of tabulation of data and plotting of graphs.

2.2 SI UNITS

Till recently in the scientific world, mainly two systems of units had been in common use. One is c.g.s. (centimetre, gram, second) which was more commonly used over the European continent and the other is f.p.s. (foot, pound and second) prevalent in England. A common system of units helps in exchanging the scientific facts and ideas originating from different countries. It is better still if the system of units could be derived from the scientific formulae or fundamental constants. This long felt need for a common system of scientific units was realised at a meeting called General Conference on Weights and Measures in 1960. At this meeting, the international scientific community agreed to adopt common units of measurements known as International System of Units. This is abbreviated as SI units from the French name, *Systeme Internationale*. In this section, we shall first state the SI units for a few basic and derived quantities. Then we shall explain the prefixes used to change the order of magnitude of the SI units. Also we shall state the rules for representing the SI units.

2.2.1 Basic Units

There are seven basic physical quantities, from which all other physical quantities can be derived. The units of these basic physical quantities are called **basic units**. The names of these quantities along with their symbols, SI units and the symbols of SI units are given in Table 2.1. Each of these seven quantities is regarded as having its own dimension. The symbol of a quantity represents its dimension as given in column (ii) of Table 2.1. The dimensions of basic quantities are useful in defining the derived physical quantities, which we shall study in subsection 2.2.2. We will be using the symbols given in column (ii) of Table 2.1 to refer to the dimensions of the basic quantities.

Table 2.1 : Basic Physical Quantities and Their SI Units

Physical Quantity (i)	Symbol of Quantity (ii)	Name of the SI Unit (iii)	Symbol of the SI Unit (iv)
Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Electric current	I	ampere	A
Temperature	T	kelvin	K
Luminous intensity	I_r	candela	cd
Amount of substance	n	mole	mol

Note that *m* (italicised) is the symbol for mass of an object, while m (roman) is the symbol of SI unit, metre.

We are not going to define kilogram, metre etc. since our aim is to use these units and not to establish the basis of these units.

2.2.2 Derived Units

All other physical quantities are regarded as being derived from the above seven basic quantities by definitions involving multiplication, division, differentiation and integration. Such quantities and their units are called **derived physical quantities and derived units**, respectively. In Tables 2.2 and 2.3, the derived SI units without and with special names are given.

For convenience, we shall use molarity (mol dm^{-3}) units for referring to the concentration of solutions

1 M = 1 mol dm^{-3} = 1000 mol m^{-3}

Table 2.2 : Derived SI Units Without Special Names

Physical Quantity (i)	Definition (ii)	Dimensional formula (iii)	Name of the SI Unit (iv)	Symbol of the SI Unit (v)
Area	Length × length	l^2	square metre	m^2
Volume	Length × length × length	l^3	cubic metre	m^3
Density	Mass/volume	ml^{-3}	kilogram per cubic metre	kg m^{-3}
Velocity	Displacement/Time	lt^{-1}	metre per second	m s^{-1}
Acceleration	$\frac{\text{(Change in velocity)}}{\text{Time}}$	lt^{-2}	metre per second squared	m s^{-2}
Molar mass	$\frac{\text{Mass}}{\text{(Amount of the Substance)}}$	mn^{-1}	kilogram per mole	kg mol^{-1}
Concentration	Amount/Volume	nl^{-3}	mole per cubic metre	mol m^{-3}

The definitions given for area and volume are of general type, although specific formulae are to be used depending on the shape or surface of an object.

Table 2.3 : Derived SI Units Having Special Names

Physical Quantity (i)	Definition (ii)	Dimensional formula (iii)	Name of the SI Unit (iv)	Symbol of the SI Unit (v)
Force	Mass × acceleration	mlt^{-2}	newton	N or kg m s^{-2}
Pressure	Force/Area	mlt^{-2}/l^2 $=ml^{-1}t^{-2}$	pascal	Pa or kg m s^{-2}/m^{-2} or kg m^{-1} s^{-2}
Energy or work	Force × distance	$mlt^{-2}l$ $=ml^2t^{-2}$	joule	J or N m or Pa m^3 or kg m^2 s^{-2}
Electic charge	$\begin{pmatrix}\text{Electric}\\ \text{current}\end{pmatrix}$ × time	It	coulomb	C or A s
Electric potential difference	$\frac{\text{Electrical energy}}{\text{Electric charge}}$	$\frac{ml^2t^{-2}}{It}$ $=ml^2I^{-1}t^{-3}$	volt	V or J C^{-1} or kg m^2 A^{-1} s^{-3}
Electric resistance	$\frac{\text{(Electric Potential difference)}}{\text{(Electric Current)}}$	$\frac{ml^2I^{-1}t^{-3}}{I}$ $=ml^2I^{-2}t^{-3}$	ohm	Ω or V A^{-1} or kg m^2 A^{-2} s^{-3}
Electric conductance	1/(Electric resistance)	$1/ml^2I^{-2}t^{-3}$ $=I^2t^3m^{-1}l^{-2}$	siemens	S or A V^{-1} or A^2 s^3 kg^{-1} m^{-2}
Frequency	$\frac{\text{(Number of waves or cycles)}}{\text{Time}}$	$\frac{1}{t}$	hertz	Hz or s^{-1}

From Tables 2.1, 2.2 and 2.3, you can find a direct correspondence between the dimensions of a physical quantity and the symbols of its SI units. For example, see how from the dimensions of acceleration, its SI units have been worked out below:

Dimensions of acceleration $= lt^{-2}$ [column (iii) of Table 2.2]
Units of acceleration $=$ m s^{-2} [columns (ii) and (iv) of Table 2.1] (in terms of symbols)

Next we shall discuss how the dimensions and the units of a physical quantity can be obtained.

Deduction of the SI Units of a Physical Quantity

We can derive the dimensions and the units of a physical quantity, provided a mathematical relationship is available between this physical quantity and other physical quantities of known dimensions. Let us illustrate this by means of the following examples:

Example 1

Suppose we want to find the dimensions and the units of the gas constant, R. The mathematical relationship to be used for this is the ideal gas equation, Eq. 2.1.

$$\left.\begin{array}{r}\text{Pressure} \times \text{volume} = \text{Amount of the substance} \times \\ \text{gas constant} \times \text{temperature}\end{array}\right\} \quad \ldots (2.1)$$

Rearranging this,

$$R = \frac{\text{Pressure} \times \text{volume}}{\text{Amount of the substance} \times \text{temperature}} \quad \ldots (2.2)$$

The dimensions of the quantities in the right hand side of Eq. 2.2 are mentioned in Tables 2.1–2.3. We used the dimensions of these quantities to derive the dimensions and the units of R as shown below :

$$\text{Dimensions of } R = \text{Dimensions of } \left[\frac{\text{Pressure} \times \text{volume}}{\text{Amount of the substance} \times \text{temperature}}\right]$$

$$= \frac{ml^{-1}t^{-2}l^3}{nT} = (ml^2t^{-2})(n^{-1})(T^{-1})$$

Hence, the units of R = joule mole^{-1} kelvin^{-1}.

Generally we represent the SI units of a physical quantity in terms of symbols in this course.

(Using the units corresponding to the dimensions mentioned in Tables 2.1-2.3)

Thus, R has the dimensions of (energy) (amount of the substance)$^{-1}$ (temperature)$^{-1}$ and the units, J mol^{-1} K^{-1}.

Example 2

We can derive the SI units of surface tension using the following relationship :

Surface tension = Force per unit length (acting perpendicular to a liquid surface)

$$= \frac{\text{Force}}{\text{Length}} \quad \text{(relationship is written to arrive at the dimensions)}$$

In a detailed way, you shall study surface tension and viscosity in Units 4 and 5 of this course.

Dimensions of surface tension $= mlt^{-2}/l$ or mt^{-2}

Units of surface tension $= \mathrm{N\,m^{-1}}$ or $\mathrm{kg\,s^{-2}}$
(in terms of corresponding units)

Example 3

Let us now derive the SI units of coefficient of viscosity. The coefficient of viscosity is defind as the (tangential) force (F) per unit area (A) offered by a liquid layer to create a unit velocity gradient (v/l). Velocity gradient means drop in velocity (v) per unit length. Unit velocity gradient means a drop in velocity of 1 m $\mathrm{s^{-1}}$ per every 1 m length.

Hence, coefficient of viscosity $=(F/A)\big/(v/l)$

Dimensions of coefficient of viscosity $=(mlt^{-2}/l^2)\big/(l/t/l)$

$= (ml^{-1}t^{-2})\,(t)$

Units of coefficient of viscosity = Pa s (using corresponding units)

In general; the following hints would be useful in the deduction of the unit of a quantity (which we name as test quantity):

i) Write an equation relating the test quantity to other quantities of known dimensions.

ii) Rearrange this equation such that only the test quantity is on the left hand side and others are on the right hand side.

iii) Substitute the dimensions of the quantities on the right hand side and simplify.

iv) Write down the units corresponding to the simplified dimensions, using Tables 2.1–2.3.

Use the above hints and work out the following SAQs.

SAQ 1

Derive the units of the second order rate constant (k) using the following equation :
Reaction rate $= k$ [reactant]^2
where reaction rate denotes the concentration of the reactant used up per unit time and [reactant] is the concentration of the reactant. Note that the concentration is to be expressed in molarity.

....

....

....

....

SAQ 2

From the equation.

kinetic energy $=1/2 \times$ mass $\times$ (velocity)^2, derive the units of kinetic energy.

....

....

....

....

2.2.3 SI Prefixes

We now discuss how to overcome the difficulty of expressing the units of physical quantities, which are either very large or very small, as compared to the SI units. We add a prefix to the SI unit such that the magnitude of the physical quantity of a substance can be expressed as a convenient number.

For example, the bond distance in hydrogen molecule is 7.4×10^{-11} m. We express it conveniently as 74 pm where pico is the SI prefix and p is its symbol. The list of SI prefixes it given in Table 2.4 and it is possible to change the order of magnitude of any unit using this table.

Prefixing of SI units helps in expressing a physical quantity, large or small, as a convenient number.

Example : $7{\cdot}4 \times 10^{-11}$m
$= 74 \times 10^{-12}$ m
$=74$ pm

Table 2.4 : SI Prefixes

Submultiple	Prefix	Symbol	Multiple	Prefix	Symbol
10^{-1}	deci	d	10	deca	da
10^{-2}	centi	c	10^2	hecto	h
10^{-3}	milli	m	10^3	kilo	k
10^{-6}	micro	μ	10^6	mega	M
10^{-9}	nano	n	10^9	giga	G
10^{-12}	pico	p	10^{12}	tera	T
10^{-15}	femto	f	10^{15}	peta	P
10^{18}	atto	a	10^{18}	exa	E

More examples for usage of prefixes are given below :

$$10^3\ \text{m} = 1\ \text{km};\ 10^{-9}\ \text{s} = 1\ \text{ns}$$

The unit for mass is kg which is already prefixed. We do not add a second prefix but rather use a single prefix on the unit gram. Thus, to represent 10^{-9} gram, the unit used is ng and not pkg. For 10^{-3} gram, mg is used not μkg.

SAQ 3

Write down the following with proper SI unit symbols and prefixes :

(a) 10^{-9} metre (b) 10^{-12} second (c) 10^3 pascal

....

....

....

....

SAQ 4

Write down 0.015×10^{-3} S using proper SI prefix.

2.2.4 Grammatical Rules for Representing SI Units

The following rules would be of immense help to you while using SI units :

i) The symbol of a unit is never to be used in plural form. Writing 10 kilograms as 10 kg is correct but not as 10 kgs.

ii) In normal usage, full stop is used to indicate the end of a sentence or the presence of an abbreviation. To denote the symbol of SI unit as an abbreviation by using a full stop is incorrect; but, if the SI unit is at the end of a sentence, then the full stop can be used.

Three no's in SI units:
No plurals:
No full stops (except at the end of a sentence):
No dashes.

iii) When there is a combination of units, there should be a space between the symbols. If the units are written without leaving any space, the first letter is taken as a prefix. Thus, m s represents metre second whereas ms stands for millisecond.

iv) Always leave a space between the magnitude and the unit symbol of a physical quantity. For example, writing 0.51 kg is correct but not 0.51kg.

v) Symbol of the unit derived from a proper name is represented using capital letters but not the name of the unit (Table 2.3). For example, writing 100 newton or 100 N is correct but not 100 Newton or 100 n.

vi) For numbers less than unity, zero must be inserted to the left of the decimal point. Thus, writing 0.23 kg is correct but not .23 kg.

vii) For larger numbers exceeding five figures, one space after every three digits (counting from the right end) must be left blank. Commas should not be used to space digits in numbers. For example 15 743 231 N is correct but not 15, 743, 231 N. It is preferable to use proper SI prefixes.

In cm unit, c (centi, 10^{-2}) is the prefix of the unit, m (metre).

viii) The degree sign is to be omitted before K while representing temperature. For example, 298 K is correct but not 298° K.

ix) You should not mix words and symbols for representing SI units. For example, it is proper to write N m^{-2} or newton per square metre and not N per square metre.

x) Exponents (or powers) operate on prefixes also. Let us derive the relationship between cm^3 and m^3 using the relation, 1 cm$=10^{-2}$ m.

$$1\ \text{cm}^3 = (1\ \text{cm})^3 = (10^{-2}\ \text{m}) \times (10^{-2}\ \text{m}) \times (10^{-2}\ \text{m}) = 10^{-6}\ \text{m}^3$$

Thus, 1 cm^3 is eqal to $10^{-6}\ \text{m}^3$ but not to $10^{-2}\ \text{m}^3$ or $10^{-3}\ \text{m}^3$

xi) To show that a particular unit symbol has a negative exponent, one may be tempted to use the sign "/ ", known as solidus. It is better to avoid the usage of this sign and if used, no more than one should be employed. For example, representing pascal (kg $\text{m}^{-1}\ \text{s}^{-2}$)as kg/m s^2 is allowed but not as kg/m/s^2.

xii) The physical quantity 'amount' should not be called ' number of moles' just as the physical quantity 'mass' , is not called number of kilograms.

So far, we studied some rules for writing SI units. Let us now discuss the dimensions of some mathematical functions which are useful in studying this course.

While representing the relationship among the physical quantities of substances, we often come across the mathematical functions like sin x, and ln x. It is to be kept in mind that trigonometric functions (sin x, cos x etc.) exponential functions functions (e^x or e^{-x}) and logarithmic functions (ln x or log x) are dimensionless quantities and hence, have no units.

You can understand the validity of this statement, once you recapitulate the definitions of these functions. We shall illustrate this for the functions, sin x and e^x.

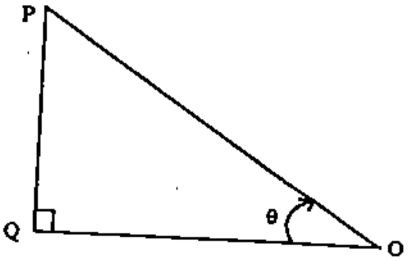


Fig. 2.1 : Right angled triangle

From the right-angled triangle PQO (Fig. 2.1),

$$\sin\theta = \frac{\text{Length of PQ}}{\text{Length of OP}}$$

Evidenly sin θ is dimensionless and has no unit. The same is true of other trigonometric functions also.

As an illustration for the exponential series, let us consider e^x

$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \cdots$$

Since addition or subtraction must be done between quantities of same dimensions, $1, x, x^2, x^3$ .... etc. in the above series must all be of the same dimensions. This indicates that x and e^x are dimensionless and unitless. Again this is true of e^{-x} and ln x or log x also.

We have to be careful in using dimensionless quantities such as logarithmic quantities in calculations. For example, while using logarithmic quantities in calculations, it is necessary to divide the physical quantities by the respective units. See the following examples:

i) log $[\text{H}^+]$/M : $[\text{H}^+]$ has molarity unit and it is divided by M to render it dimensionless; this is used in SAQ 12 of this unit in subsec 2.4.4.

ii) log $(V_\infty - V_t)$/cm^3 : V_∞ and V_t are volumes of nitrogen gas at infinite time and at time t; in order to render $(V_\infty - V_t)$ dimensionless, it is divided by cm^3 unit. See Example 14 in Sec. 2.6 of this unit.

$$e^x = 1 + \frac{1}{1!} + \frac{1}{2!} + \frac{1}{3!} + \frac{1}{4!} + \cdots = 2.718$$

1! is to be read as ' factorial' 1;

2! is to be read as 'factorial' 2;

3! is to be read as 'factorial 3; etc.

Also 1! = 1; 2! = 1 × 2;

3! = 1 × 2 × 3;

4! = 1 × 2 × 3 × 4; etc.

Further, '.....' refers to the other members of the exponential series.

SAQ 5

State the SI units of R using a solidus.

. . . .

. . . .

. . . .

2.3 SOME USEFUL MATHEMATICAL OPERATIONS

It is useful to recapitulate some mathematical operations involving the exponents (or powers) as given in Table 2.5.

Table 2.5 : Operations Involving the Exponents

Operations	Formula		Example
Multiplication	$N^x N^y = N^{x+Y}$		$10^5 \times 10^3 = 10^8$
Division	$N^x/N^y = N^{x-y}$		$10^5/10^3 = 10^2$
Raising to a power	$(N^x)^y = N^{xy}$		$(10^5)^3 = 10^{15}$
Taking a power root	$\sqrt[y]{N^x} = N^{x/y}$	(i)	$2\sqrt{10^8} = 10^{8/2} = 10^4$
		(ii)	$3\sqrt{10^{12}} = 10^{12/3} = 10^4$

Having seen the exponential operations, let us see how to express the numbers in scientific notation.

2.3.1 Scientific Notation

Usually during multiplication and division, we come across numbers greater than 10 or less than 1. It is convenient to express such numbers in scientific notation. You may have studied this in your earlier classes. For transforming a number into scientific notation, use the following steps:

i) Write the number with the decimal after the first nonzero digit. This is called the coefficient term.

ii) Multiply the number written in (i) by 10 raised to an integral exponent; this exponent is equal to the number of spaces the decimal has to be moved to bring it after the first nonzero digit. The exponent is positive if the decimal is moved to the left (the number is 10 or greater); the exponent is negative if the decimal is moved to the right (the number is less than 1).

'Exponent' means 'power' of a number.

In case of integers (such as 307 or 2325 given in Table 2.6), the decimal is assumed to be present after the last digit. Thus in 307, the decimal is assumed to be present after 7; to convert it into scientific notation, the decimal is taken two places to the left, i.e., before 7 and 0. Hence, the exponent is +2 (or simply 2).

$307 = 3.07 \times 10^2$

Similarly $2325 = 2.325 \times 10^3$

[The decimal assumed to be present after 5 is taken three places to the left before 5, 2 and 3.]

The examples given in Table 2.6 should help you in understanding the above steps.

Table 2.6 : Scientific Notation for Numbers

Number	First nonzero digit	Decimal movement	Scientific notation	Coefficient term	Exponent
307	3	2 places to the left	3.07×10^2	3.07	2
2325	2	3 places to the left	2.325×10^3	2.325	3
0.00607	6	3 places to the right	6.07×10^{-3}	6.07	–3

Cont...

0.04325	4	2 places to the right	4.325×10^{-2}	4.325	–2
30700	3	4 places to the left	3.07×10^{4}	3.07	4
232500	2	5 places to the left	2.325×10^{5}	2.325	5

The numbers between 1 and 10 do not require the scientific notation. Thus the number, 3.2, can be written as such; its scientific notation is 3.2×10^0 and, $10^0 = 1$.

Remember that 'ln' means natural logarithm and it is to the base *e*; and, 'log' means common logarithm and it is to the base 10. These two logarithmic functions are related as follows:

$\ln x = 2.303 \log x$

In this course, we make use of logarithm to the base 10 only for calculations.

2.3.2 Using the Table of Logarithms

Often you have to use the table of logarithms during calculations. You may be knowing

- how to obtain the logarithm of a number and also
- how to obtain the number from its logarithm through the usage of antilogarithms. It is useful to recall the rules stated in Table 2.7 while using a logarithmic table.

Table 2.7: Rules Useful in Evaluating Logarithmic Expressions

	Rule		Example
(i)	$\log m^a = a \log m$	(i)	$\log 10^3 = 3 \log 10$ $= 3 \times 1 = 3$
		(ii)	$\log 10^{-3} = -3 \log 10$ $= -3 \times 1 = -3$
(ii)	$\log mn = \log m + \log n$	(i)	$\log 567.0$ $\log 5.670 \times 10^2$ $= \log 5.670 + \log 10^2$ $= \log 5.670 + 2 \log 10$ $= 0.7536 + 2 = 2.7536$
		(ii)	$\log 0.002291$ $= \log 2.291 \times 10^{-3}$ $= \log 2.291 + \log 10^{-3}$ $= 0.3600 - 3 \log 10$ $= 0.3600 - 3$ or $\bar{3}.3600 = -2.6400$
(iii)	$\log m/n = \log m - \log n$		$\log (5.612/1.608)$ $= \log 5.612 - \log 1.608$ $= 0.7492 - 0.2062 = 0.5430$
(iv)	$\log m/n = -\log n/m$ $= -(\log n - \log m)$		$\log (1.608/5.612)$ $= -[\log 5.612/1.608]$ $= -0.5430$ (or $\bar{1}.4570$)
(v)	$N = e^Y$ $\log_e N = \ln N = \ln e^Y$ $= y \ \ln e = y$		$7.389 = e^2$ $\ln 7.389 = \ln e^2$ $= 2 \ln e$ $= 2 \times 1$ $= 2^*$

$\log_{10} 10 = \log 10 = 1$, since $10^1 = 10$

$\log_{10} 1 = \log 1 = 0$, since $10^0 = 1$

Logarithm of a number greater than 1 is positive.

Logarithm of a positive fraction is negative.

When you want to see logarithm of a quantity such as *m/n* where *m* (the numerator) is greater than *n* (the denominator), use rule (iii). On the other hand, if *m* is less than *n*, then use rule (iv). Try to understand the examples given for rules (iii) and (iv) in Table 2.7.

Rule (v) involving logarithm to the base *e* is given only for showing the similarity with logarithm to the base 10

$\log_e e = \ln e = 1$

$\log_e 1 = \ln 1 = 0$

---

*The answer '2' has to be written as 2.000 for keeping the significant figures. We shall discuss this in Sec. 2.4 of this unit.

In case you have any problem in understanding the examples worked out in Table 2.7 or in finding the logarithm of a number, use the following steps, which are illustrated in Table 2.8.

i) Write the scientific notation of the given number.

ii) The mantissa is equal to the logarithm of the coefficient term; you can see logarithms from the tables given towards the end of this block.

iii) The characteristic is equal to the exponent (or power of 10) in the scientific notation.

iv) Add the characteristic and mantissa as per rule (ii) explained in Table 2.7; the sum is the logarithm of the given number.

For the number, 607.0, the logarithm is 2.7832. Here '2' is the characteristic and "0.7832" is the mantissa. For explanation, see Table 2.8.

While expressing the logarithm of a number less than one, the characteristic (and the logarithmic value) can be expressed either with

(i) a negative sign or

(ii) with a bar sign (i.e. "—" sign over the number representing the characteristic).

If you are not aware of using the table of logarithms and antilogarithms, consult your c o

The former is useful in representing the logarithm of a number such as in pH calculations in Experiment 8 of Block 3 of this course. The latter is useful while carrying out multiplication or division.

A few examples are discussed in Table 2.8.

Table 2.8 : Finding the Logarithm of Given Number

Number	**Scientific notation**	**Coefficient**	**Mantissa = log (coefficient)**	**Exponent**	**Characteristic =Exponent**	**Logarithm of the number =characteristic +mantissa**
8.000	8.000×10^0	8.000	log 8.000 =0.9031	0	0	0+0.9031 =0.9031
80.00	8.000×10^1	8.000	log 8.000 =0.9031	1	1	1 +0.9031 =1.9031
607.0	6.070×10^2	6.070	log 6.070 =0.7832	2	2	2 +0.7832 =2.7832
2325	2.325×10^3	2.325	log 2.325 = 0.3664	3	3	0.3664 + 3 = 3.3664
0.8000	8.000×10^{-1}	8.000	log 8.000 = 0.9031	–1 or $\bar{1}$	–1	–1 + 0.9031 = –0.0969 (or $\bar{1}$.9031)
0.006070	6.070×10^{-3}	6.070	log 6.070 = 0.7832	– 3 or $\bar{3}$	–3	0.7832 – 3 = –2.2168 (or $\bar{3}$.7832)

$\bar{1}$ is to be read as "one bar"

From Table 2.8, you can see that the logarithm of a number greater than 1 is positive; the logarithm of a number less than 1 (but greater than 0) is negative. It is so since log 1 is zero. It is meaningless to look for the logarithm of a negative quantity.

2.3.3 Finding the Number from their Logarithms

Eq. 2.3 is useful in finding out 10^x whether x is positive or negative.

To find a number from its logarithmic value, we have to find out the antilogarithm. We shall use the following relationships while looking for antilogarithms.

$$\log N = x$$
$$N = 10^{x} = \text{antilog}\, x \qquad \ldots (2.3)$$

Let us see some examples,

i) When x is positive

When the exponent x is positive, use the following steps for finding N as per Eq. 2.3.

i) The digit(s) before the decimal in the given logarithmic value should be identified as the characteristic and must be converted into the exponent term.

$$\text{Exponent term} = 10^{(\text{characteristic})} \qquad \ldots (2.4)$$

ii) The digit(s) after the decimal in the logarithmic value should be taken as the mantissa and must be converted into the coefficient term by looking for the antilogarithms given towards the end of this block.

$$\text{Coefficient term} = \text{antilog (mantissa)} \qquad \ldots (2.5)$$

iii) The answer is obtained by multiplying the coefficient term and the exponent term.

$$\text{Answer} = \text{Coefficient term} \times \text{exponent term} \qquad \ldots (2.6)$$

Example 4

Finding N if $\log N = 1.5100$

In this case, characteristic $= 1$ and,
mantissa $= 0.5100$

Using Eq. 2.4, the exponent term $= 10^{(\text{characteristic})} = 10^{1}$

Using Eq. 2.5, the coefficient term $=$ antilog (mantissa)

$=$ antilog 0.5100

$= 3.236$

Using Eq. 2.6, $N = 3.236 \times 10^{1}$ or 32.26

Example 5

Finding N if $\log N = 2.3510$

Here, characteristic $= 2$ and
mantissa $= 0.3510$

Using Eq. 2.4, the exponent term $= 10^{2}$

Using Eq. 2.5, the coefficient term $=$ antilog 0.3510
$= 2.244$

Hence $N = 2.244 \times 10^{2} = 224.4$

Example 6

Finding N, if $\log N = 0.3510$

This is similar to previous example except that '0' is the characteristic.

Hence N $=2.244 \times 10^0$

$=2.244$ [since $10^0 = 1$]

ii) When x is negative

When x is negative, use the following steps for finding N, as per Eq. 2.3.

Note that characteristic may be either positive or negative; the mantissa is always positive.

i) The negative number is shown as the sum of a negative integer and a positive fraction.

ii) The negative integer is considered to be the characteristic (or a number having a bar above) and is to be converted into the exponent term using Eq. 2.4. **Note that you get a negative exponent for 10 in this case.**

iii) The positive fraction is equal to the mantissa and is to be converted into the coefficient term by looking for the antilogarithms. For this, you use Eq. 2.5.

iv) The anwer is obtained by multiplying the coefficient term and the exponent term as given in Eq. 2.6.

Use the following examples to understand these steps :

Example 7

Finding N, if $\log N = -4.5000$

We have to find antilog (-4.5000)

Step (i) : $\log N = -5 + 0.5000$ (or $\bar{5}.5000$)

Step (ii) : characteristic $= -5$

Using Eq. 2.4, exponent term $= 10^{-5}$

Step (iii) : Mantissa $= 0.5000$

Using Eq. 2.5, coefficient term $=$ antilog (0.5000)

$= 3.162$

Step (iv) : Using Eq. 2.6, N $=$ Coefficient Term $\times$ exponent term

$N = 3.162 \times 10^{-5}$

In other words, $10^{-4.5000} =$ antilog $(-4.5000) = 3.162 \times 10^{-5}$

Example 8

Finding N, if $\log N = -0.3260$

Step (i) : $\log N = -1 + 0.6740$ (or $\bar{1}.6740$)

Step (ii) : characteristic $= -1$;

Hence, exponent term $= 10^{-1}$

Step (iii) : Mantissa $= 0.6740$

Hence, coefficient term $=$ antilog $0.6740 = 4.721$

Step (iv) : $N = 4.721 \times 10^{-1} = 0.4721$

In other words, $10^{-0.3260} = 0.4721$

Many a times, we have to find the square root, cube root etc. of a number. Now let us study the method of finding a specified root of a number.

Finding the roots using logarithms

To find the specified root of a number using logarithms, do as in the examples discussed below for two different cases.

Finding the specified root of a number greater than 1

Example 9

Find $44300^{1/3}$

$44300^{1/3} = \text{antilog}\ (\log 44300^{1/3})$

First find $\log 44300^{1/3}$

$\log 44300^{1/3}$

$= 1/3 \log 44300$ (using rule (i) of Table 2.7)

$= 1/3\ (4.6464)$ (Go to the next step by doing ordinary division)

$= 1.5488$

For finding the root, we use the principle that.

antilog (log N) $= N$

From the above log value, find the antilog value as stated in the previous examples.

antilog (1.5488) = 35.38

Therefore $44300^{1/3}$

$= \text{antilog}\ (\log 44300^{1/3})$

$= 35.38$

Finding the specified root of a positive fraction

Example 10

Find $(0.000004000)^{1/3}$

When the given root of a positive fraction is to be found out, first rewrite the problem using scientific notation.

$(0.000004000)^{1/3} = (4.000 \times 10^{-6})^{1/3}$

While taking cube root, we should see whether the exponent in the scientific notation is exactly divisible by 3. In the present case, the exponent (– 6) is exactly divisible 3. In such cases we proceed as follows :

$(4.000 \times 10^{-6})^{1/3} = \text{antilog}\ (\log\ (4.000 \times 10^{-6})^{1/3})$

Step (i) : Find the log value of the number in scientific notation.
$\log\ (4.000 \times 10^{-6})^{1/3}$

$=1/3\ [\log 4.000 + \log 10^{-6}]$

$=1/3\ [\log 4.000 - 6 \log 10]$

$=1/3\ [0.6021 - (6 \times 1)]$ [since log 10 = 1]

$=0.2007 - 2$

Step (ii) : Find the antilog value for the answer obtained above using the principles stated previously.

In this section, we have explained the use of logarithms and antilogarithms during calculations. It is preferable to maintain significant figures also during calculations. This aspect will be discussed in Sec. 2.4.

Characteristic $=-2$

Hence, exponent $=10^{-2}$

mantissa $=0.2007$

Hence, coefficient term = antilog 0.2007

$=1.588$

Hence, the answer should be 1.588×10^{-2}

i.e. $(0.000004000)^{1/3} = (4.000 \times 10^{-6})^{1/3}$

$=\text{antilog}\ (\log 4.000 \times 10^{-6})^{1/3}$

$=1.588 \times 10^{-2}$

Example 11

Find $(0.0004600)^{1/3}$.

$(0.0004600)^{1/3} = (4.600 \times 10^{-4})^{1/3}$

In this case, the exponent term (– 4) is not exactly divisible by 3. In such cases, it is better to convert the exponent term into the nearest lower number that is exactly divisible by 3. In the above example, the exponent term is converted from 10^{-4} to 10^{-6}, since –6 is the nearest number that is lower than –4 and is exactly divisible by 3.

$(4.600 \times 10^{-4})^{1/3} = [460.0 \times 10^{-6}]^{1/3}$

$=\text{antilog}\ [1/3\ (\log 460.0 \times 10^{-6})]$

$=\text{antilog}\ [(1/3 \times 2.6628) + (1/3 \times (-6))]$

$=\text{antilog}\ [0.8876 - 2]$

Characteristic $=-2$ and so, exponent term $=10^{-2}$

Mantissa $=0.8876$ and so, coefficient term $=7.720$

Hence antilog $[0.8876 - 2] = 7.720 \times 10^{-2}$

i.e., $(4.600 \times 10^{-4})^{1/3}$

$=\text{antilog}\ (\log (4.600 \times 10^{-4})^{1/3})$

$=7.720 \times 10^{-2}$

In this section, we saw the use of some mathematical operations, logarithms and antilogarithms. We must use them in our calculations subject to the following condition:

"The accuracy in the final result in terms of number of digits should be in keeping with the accuracy of the measurements made during the experiment".

To understand the importance of this principle, we must understand the concept of significant figures. This is dealt with in the next section.

In the previous examples, you studied the methods for finding out the cube root. In the following SAQ, you are asked to find out the square root. Try to work out this.

SAQ 6

The solubility product (K_{sp}) of manganous sulphide is given by the formula,

$$K_{sp} = S^2$$

where S is the solubility of manganous sulphide (in molarity units) in water.

You shall study the method of finding K_{sp} in Unit 9 of Block 3

If K_{sp} for manganous sulphide is 3.000×10^{-13}, find its solubility in mol dm^{-3} units. (Note that is a convention to express K_{sp} as a dimensionless number. You take square root of the given K_{sp} value, which will give S in mol dm^{-3} units.)

....

....

....

....

2.4 SIGNIFICANT FIGURES

In Sec. 2.2, we discussed the units of physical quantities. Let us now focus our attention on the magnitude of physical quantities. Whenever we try to make any measurement, we are not certain about the actual value. Errors may creep in due to many reasons. Many a times, the calibration just as in a burette or in a graduated pipette may not be exact. Even the conditions of measurement may vary. For example, warmth expands a scale (ruler) by constant use, or it may get shortened due to rubbing against surfaces. Also, we are limited by the degree of accuracy to which our eyes can read the scales. Finally, our work is always subject to personal error. Since our measurements are uncertain, our report of the measurements taken from experiments should reflect only what we are reasonably sure of. Suppose that an analysis involves a number of measurements. Of these measurements, the one which involves the least accuracy is called the **limiting measurement**. The final calculation would be meaningful if it reflects the accuracy of the limiting measurement. In other words, the final result should not be more accurate than the limiting measurement.

For example in an experiment involving the calculation of molarity of hydrochloric acid using standard sodium carbonate solution, the following two measurements are involved.

Accuracy is the degree of agreement between the measured value and the theoretical value. Accuracy relates to the reliability of the results.

Precision is defined as the degree of agreement between repeated measurements. Precision relates to the reproducibility of the results. Precision does not assure accuracy. An example is finding the mass of a substance repeatedly wherein one of the weights used is in error. Same error occurs in each measurement and the answer would be the same during repeated experiments, but still is not exact. That is, the result has precision but not accuracy.

Accuracy in the expression of experimental results should be in keeping with the accuracy in the performance of the experiment. Maintenance of significant figures during calculation helps in avoiding the hyprocrisy of expressing the result which seems to be more accurate than the performance of the experiment!

(i) finding the mass of solid sodium carbonate in an analytical balance accurate to four decimals; this is followed by dissolving it in water and making up to a known volume to prepare a standard solution of sodium carbonate.

(ii) finding the titre value of standard sodium carbonate solution for reaction with a known volume of hydrochloric acid; the titre value is known to one decimal only.

Of the two measurements involved, the titre value (running for one decimal) has less accuracy than the mass weighed (running for four decimals); hence titre value represents the limiting measurement. This fact should be borne in mind while calculating the molarity of hydrochloric acid. In order to understand the way of representing the final result in keeping with the accuracy of the limiting measurement, we should understand the concept of significant figures.

2.4.1 Calculation of Significant Figures in a Number

The significant figures can be defined as the number of digits necessary to express the results of the experiments consistent with the precision in measurements. Significant figures include all digits of the number representing measurable divisions and one digit representing an estimated division. The significant figures in a measurement are determined using the following rules.

i) The digits 1 to 9 are all important. So the number, 45, has two significant figures; and, the number, 4.946, has four significant figures.

ii) If zero is placed between two non-zero digits, then it is significant. For example, both 3.0045 and 30045 have five significant figures.

iii) If zero is to the right of the decimal point forming the final digit(s), then also it is significant. For example, 42.0, 4.20 and 0.420 all have three significant figures.

iv) Zero is not significant when it is used to mark the position of the decimal point in a number less than one. For example, 0.1235 and 0.0001235 both have only four significant figures. The zero in 0.1235 and all the four zeros in 0.0001235 are used to mark the position of a number less than one; hence, these zero's are not significant.

v) A zero that is used to mark the decimal place in a number greater than one is usually not significant. Specially when the zeros are used as place markers rather than being part of the actual measurement, they are not significant. For example, consider the volume of a liquid measured as 600 cm^3 using a measuring jar. Let us examine this for the purpose of significant figure calculation. It is not possible to determine whether the zeros are used merely to place the decimal point or whether they are a part of the measurement. The accuracy depends on whether the subdivisions in the measuring jar are in terms 100 cm^3 or 10 cm^3. In such large-volume measuring jars, 1 cm^3 subdivisions are not made. In the former case, 600 cm^3, represents a significant figure of one and in the latter case, it is two.

The job is made much easier, if you represent the numbers using the scientific notation. **The significant figure in a number is equal to the total number of digits in the coefficient of scientific notation of that number.** For example the number 30900 has its significant figure value depending on the way the coefficient is represented. See the following three cases.

Case i) : $30900 = 3.09 \times 10^4$; significant figure is 3; the subdivisions used in the measurement are in terms of hundreds.

Case ii) : $30900 = 3.090 \times 10^4$; significant figure is 4; the subdivisions used in the measurement are in terms of tens.

Case iii) : $30900 = 3.0900 \times 10^4$; significant figure is 5; the subdivisions used in the measurement are in terms of units (ones).

We can take yet another example, say 0.003061. Its scientific notation is 3.061×10^{-3}. Obviously, this has four significant figures; note that all the zero's before '3061' are not significant.

vi) **The significant figure calculation arises only for measured quantities of an experiment wherein some uncertainty is possible.** The universal constants (such as gas constant, velocity of light etc.), the quantities obtained by counting and, the quantities arising out of definitions (such as 1 inch =2.54 cm) are considered to be exact. **For these exact quantities, we need not calculate the significant figures.** The exact quantities are assumed to have infinite number (i.e., a very large number) of significant figures. Let us see the following examples to understand the significance of exact numbers.

i) For the relationship,

Volume of a sphere $= \frac{4}{3}\pi\ (\text{radius})^3$,

The significant figures in volume and radius should be the same; 4, 3 and π are considered exact since these are constants and, are assumed to have a large number of significant figures. For example, if the radius is 2.4 cm,

then volume of the sphere $= \frac{4}{3} \times \frac{22}{7} \times (2.4)^3\ \text{cm}^3$

$= 58\ \text{cm}^3$ (to two signficant figures)

Table 2.9 : Significant Figures and Scientific Notation

Number (i)	Scientific notation (ii)	Coefficient (iii)	Number of digits in the coefficient (iv)	Number of significant figures in the coefficient (v)	Explanation (vi)
307	3.07×10^2	3.07	3	3	All digits are significant. In each case, the decimal point in the number given in column (i) is understood to be after the last digit.
2325	2.325×10^3	2.325	4	4	
(i)	(ii)	(iii)	(iv)	(v)	(vi)
307.00	3.0700×10^2	3.0700	5	5	All zeros after the decimal point are significant (since these succeed nonzero digits).
2325.0	2.3250×10^3	2.3250	5	5	
0.00307	3.07×10^{-3}	3.07	3	3	All zeros after the decimal point but before the first nonzero digit are not significant because they only locate the decimal point.
0.02325	2.325×10^{-2}	2.325	4	4	
30700	3.07×10^4	3.07	3	3	All zeros after the last nonzero digit are considered not significant, unless the accuracy of the measurement is known. As per the accuracy of the measurement, the scientific notation is to be written and significant figures calculated accordingly.
	3.0700×10^4	3.0700	5	5	
232500	2.325×10^5	2.325	4	4	
	2.32500×10^5	2.32500	6	6	

The first nonzero digit

(i) in 0.00307 is 3 and

(ii) in 0.02325 is 2

The last nonzero digit

(i) in 30700 is 7 and

(ii) in 232500 is 5.

Note that the answer ('58 cm^3') has two significant figures, since the radius ('2.4 cm') has only two significant figures. We are not concerned with the significant figures, of 4, 3 and π (i.e., 22/7), since these are exact quantities and are assumed to have a large number of significant figures.

ii) Sometimes , in an experiment we may have to count the number of [illegible] species. For example in Unit 4, you shall study the 'drop number method' for determining the surface tension of liquids. In this method, one of the measurements relates to the counting of number of drops of a liquid falling through a narrow tube. The number of drops must be a whole number and could be counted exactly. Hence, we need not calculate the significant figures for the drops, (use this idea in SAQ 11 of this unit and in SAQ 3 of Unit 4).

More examples for significant figure calculation are given in Table 2.9.

Before trying to know about arithmetic operations involving significant figures, work out the following SAQ.

SAQ 7

Determine the significant figures for the following:

(i) 7.336 (ii) 8.30 (iii) 1030 (two possible answers)

(iv) 5.4121 (v) 00.00030

. . . .

. . . .

. . . .

2.4.2 Addition and Subtraction Maintaining Significant Figures

The thumb rule in maintaining the significant figures during addition and subtraction is given below :

The number of decimal places in the result should be the same as the smallest number of decimal places among the data.

If you follow the steps in the same order as given below, addition and subtraction would be easier during the scientific calculations :

i) Write down the numbers to be added or subtracted one below the other in a spacious way and also find out the calculated value as per addition or subtraction.

ii) Put a circle round the significant digit at the right end of each number; this circle indicates the uncertain or estimated figure.

iii) At the top of the numbers, give the column number from right to left in Roman numerals.

iv) For each of the data, locate the column number containing the uncertain or estimated figure. Among the column numbers containing uncertain figures, the highest is noted.

v) The final answer must contain digits only upto this highest column.

Example 12

To illustrate the use of the above rules during addition, an example is given in Table 2.10. This example concerns the following addition :

5.311 +28.12 +1.5102

Table 2.10 : Addition involving significant figures

	Column numbers from right to left						Column number containing the uncertain figure	Highest column number containing uncertain figure
	VI	V	IV	III	II	I		
		5.	3	1	①		II	
	2	8.	1	②			III	III
		1.	5	1	0	②	I	
Calculated answer	3	4.	9	4	1	2		
Final answer is	34.94							

First nonsignificant digit (it is less than 5 and hence is dropped; for explanation see below).

The answer contains only upto column III from right; it is got by rounding off the first nonsignificant digit (1 in column II).

Note that 28.12 has two decimal places while 5.311 and 1.5102 have three and four decimal places, respectively. Hence, the lowest of decimal places in the given data is two. The answer, 34.94 must have two decimal places only in conformity with the thumb rule stated above.

Another fact to be kept in mind while applying the above rules is that the nonsignificant figures are to be rounded off before discarding them. The following principles are used for purposes of rounding off.

a) If the first nonsignificant digit is less than 5, that digit is dropped as such. For the example discussed in Table 2.10, the first nonsignificant digit is 1 and it is dropped (in fact, 0.0012 is dropped as such).

b) If the first nonsignificant digit is equal to or greater than 5, that digit is dropped and the last significant digit is increased by 1. For example, if 5.316, 28.12 and 1.5102 are added, the calculated answer is 34.9462. Similar to the principles illustrated above, 0.0062 is to be omitted. But since the first nonsignificant digit is 6, the final answer is 34.95, (got by rounding off the last significant digit from 4 to 5).

Example 13

An example for subtraction using significant figures has been given in Table 2.11. The example concerns the following subtraction:

Remember that the steps to be followed are the same for both addition and subtraction.

17.58 – 1.246

Table 2.11 : Subtraction involving significant figures

	Column numbers from right to left					Column number containing the uncertain figure	Highest column number containing uncertain figure
	V	IV	III	II	I		
	1	7.	5	⑧		II	II
(−)		1.	2	4	⑥	I	
Calculated answer is	1	6.	3	3	4 ← nonsignificant digit (it is less than 5 and hence, is dropped).		
Final answer is	16.33						

The answer contains only upto column II from right; it is got by rounding off the nonsignificant digit (4 in column I).

Among the two numbers, 17.58 has two decimal places while 1.246 has three decimal places. Evidently the final answer, 16.33, also has two decimal places.

So far we studied the methods of carrying out addition and subtraction maintaining significant figures. Let us next do multiplication and division maintaining significant figures. Before that try the following SAQs.

SAQ 8

Using the individual atomic weights given below, calculate the formula weight of Ag_2MoO_4 maintaining significant figures

Silver	:	107.870
Molybdenum	:	95.94
Oxygen	:	15.9944

SAQ 9

Carry out the following maintaining the significant figures :

6.37 − 4.675

2.4.3 Multiplication and Division Maintaining Significant Figures

The common steps to be followed in multiplication and division maintaining significant figures are given below. You can verify their application using Table 2.12.

i) For each number involved in the multiplication and division operations, write down the scientific notation and the coefficient.

ii) Find out the significant figure value of each coefficient; identify the lowest among these significant figures.

iii) Do the actual multiplication or division using the scientific notation of the numbers. Reduce the answer to the lowest significant figure obtained in step (ii) above. The thumb rule in maintaining significant figures during multiplication and division operations is as follows :

"A product or quotient will contain as many significant figures as the coefficient of the term with the smallest value for significant figure".

You will be able to understand this much better by seeing how the multiplication (25.72 × 221) and the division (666/0.06000) are done in Table 2.12.

Table 2.12 : Multiplication and Division Maintaining Significant Figures

Problem	Number			Lowest of the significant figures	Calculated Value		Coefficent reduced to lowest of the significant figures as given in (v)	Final answ
	Scientific notation	Coefficient	Significant figure		Normal represen-tation	Scientific notation		
(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)	(ix)
25.72×221	2.572×10^{1}	2.572	4	3	5684.12	5.68412×10^{3}	5.68 (to three significant figures)	5.68×10^{3}
	2.21×10^{2}	2.21	3					
$\frac{666}{0.06000}$	6.66×10^{2}	6.66	3	3	11100	1.11×10^{4} or 1.110×10^{4} or 1.1100×10^{4}	1.11 (to three significant figures)	1.11×10^{4}
	6.000×10^{-2}	6.000	4					

As a test of understanding Table 2.12, work out the following SAQs.

SAQ 10

Carry out the following operations and report the answer with proper significant figures :

i) 19.0 × 20.00

ii) 0.79/1.516

. . . .

. . . .

. . . .

SAQ 11

In Unit 4, you shall study 'drop number method', using which the following relationship between the surface tension values of two liquids such as, mercury and water (r_{Hg} and r_w), can be compared. To do this, number of drops of mercury and water (n_{Hg} and n_w) in the same volume of each liquid and the densities of the two liquids (d_{Hg} and d_w) must be known.

$$\frac{n_w}{n_{Hg}} = \frac{r_{Hg}}{r_w} \cdot \frac{d_w}{d_{Hg}}$$

Using the following data at 293 K, calculate the significant figures in the final answer for n_w/n_{Hg} (the ratio of the number of drops of water to those of mercury). You shall do the actual calculation in SAQ 3 of Unit 4 of Block 2 of this course.

Don't be afraid on seeing the length of SAQ 11 ! Most of it is meant to give you background information. The actual question is given in bold letters.

$$r_{Hg} = 0.472 \text{ N m}^{-1}$$

$$r_w = 0.07288 \text{ N m}^{-1}$$

$$d_{Hg} = 13.6 \text{ kg dm}^{-3}$$

$$d_w = 1.00 \text{ kg dm}^{-3}$$

Hint : Although n_w and n_{Hg} are exact numbers as per the discussion is Subsec. 2.4.1 of this unit, n_w/n_{Hg} is not an exact number; the significant figures in the left side should be equal to those in right side of the relationship stated above.

....

....

....

....

2.4.4 Taking Logarithms and Antilogarithms Maintaining Significant Figures

In changing from logarihms to antilogarithms, and vice versa, the number being operated and the logarithm mantissa have the same number of significant figures. **All zeros in the mantissa are significant.**

Taking logarithms Maintaining significant figures

In Column (vi), rounding off is done only, if the significant figures stated in (iv) are less than four.

Any number having more than four digits, should be rounded off to four digits and logarithm should be taken. Any number with less than four digits should be added required number of zero's for the purpose of using four figure logarithms. But the significant figures in the number and those of mantissa should match as shown in the examples below. For this purpose, rounding off procedure is used, wherever required. Go through the examples in Table 2.13.

Table 2.13 : Calculation of Logarithms Maintaining Significant Figures

Example number	Problem	Coefficient value	Number of significant figures	Mantissa		Characteristic	Final answer (viii) [(vi) + (vii)]
				As per four figure logarithms	Rounded off as per column (iv)		
(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)
1	$\log 2.750 \times 10^{-3}$	2.750	four	0.4393	0.4393 (to four significant figures)	-3	$\log 2.750 \times 10^{-3}$ $= -2.5607$
2	$\log 2.75 \times 10^{-3}$	2.75	three	0.4393	0.439 (to three significant figures)	-3	$\log 2.75 \times 10^{-3}$ $= -2.561$
3	$\log 2.0 \times 10^{3}$	2.0	two	0.3010	0.30 (to two significant figures)	3	$\log 2.0 \times 10^{3}$ $= 3.30$

From the above examples, you can see that the mantissa is rounded off to the same number of significant figures as those in the coefficient of the given quantity in scientific notation. Final answer is expressed with one more significant figure (which is due to the characteristic). Thus, 2.750 in Example (1) of Table 2.13 has four significant figures, whereas the answer, −2.5607 has five significant figures; four due to mantissa and one due to the characteristic.

Taking antilogarithms Maintaining Significant Figures

As said for logarithms, the significant figures in the mantissa and the coefficient in the scientific notation must match. Necessary rounding off is done with four figure antilogarithms. Study the following examples in Table 2.14. All problems follow the equation,

$$\log N = x$$

In each case, x is given and N is to be found out using the relationship, $N = \text{antilog } x$. The x value is written in a rearranged form in column (iii) to show the characteristic and mantissa parts separately.

Table 2.14 : Calculation of Antilogarithms Maintaining Significant Figures

Example Number (i)	x (ii)	Rearranged x (iii)	Mantissa (with proper significant figures) (iv)	Coefficient = antilog (mantissa) (v)	Characteristic (vi)	Exponent term (vii)	Answer in scientific notation: N=antilog x (viii)
1.	−4.7166	−5 +0.2834	0.2834 (four singnificant figures)	1.921 (four significant figures)	−5	10^{-5}	antilog (−4.7166) $=1.921 \times 10^{-5}$
2.	−2.70	−3 +0.30	0.30 (two significant figures)	2.0 (1.995 rounded to two significant figures)	−3	10^{-3}	antilog (−2.70) $=2.0 \times 10^{-3}$
3.	6.5100	6 +0.5100	0.5100 (four significant figures)	3.236 (four significant figures)	6	10^{6}	antilog (6.5100) $=3.236 \times 10^{6}$
4.	6.510	6 +0.510	0.510 (three significant figures)	3.24 (3.236 rounded to three significant figures)	6	10^{6}	antilog (6.510) $=3.24 \times 10^{6}$

In the next section, we shall discuss the method of maintaining the laboraory note book.

Using the above ideas, work out the following SAQ.

SAQ 12

Using the relationship, $\text{pH} = -\log [\text{H}^+]$

where $[\text{H}^+]$ is in molarity, calculate $[\text{H}^+]$ of a solution for which pH is 4.70, maintaining the singificant figures. Express the answer in molarity.

Note: During calculation, the equation, pH =– log $[H^+]$ should be considered as the expression, pH=– log $[H^+]/M$ where M is the symbol of molarity unit. To understand this, see subsec. 2.2.4.

. . . .

. . . .

. . . .

2.5 LABORATORY NOTE BOOK

It is essential to keep a proper record of the work that has been done. The record should reflect all the observations at various stages of the experiment. The observations prove helpful in correct interpretation of an experimental result.

While preparing a laboratory note book, the following important features may be kept in mind.

- The laboratory note book is a complete record of all operations. Date, time, the number and the title of each experiment must be entered regularly.
- Record all observations and data in the note book at the time they are obtained. Never use scraps of paper for noting particulars like masses of substances weighed, melting points, titre values etc. They might get lost or mixed up.
- The record should be clearly written and well organised. On reading it, one should be able to understand what has been done. It may not be necessary to copy out the exact procedure, since this is given in your laboratory manual. Detailed calculations are to be shown. Results should be summarised, conclusions drawn for each experiment and explanation provided, if the results vary from those expected. **Certain marks have been allotted for maintaining a good laboratory note book.**

Some of the important points to remember in maintaining a laboratory note book are given below:

From a stationery shop, buy your record note book and graph sheets.

- A bound note book should be used for laboratory record. You may use a laboratory note book in which one side has ruled pages and other side is unruled.
- All entries must be made in ink. If you commit a mistake, it should be crossed and correct entry should be made.
- The first few pages in the note book should be left for making a list of contents.
- Graphs drawn should be attached to the laboratory note book.

2.6 TABULATION OF DATA AND PLOTTING OF GRAPHS

While doing calculations, unit of the physical quantities must be mentioned. Tabular columns must have relevant titles. While tabulating the data, the physical quantities should be represented as dimensionless quantities by dividing the physical quantities by appropriate units. Thus, in the titration table given in Sec. 1.7 of Unit 1, the volume of the solution is divided by cm^3 units to facilitate the entries as mere numbers. In the examples given in Sec. 1.6 and 1.7 of Unit 1, we showed how to enter the data for weighing and calculation of molarity.

y165E

Plotting a Graph

Often experimental data can be analyzed by plotting a graph. While plotting a curve, x– and y– coordinates must be represented as dimensionless quantities by dividing the physical quantities by appropriate units. Proper scales should be chosen. The graph should be given a suitable title. In many cases, we come across straight line plots. You shall come across straight line plots in Units 11, 12, 13, 15 and 16. The straight line plots help us in confirming a linear relationship between the quantities plotted. For this, we have to calculate the slope of a straight line plot. If the slope is positive, there is a direct proportionality between the two quantities; if the slope is negative, there is an inverse relationship between the two. To find the slope of a straight line, select two points (x_1, y_1) and (x_2, y_2) on the straight line and apply the formula:

A linear relationship is said to exist if increase in y *is proportional to increase or decrease in* x (but not to increase or decrease in $x^2, x^3, x^{-2}, x^{-3}, e^x$, etc. values).

A straight line curve obeys the equation,

$$y = mx + c$$

where m and c are the slope and the y – intercept, respectively.

$$\text{Slope} = \frac{(y_2 - y_1)}{(x_2 - x_1)} \qquad \ldots (2.7)$$

Example 14

To understand the above, let us discuss an example. In this example, the graphical method of calculation of the first order rate constant for the hydrolysis of benzene diazonium chloride is illustrated. Benzene diazonium chloride gets hydrolysed as follows:

$$C_6H_5N_2Cl \longrightarrow C_6H_5OH + N_2 + HCl$$

The volumes of nitrogen liberated at various time intervals (t) are denoted by V_t while the volume of nitrogen liberated at infinite time is denoted by V_∞. The first order rate constant, k, is given by the equation.

$$\log (V_\infty - V_t) = \log V_\infty - \frac{k}{2.303} t \qquad \ldots (2.8)$$

This is of the form, $y = c + mx$, which is an equation for a straight line.

Comparing these two equations,

$$\text{Slope} = m = -\frac{k}{2.303}$$

$$k = - 2.303 \times \text{slope} \qquad \ldots (2.10)$$

In other words, from the slope of $\log (V_\infty - V_t)$ against t plot, k can be obtained.

We now state in this example,

- the way of representing the data for plotting a curve,
- the actual plot and
- the way of calculating the slope using Eq. 2.7.

Data for the hydrolysis of benzene diazonium chloride

t/s	0	1500	3000	4500
$(V_\infty - V_t)$/cm^3	81.0	74.6	68.9	63.4
$\log (V_\infty - V_t)$/cm^3	1.908	1.873	1.838	1.802

During calculation, we write the left hand side of Eq. 2.8 as $\log (V_\infty - V_t)/\text{cm}^3$, in order to represent it as a dimensionless quantity. In order to understand this, see subsec. 2.2.4.

Using these data, $\log (V_\infty - V_t)$ against t plot is made as shown in Fig. 2.2.

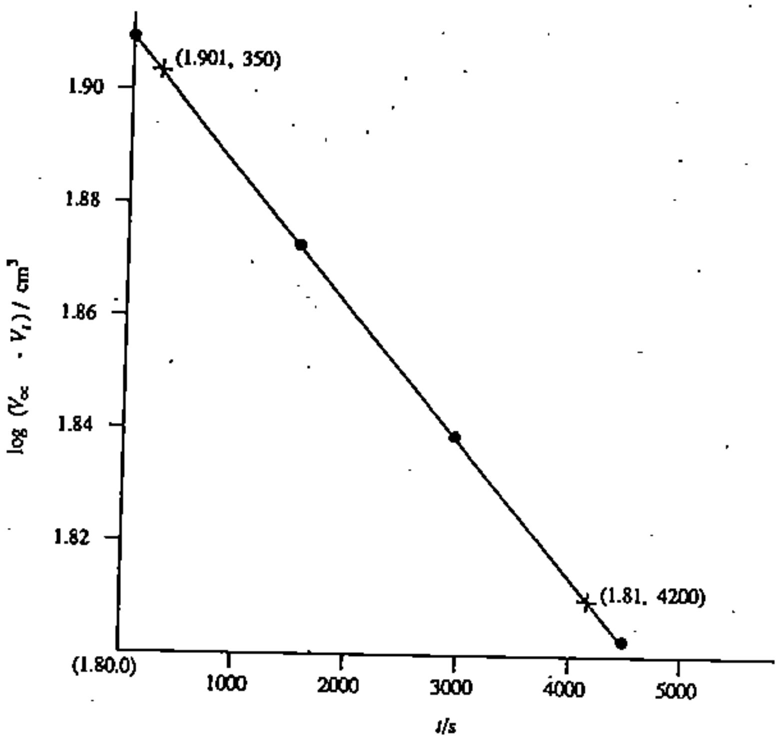


Fig. 2.2 : $\log (V_\infty - V_t)$ against t plot

For calculating the slope, choose two points on the straight line and indicate them by '×' mark. Find the x and y coordinates corresponding to these two points. Substitute these values in Eq. 2.7 and calculate the slope of the straight line. This is illustrated below:

The unit of slope

$$= \frac{\text{Unit of } y \text{ coordinate}}{\text{Unit of } x \text{ coordinate}}$$

$$= \frac{\text{Unit of } \log(V_\infty - V_t)/\text{cm}^3}{\text{Unit of } t}$$

$$= \frac{1}{s} \text{ or } s^{-1}$$

Using Eq. 2.7, slope $= \dfrac{(1.81 - 1.901)}{(4200 - 350)\,s}$

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

Using Eq. 2.10, k $= -2.303 \times \text{slope}$

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

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

While drawing a straight line, sometimes all the points may not fall on a line. In such cases, draw the straight line in such a way that (i) it passes through as many points as possible or (ii) the points are scattered symmetrically around the straight line.

Test Value : The value which is to be determined using an experiment.

Sometimes it may be necessary to find the x-coordinate, corresponding to a y-coordinate and vice versa, using the straight line plot as such, Fig. 2.3. This is called **interpolation**. In this case, the test value of x (or y) falls in between the extreme limits of x coordinates (or y coordinates) of points used for plotting the graph. The interpolation of a value is done within the experimentally tested range of linear relationship.

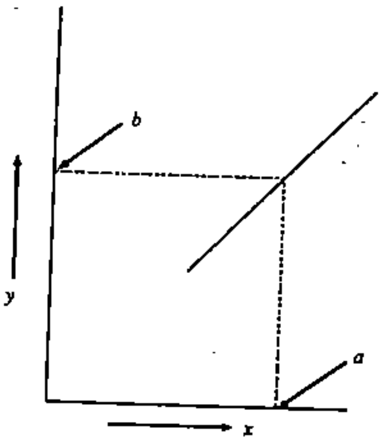


Fig. 2.3 : Interpolation method; *a* and *b* are the values of *x* and *y* coordinates for the test case. If *a* (or *b*) is found out by experiment, then *b* (or *a*) can be known by drawing dotted lines intercepting the straight line as shown in the figure.

To cite an example, we can use interpolation method in colorimetric experiment to find the concentration of a given solution from its absorbance value (or meter response) using the absorbance (or meter response) against concentration plot. We shall study this in Sec. 3.2 of Unit 3.

In certain situations, we may have to extend a straight line graph to obtain *x*– (or *y*– coordinate) from the known *y*– (or *x*–coordinate). This is called extrapolation. Extrapolation is not always reliable because the testing of a quantity is done beyond the experimentally tested limits of linear relationship. Any deviation from linear relationship will result in yielding an inaccurate result. For example, Beer-Lambert law, which is the guiding principle for colorimetry, holds over limited concentration ranges. Extrapolation is not allowed in this case.

2.7 SUMMARY

In this Unit, we discussed the SI units of basic and derived physical quantities. We explained the method of representing a number using scientific notation . We defined the term, significant figure. We explained the ways of maintaining significant figures while carrying out calculations. We discussed some features regarding the recording of observations, tabulation of data and plotting graphs.

2.8 ANSWERS

Self Assessment Questions

1) Units of k = units of (reaction rate/ $[\text{reactant}]^2$)

$$= \text{M s}^{-1}/\text{M}^2 = \text{M}^{-1}\text{ s}^{-1}$$

where $\text{M} = \text{mol dm}^{-3}$

2) Units of kinetic energy = Unit of (mass × $(\text{velocity})^2$)

$$= \text{kg m}^2\text{ s}^{-2}$$

$$= \text{J}$$

3) (a) nm (b) ps (c) kPa

4) 0.015×10^{-4} S $= 1.5 \times 10^{-6}$ S

$= 1.5\ \mu S$

5) Units of R = J mol^{-1} K^{-1}

= J/mol K

6) $S = (K_{sp})^{1/2}$

$= (3.000 \times 10^{-13})^{1/2}$ mol dm^{-3}

$= (30.00 \times 10^{-14})^{1/2}$ mol dm^{-3}

$= 5.476 \times 10^{-7}$ mol dm^{-3}

7) (i) 4 (ii) 3 (iii) 4 (in 1.030×10^3) and 3 (in 1.03×10^3) (iv) 5 (v) 2 (all the five zeros before 3 are nonsignificant whereas zero after 3 is significant).

8)

	215.740 (2 × Atomic weight of Ag)
	95.94 (1 × Atomic weight of Mo)
	63.9776 (4 × Atomic weight of oxygen)
Calculated answer	375.6576

Final answer = 375.66 (rounded to two decimal places since the data 95.94, which has the least number of decimals, has two places.)

9)

	6.37
	− 4.675
Calculated answer	1.695

Final answer = 1.70 (rounded to two decimal places since 6.37 has two decimal places while 4.675 has three decimal places).

10) i) 3.80×10^2 (to three significant figures)
ii) 5.2×10^{-1} (to two significant figures)

11) Of the various terms in the given relationship, except r_w, which has four significant figures, all the others (r_{Hg}, d_{Hg} and d_w) have only three significant figures. Hence the final answer also should have three significant figures.

12) pH = −log [H$^+$]/M = 4.70

log [H$^+$]/M = − 4.70

= − 5 + 0.30

Since mantissa (0.30) has two significant figures, the coefficient also has two significant figures. Coefficient term = antilog (0.30)

= 2.0

Exponent term = 10^{-5}

∴ [H$^+$] = Coefficient term × exponent term

$= 2.0 \times 10^{-5}$ M

Logarithms

	0	1	2	3	4	5	6	7	8	9	differences								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	5	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

	0	1	2	3	4	5	6	7	8	9	differences								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

Antilogarithms

	0	1	2	3	4	5	6	7	8	9	differences								
											1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1302	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

	0	1	2	3	4	5	6	7	8	9	differences 1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	21

UNIT 3 LOW-COST INSTRUMENTS

Structure

3.1 Introduction
  Objectives
3.2 Colorimetry
  Beer-Lambert Law
  Principle of Colorimeter
  Various Controls of the Low-Cost Colorimeter
  Demonstration Experiment 1 : Colorimetric Estimation of Copper Sulphate
3.3 Conductometry
  Theory
  Various Controls of the Low-Cost Conductometer
  Method of Operation
  Demonstration Experiment 2 : Determination of conductance of Given Sodium Hydroxide Solution
3.4 Potentiometry
  Galvanic Cells and Cell Reaction
  Measurement of E.M.F.
  Nernst Equation
  Types of Electrodes
  Various Controls of the Low-Cost mV/pH Meter
  Method of Operation
  Demonstration Experiment 3 : Construction of Daniell Cell and Measurement of E.M.F.
3.5 Summary
3.6 Answers

3.1 INTRODUCTION

In this unit, we shall discuss the basic principles of colorimetry, conductometry and potentiometry. We shall explain the procedure for using low-cost instruments such as colorimeter, conductometer and mV/pH meter. You will be using these instruments for some of the experiments in this course. Three demonstration experiments will also be discussed to illustrate the use of these instruments.

Objectives

After studying this unit, you should be able to :

- state the principles of colorimetry, conductometry and potentiometry,
- explain the procedure for operating the controls in colorimeter, conductometer and mV/pH meter, and
- explain the methods of recording absorbance or conductance or e.m.f. of the given solution or system.

3.2 COLORIMETRY

Chemical analysis based on measurement of intensity of light absorbed in the visible region is termed colorimetry. Any coloured substance may be analysed by this method. If a substance is colourless, it can be made to form a coloured compound by the addition of a suitable reagent and then analysed colorimetrically. In colorimetry, generally the concentration of a substance is obtained from the intensity of light absorbed. In order to accomplish this, experiments are carried out to obtain the intensities of light absorbed by the substance in solutions of known concentrations. The simple instrument used for this measurement is termed a colorimeter. Colorimetric methods provide a simple and rapid method of estimating minute quantities of substances in solution. Hence the technique can be used to perform a wide variety of experiments such as monitoring a reaction colorimetrically in kinetics, determining equilibrium concentrations for the determination of equilibrium constants, etc. Let us now discuss Beer–Lambert law which summarises the basic principle of colorimetric estimation.

For a detailed study of Beer–Lambert law, see Unit 5 of CHE–03 (L) and Unit 8 of CHE–01 courses.

3.2.1 Beer–Lambert Law

The wavelength at which a substance exhibits maximum absorption depends on its structure.

When light of an appropriate wavelength is passed through a coloured solution contained in a cell, a fraction of the light is absorbed. The intensity of light absorbed depends on the nature or structure of the substance, its concentration in solution and the thickness of the absorbing medium. The part of light, which is not absorbed, is transmitted. Though some light is reflected back from the solution, its amount is negligibly small and is eliminated by using a control. For all practical purposes we may say,

$$I_0 = I_a + I_t$$

where,

I_0 = Intensity of incident light

I_a = Intensity of light absorbed

I_t = Intensity of transmitted light.

Beer–Lambert law relates I_0 to the thickness and concentration of the medium. Let us understand Beer–Lambert law.

Beer–Lambert law is a combination of the two laws, Beer's law and Lambert's law. We are not going to discuss these two laws separately. Beer–Lambert law states that the fraction of light absorbed by a given absorbing medium is directly proportional to the thickness of the medium and the concentration of the absorbing species. The mathematical expression of this law is given below:

$$\log I_0/I = A = \varepsilon cl \qquad \ldots (3.1)$$

where,

I_0 = Intensity of incident light

I = Intensity of transmitted light

A = Absorbance

l = Thickness of the medium

c = Concentration in mol dm^{-3}

ε = Molar absorption coefficent

Eq. 3.1, $A = \varepsilon cl$, is of the type "$y=mx$", which is an equation for a straight line passing through the origin. The slope ("m") of the straight line plot of A against c is equal to the product, εl. Hence, from the values of the slope and l, ε can be found out.

$$\varepsilon = \frac{\text{slope}}{l}$$

ε, the molar absorption coefficient, is the absorbance of a solution having unit concentration (c = 1 M) placed in a cell of unit thickness, (l = 1 cm). Absorbance is also called **optical density (OD)**.

ε can be expressed in the unit, $m^2\ mol^{-1}$ or $cm^2\ mol^{-1}$. If l is in m unit and c is in mol m^{-3} units, then ε is in $m^2\ mol^{-1}$ units. On the other hand, if l is in cm unit and c is in molarity unit (mol/1000 cm^3 or mol/dm^3 units), then ε is in $cm^2\ mol^{-1}$ units.

According to Eq. 3.1, the absorbance or OD of a solution in a container of fixed path length is directly proportional to the concentration of a solution. A plot between absorbance and concentration is expected to be linear. Such a straight line plot (passing through the origin) shows that Beer–Lambert law is obeyed. The straight line so obtained is known as **calibration curve.** A calibration curve is useful in finding the concentration of a given solution. We shall discuss this aspect in Demonstration Experiment 1 of this unit. Dilute solutions obey Beer–Lambert law over a considerable concentration range, the upper limit varying from system to system.

Deviations from Beer–Lambert Law

Beer–Lambert law does not hold good over a wide range of concentrations, if the nature of the absorbing species changes with concentration; for example, when the species ionises, dissociates or associates in solution. Addition of large amounts of noninterfering electrolytes may shift the wavelength at which maximum asportion occurs and may also change the value of molar absorption coefficient. Also discrepancies may occur when the light used is not monochromatic.

Monochromatic light has more or less only one wavelength value.

3.2.2 Principle of Colorimeter

It is difficult to quantify colour visually. For this we need the help of a measuring device. A colorimeter is such a device. A colorimeter measures the intensity of light before passing through the solution and after passing through the solution. From the intensity measurements, we can estimate the concentration of a solution. You are provided with a low cost colorimeter for measurement of light intensity.

In general, the apparatus for colorimetry includes a

- light source
- slits and lenses to focus a sharp beam of light,
- filters to transmit a narrow range of wavelengths,
- a cuvette which is a small vessel in which the solution is taken,
- cuvette holders, and,
- a receiver which is helpful in determining the intensity of the transmitted beam.

The instruments of this type are known as filter colorimeters or filter photometers. A schematic diagram of a colorimeter is given in Fig.3.1. The diagram of a low-cost colorimeter is given in Fig.3.2.

A colorimeter operates on a broad range of wavelengths.

A colorimeter is useful in visible region only. But a spectrophotometer is useful in u.v. and visible regions. A spectrophotometer has special facilities for generation and selection of specific wavelength.

Fig.3.1 : Schematic diagram of a colorimeter

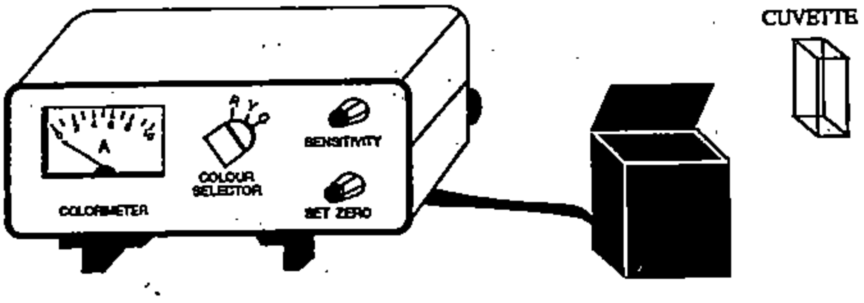


Fig. 3.2 : Low–cost colorimeter.

The diodes have the property of permitting current to flow with practically no resistance in one direction and offer nearly infinite resistance to current flow in the opposite direction. In electronic circuits, diodes have numerous applications.

A photocell converts light into electricity.

The reference sample may be pure solvent or a solution of lower concentration.

Three light emitting diodes (LEDs) are available in the low-cost colorimeter as light source. These emit light of different colours such as red, yellow or green. You would be using one of them depending on the colour of absorbing medium. The light from the source is made to pass through a slit so that we get a thin ray, which falls on the cell containing the solution. Some of the light is absorbed and the rest is transmitted. The light transmitted by the solution falls on the photocell where a current is generated. The magnitude of this current is proportional to the intensity (I) of the light transmitted by the solution. The current signal is suitably amplified and then measured with the help of an ammeter. The intensity of incident light (I_0) is measured by passing the light from the same source through distilled water taken in the cuvette. Under this condition, no light is absorbed and the whole of it falls on the photocell. In case the solution is made in a solvent other than water, the pure solvent may be taken as the reference sample. The difference between the two readings gives the amount of light absorbed. Next let us discuss the controls of the low-cost colorimeter.

3.2.3 Various Controls of the Low–Cost Colorimeter

The meter reading is called the meter response. Instead of absorbance values, meter response values are used in low-cost colorimeter experiments.

Power Switch	:	This is a switch on the back of the instrument and is used to switch the instrument on or off. When the instrument is connected to the mains and switched on, the LED on the front panel will glow.
Colour Selector	:	This control is on the front panel of the instrument with the positions marked R, Y and G signifying the three colours, red, yellow or green.
Meter Scale	:	The scale in the colorimeter (marked A) has markings from 1 to 10. These markings are meter response values.

Set Zero :	This control is again on the front panel of the instrument. This is adjusted to set the meter response to zero when the solvent or reference solution is taken in the cuvette.
Sensitivity :	This control is also on the left front panel of the instrument. This is used to give any desired scale for the range of concentrations under consideration. Suppose that in an experiment, we have solutions of concentrations varying from 0 to 8% (mass by volume). With the solvent, the set zero knob is adjusted to set the meter response to zero. Then with the 8% solution, the sensitivity knob is adjusted to set the meter response to 9.0. Let us say, in another experiment, we have solutions from 0–6% only. Instead of using the same adjustment, we could have a better scale. After setting zero with the solvent, we take the 6% solution and readjust the sensitivity knob to set the meter response to 9.0. Remember, the earlier setting gives a scale of 0–9 for concentrations 0–8%, whereas the latter setting gives a scale of 0–9 for a smaller concentration range 0–6%.

Method of Operation

1) Before connecting the instrument to the mains, check whether the needle coincides with zero in the meter. If the needle is not coinciding with zero, make it read zero using a small screw driver into the hole under the meter. Then connect the instrument to the mains and put on the power switch at the back.

2) Set the colour selector knob at the desired colour. For an unknown solution, the knob for the colour selector is set at R or Y or G depending on which LED gives the highest meter response, (i.e., the largest absorbance), when the light from LED is passed through the solution in the cuvette.

3) Take a clean cuvette and fill it with [illegible] water (or the reference sample). Wipe the outside dry with tissue paper. Make an identifying mark on one plain side of the curvette at the top and insert the curvette into the holder in such a way that the marked plain side is towards the LED. **Maintain this position everytime you insert the curvette into the holder.** Close the lid of the holder.

4) Adjust the set zero control to make the meter read zero.

5) Next rinse and fill the same cuvette with the solution of maximum concentration. Wipe the outside dry. Insert into the holder and close the lid.

6) Adjust the sensitivity control to set meter response near the end of the scale, say 9.0. Do not disturb this knob after this adjustment.

7) Rinse and fill the same cuvette again with distilled water (or the reference sample) and insert into the holder after wiping the outside dry. Check if the meter reads zero. If not, use the set zero control to get a meter reading zero. After this, do not disturb this knob. The instrument is now set for a calibration experiment or a kinetic experiment.

Precautions

1) You should not use a plastic cuvette while using organic solvents like chloroform, acetone, etc.

2) The reference sample, which is used to set the meter response to zero with the set zero control, should consist of the solvent (or a solution of lower concentration) and all reagents except the specific light-absorbing substance being studied.

3) Wash the cuvette thoroughly. Rinse it with the solvent or the solution depending on which is going to be taken in it for colorimetric measurement.

4) See to it that you do not leave any finger marks on the cuvette.

5) Keep the cuvette in the same position each time you insert it in the holder.

6) Never touch the faces of the cuvette through which light is transmitted.

7) Wipe the outside of the cuvette dry after filling and before inserting in the holder.

3.2.4 Demonstration Experiment 1 : Colorimetric Estimation of Copper Sulphate

Calibration of a colorimeter is the first step in estimating the concentration of a solution colorimetrically. In this experiment, we shall discuss the method of obtaining the calibration curve and estimating the concentration of given solution of copper sulphate.

Aim : i) To draw concentration – absorbance calibration curve for copper sulphate solution.

ii) To determine the concentration of a given copper sulphate solution.

Requirements

Apparatus

Colorimeter	–	1
Volumetric flask (100 cm^3)	–	1
Test tubes	–	10
Test tube stand	–	1
Measuring cylinder (10 cm^3)	–	1
Beaker (250 cm^3)	–	2
Burettes (50 cm^3)	–	2
Burette stand	–	2

Chemicals

Stock solution of copper sulphate (10% m/V)
copper sulphate solution of unknown concentration

Procedure

Copper sulphate solutions of various concentrations are prepared in six labelled test tubes using the stock solution. For this purpose the required volumes of water and copper sulphate solution (stock solution) are added as shown below :–

Water and copper sulphate solutions are taken in two burettes, one containing the stock solution and the other containing water.

Sample number	Volume of stock solution	Volume of distilled water	Mass by volume percentage of solution
1	0	10	0
2	2	8	2
3	4	6	4
4	6	4	6
5	8	2	8
6	10	0	10

While verifying the mass by volume percentage values entered in the table, remember that the stock solution is 10% *m/V* in strength.

It can be seen that the concentration of the six samples vary from 0 to 10% of copper sulphate (m/v).

Before estimating Cu^{2+} ions in an unknown solution, a calibration curve will have to be plotted between the concentration and the meter response in the instrument. For this we shall follow all the instructions listed under 'Method of Operation'. In keeping with instruction 2 stated there, set the selector knob on R, since copper sulphate solution has an absorption maximum in the red region. After adhering to the instructions 1 and 3 to 7, the following is done without distributing the set zero and the sensitivity knobs.

The cuvette is cleaned throughly, rinsed with sample (1) mentioned above and filled with the same. The cuvette is placed in the cuvette holder in the instrument and the meter response is recorded in observation Table 3.1. Then sample (1) is removed and the cuvette is rinsed and filled with sample (2). The cuvette with sample (2) is placed in the cuvette holder and the meter response is again noted. This procedure is repeated with the samples kept in tubes (3), (4), (5) and (6), each time noting the meter response in Table 3.1.

The cuvette is again washed, rinsed with the solution of unknown concentration (sample 7) and filled with it. The cuvette is placed in the cuvette holder and the meter response is noted in the table.

Table 3.1 : Meter Response as a Function of Concentration of Copper Sulphate

Sample number	Strength of copper sulphate in % m/v	Meter response
1	0	....
2	2	....
3	4	....
4	6	....
5	8	....
6	10	....
7	Unknown solution	

Calibration Curve

The calibration curve (Fig. 3.3) is plotted in a graph sheet using the values of strength of copper sulphate solution and meter response from Table 3.1.

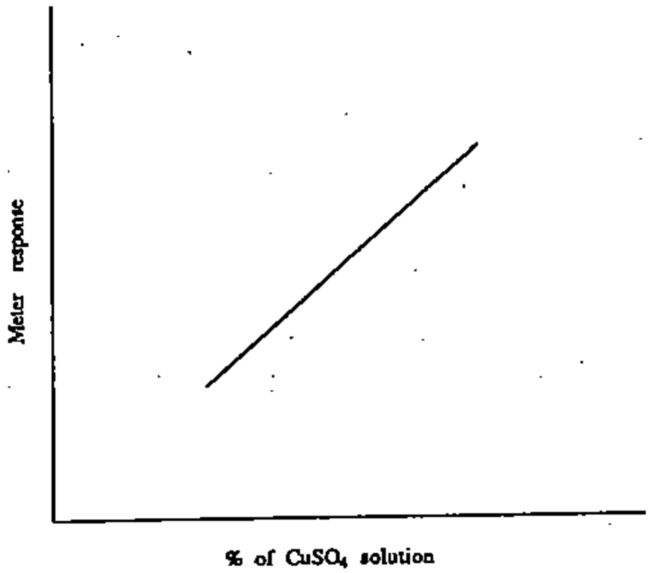


Fig.3.3 : Calibration Curve.

Using the Calibration Curve

In the interpolation method, the concentration of the unknown solution lies between the upper and lower limits of concentrations of standard solutions used for colorimetric measurement.

The concentration of the test solution (solution of unknown concentration of copper sulphate) is found out by interpolation method. For this, a dotted straight line is drawn from the point corresponding to the meter response of the test solution. The x–coordinate corresponding to the point of intersection of the calibration curve and the dotted line gives the strength of the test solution as shown in Fig. 3.4.

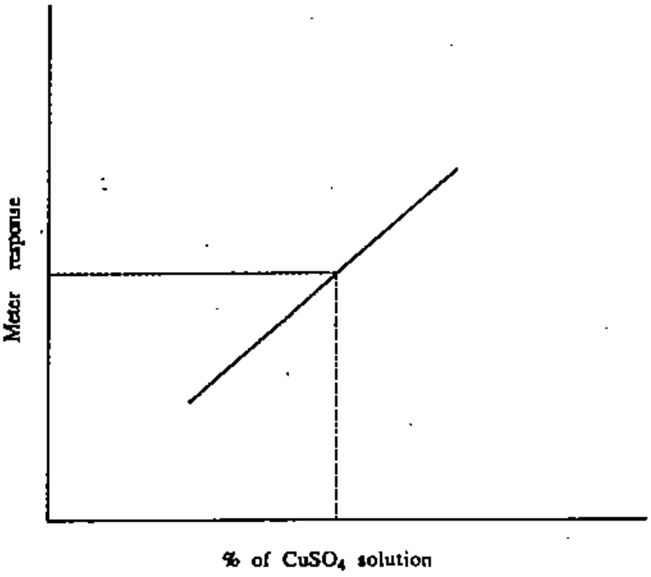


Fig. 3.4: Finding the concentration of the unknown solution using the interpolation method.

Result

From the graph, % of copper sulphate solution = ... % m/V

SAQ 1

For a substance, ε is equal to 245 $m^2\,mol^{-1}$ at a wavelength of 450 nm. Calculate the concentration (in molarity units) of its solution which has an absorbance of 0.1250, when placed in a cell of thickness 1.00×10^{-2} m.

Hints : (i) Use Eq. 3.1 (ii) Note that ε is in $m^2\,mol^{-1}$ units and l is in m unit. Hence c will be in $mol\,m^{-3}$ units.

To get c in molarity unit, use the following relationship:

$$1\ mol\ m^{-3} = 1\ mol\ (10\ dm)^{-3}$$

$$= 1 \times 10^{-3}\ mol\ dm^{-3}$$

$$= 1 \times 10^{-3}\ M$$

$$[\text{since } 1\ M = 1\ mol\ dm^{-3}$$

$$= 1\ mol\ per\ litre]$$

. . . .

. . . .

. . . .

3.3 CONDUCTOMETRY

Conductometry deals with the measurement of electrical conductance of solutions containing ions. These solutions conduct electric current due to the movement of ions towards oppositely charged electrodes. The ability of a solution to conduct current is given by its conductivity. The conductivity of a solution is proportional to the number of ions, the charge on each ion and the speed with which the ions move. The speed with which an ion moves in turn depends on the nature of the ion, nature of the solvent, presence of other ions, temperature and the applied field.

Conductometric measurements find a wide range of applications. These are used in determining equilibrium constants, e.g. ionisation constants of weak electrolytes, solubility products of sparingly soluble salts, hydrolysis constant, etc. Reactions that proceed with the formation or disappearance of ions can be conveniently monitored conductometrically for getting their kinetic parameters. Some substances which cannot be volumetrically or potentiometrically analysed can be estimated conductometrically with ease.

3.3.1 Theory

Ionic solutions obey Ohm's law just as metallic conductors do. In accordance with Ohm's law, the current I passing through a given solution is proportional to the potential difference, E. The proportionality constant R is the resistance of the solution.

$$E = IR \qquad \dots (3.2)$$

The conductance G is defined as the reciprocal of resistance.

$$G = 1/R \qquad \dots (3.3)$$

Resistance is measured in ohm (Ω)and conductance in siemens (S), 1S = 1 Ω^{-1}.

The resistance of a homogeneous body of uniform cross section is proportional to its length, l and inversely proportional to its cross-section; A. The proportionality constant is called the resistivity (specific resistance), ρ. The units of ρ are Ω m.

$$R = \rho\,(l/A) \qquad \ldots (3.4)$$

The conductivity κ (Kappa) is the inverse of resistivity.

i.e.,
$$\kappa = \frac{1}{\rho} \qquad \ldots (3.5)$$

The units of κ are S m^{-1}.

Conductivity of a solution can be defined as the conductance of a solution contained between two parallel electrodes which have cross-sectional area 1 meter square and which are kept 1 meter apart.

Taking the inverse of Eq. 3.4, $\frac{1}{\mathrm{R}} = \frac{1}{\rho} \cdot \frac{1.}{(l/A)}$

$= \kappa/(l/A)$ (using Eq. 3.5)

using Eq. 3.3., $G = \kappa/(l/A)$

or
$$\kappa = G\,(l/A) \qquad \ldots (3.6)$$

The ratio l/A is called the cell constant and it depends on the geometry of the cell — the distance between the electrodes (l) and the area of the electrodes (A). Eq. 3.6 can be written as

Conductivity = Conductance × cell constant ... (3.7)

The cell constant values are usually obtained by an indirect method and not by measuring l and A directly. The indirect method involves measuring the conductance G of a standard solution of KCl of known conductivity, κ. Table 3.2 gives the κ values of KCl solutions at three different concentrations and at three different temperatures.

Table 3.2 : Conductivity of KCl solutions

[KCl]/M	κ/S m^{-1} at 20°C	κ/S m^{-1} at 30°C	κ/S m^{-1} at 40°C
0.10	1.167	1.412	1.662
0.02	0.250	0.304	0.357
0.01	0.127	0.154	0.179

Standard KCl solution is taken in the cell for which cell constant is to be determined. Conductance of this solution is then measured and its temperature is noted. The conductivity at the temperature is obtained from Table 3.2.

We can get the κ value of KCl at temperatures other than those given in Table 3.2 from a plot of conductivity against temperature using the values given inTable 3.2.

Then the cell constant can be calculated using Eq. 3.7:

$$\text{Cell constant} = \frac{\text{Conductivity of KCl solution}}{\text{Conductance of the same solution}} \qquad \ldots (3.8)$$

This cell of known cell constant is used for finding out the conductivity of any other sample. For this, we have to measure the conductance of a given sample and then use Eq.3.7.

Conductivity of a molar solution is termed molar conductivity. Molar conductivity is represented by the symbol, Λ_m.

$$\Lambda_m = \frac{\kappa}{c} \qquad \ldots (3.9)$$

where κ is the conductivity of a solution of concentration c mol m^{-3}. Λ_m is expressed in units of S m^2 mol^{-1}.

Concentration in mol m^{-3} units = Concentration in molarity × 1000

You are provided with a low-cost conductometer (Fig. 3.5) for conductance measurement. It has an operational amplifier based circuit. Operational amplifier consists of many components mounted on a single silicon chip. Operational amplifiers have a variety of uses and, are particularly useful in low-cost instruments. We shall not discuss the principle behind the functioning of operational amplifiers, since the same is not necessary to do our experiments. For a detailed discussion on operational amplifiers, you are advised to go through Unit 9 of Block 3 of Electrical circuits and Electronics (PHE-10) course.

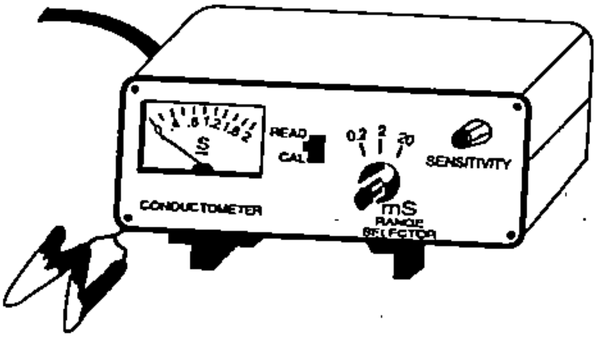


Fig. 3.5 : Low cost conductometer

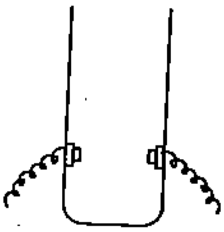


Fig. 3.6 : Low cost conductivity cell

The low cost conductometer is easy to assemble and maintain. The low cost conductometer is more convenient to use, especially for studying reactions conductometrically in kinetics experiments; we shall be using this instrument in Experiment 21 of this course.

The commercial conductometers are based on wheatstone bridge principle which is explained in Unit 16 of Block 4 of Physical Chemistry (CHE-04) course.

The commercial conductivity cells are expensive due to the usage of platinum electrodes. On the other hand low-cost conductivity cell (Fig. 3.6) is made of zero-cost carbon rods. These carbon rods are obtained from exhausted dry batteries. Using these carbon rods, conductivity cells of various designs can be easily made.

The conductance of solutions increases with increase in temperature. This is due to the increase in the velocity of ions, decrease in the viscosity of the medium, and decrease in the interactions between ions. In the case of weak electrolytes, the increase in the degree of ionisation with increase in temperature also contributes to the increase in conductance. Generally the conductivity of aqueous solutions increases by about 2% per degree celsius rise in temperature. Hence it is advisable to keep solutions in a thermostat till they acquire constancy in temperature. Conductance, conductivity and molar conductivity values are to be given along with the temperature values.

As ordinary distilled water contains impurities like CO_2, metal silicates, etc., it cannot be used for preparing solutions for very accurate conductance measurements. When conductance values of high accuracy are required, conductivity water is to be used.

For the conductance experiments of this course, distilled water or deionised water is adequate, as long as the conductivity of water is not more than 10^{-5} S cm^{-1} or 10^{-3} S m^{-1}

3.3.2 Various Controls of the Low-Cost Conductometer

Power Switch

This switch is on the back of the instrument. This is used to turn the instrument on or off. When the instrument is connected to the mains (220 V, AC supply) and switched on, the indicator LED on the front panel glows.

Range Selector

This control is on the front panel of the instrument. It has positions marked 0.2, 2, 20. These numbers stand for the full scale meter values in millisiemens (mS). This means, for example, when the selector is at 20, the meter reads between 0 and 20 mS.

Mode Selector

This control is also on the front panel of the instrument. It has positions marked CAL and READ. This is used to set the instrument in either the calibration (CAL) or read (READ) mode. The instrument is kept on CAL mode when the meter is being calibrated to read 0.1, 1, or 10 mS (mid point of the scale in the range 0.2, 2, or 20 mS, respectively) using the sensitivity control. When the instrument is on CAL mode, a standard resistor inside the instrument replaces the conductivity cell in the circuit. The cell is in circuit only when the control is on READ mode.

Sensitivity

This control, which is also on the front panel, is used while calibrating the meter.

3.3.3 Method of Operation

The following instructions will help you in using the conductometer.

1) Check the mechanical zero of the meter before connecting the instrument to the mains. If the needle is not showing zero, then adjust this using a small screw driver inserted into the hole under the meter. Then connect the instrument to the mains and switch on the instrument using the power switch.

2) Take the minimum volume of the solution (for which conductance is to be measured) in the conductivity cell and, connect the cell to the instrument.

3) Keep the mode selector at READ.

4) Set the range selector at one of the positions, 0.2. or 2 or 20, such that the position which gives a meter reading is around the middle of the scale.

5) Shift the mode selector at CAL. Then adjust the sensitivity control to set the meter reading to mid–scale. After this adjustment, do not disturb the sensitivity control. The steps 1 to 5 are collectively known as **calibration** of the conductometer.

A minimum volume of solution is required to be taken in the cell for measuring the conductance of the solution. This varies from cell to cell and has to be experimentally obtained. This minimum volume is little more than the volume of solution required to just immerse the electrodes. This volume can be determined by taking a strong electrolyte, for example, a solution of KCl. Measure out a volume, say 5 cm^3, into the cell, calibrate the meter and determine the conductance. Then add KCl solution in 1 cm^3 lots and measure the conductance after each addition. The volume of solution beyond which conductance remains constant is the minimum volume. This volume can also be obtained graphically by plotting conductance vs volume of solution (Fig. 3.7).

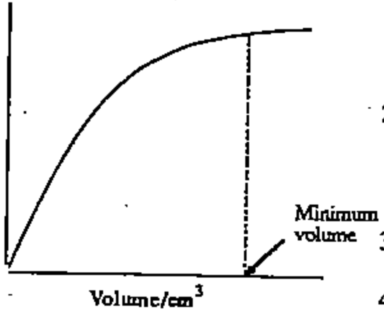


Fig. 3.7 : Conductance vs. volume of solution plot for determining the minimum volume.

For any conductance measurement using this cell, the volume of solution to be taken has to be equal to or more than the minimum volume.

6) Set the Mode selector to READ and read the meter to get the actual conductance value of the solution.

Precautions

1) Measurement of conductance in the course of a titration or a kinetic experiment may require shifting the Range Selector control. Every time you change the range, you have to check if the meter calibration is alright.

2) Conductivity cells should never be left with any solution or without proper cleaning after an experiment. After cleaning and rinsing well with distilled water or deionised water, leave the cell with electrodes well immersed in distilled/deionised water.

3) Rinse the conductivity cell well with the test solution a couple of times before filling the cell for measuring conductance.

4) You must keep the mode selector at CAL (and not at READ) under the following conditions:

    - at the time of disconnecting the conductivity cell
    - changing the solution in the cell
    - at the time of connecting the cell but before pouring the solution into it.

5) If for any experiment you have to stir the solution in the conductivity cell, then keep the stirring rod above the solution while reading the meter.

The method of measuring the conductance of a solution can be understood from Demonstration Experiment 2.

3.3.4 Demonstration Experiment 2: Determination of Conductance of Given Sodium Hydroxide Solution

We shall use the low-cost conductometer to find out the conductance of 0.01275 M NaOH solution. This experiment will help you in doing Experiment 21 of this course which deals with the kinetics of saponification of ester.

Aim : To find the conductance of 0.01275 M NaOH solution.

Requirements

Apparatus

Conductometer	–	1
Conductivity cell	–	1
Wash bottle	–	1

Chemicals

0.01275 M sodium hydroxide solution

Deionized water

Procedure

Before filling the conductivity cell with 0.01275 M NaOH solution, it is washed with water and rinsed with the given NaOH solution. The instructions 1 to 4 given under "method of operation" are followed. We find out that it is preferable to place the range selector at 20, since it leads to a meter reading around the middle of the scale. The sensitivity control is adjusted to set the meter reading to midscale. After this adjustment, the sensitivity control is not disturbed. The mode selector is shifted to "READ" position. The conductance of the given NaOH solution is found out and the value is entered as shown below:

The conductance of 0.01275 M NaOH solution = ... mS

SAQ 2

The conductivity of 0.1000 M potassium chloride solution is 1.167 S m^{-1} at 293 K. Calculate its molar conductance. (**Hint** : Use Eq. 3.9).

. . . .

. . . .

. . . .

3.4 POTENTIOMETRY

Potentiometry deals with the measurement of difference in potential between two electrodes which have been combined to form an electrochemical cell. The electrochemical cells are of two types, galvanic cells and electrolytic cells. In galvanic or voltaic cells, chemical energy is transferred into electrical energy. As a result of this, galvanic cells act as a source of electrical energy. Daniell cell which we are going to study in detail, is a familiar example of a galvanic cell. In electrolytic cells, electrical energy is transformed into chemical energy. In electrolytic cells, application of voltage higher than that of the cell results in a chemical reaction. For example, passage of electricity through acidified water causes electrolysis of water. It results in the production of hydrogen and oxygen at the cathode, and anode respectively.

The difference in potential between the two electrodes of a galvanic cell is known as cell potential. The cell potential depends on the composition of the electrodes, concentrations of the solutions (or pressures of gases) and the temperature. Relationship connecting the cell potential with the concentration of the species involved in the concerned chemical reaction, known as Nernst equation, can be derived using thermodynamic principles. A detailed discussion is given regarding this in Sec. 17.6 of Unit 17 of Physical chemistry (CHE-04) course. Based on the dependence of cell potential on the concentration of the species in the cell, we have used mV/pH meter in CHE-03(L) course as an analytical tool in acid-base titration. In this course, we shall use mV/pH meter for the determination of pH of buffer solutions and the solubility product of silver chloride. In order to understand the above two experiments, we shall study the galvanic cells in a detailed way.

The mV/pH meter owes its name to the fact that it is useful in measuring the potential difference of cells (in mV units) and in determining pH of the solutions.

3.4.1 Galvanic Cells and Cell Reaction

There are many types of galvanic cells. We are interested in such galvanic cells in which the electrodes are dipped in different electrolytes. We shall illustrate the functioning of galvanic cells using Daniell cell (Fig. 3.8).

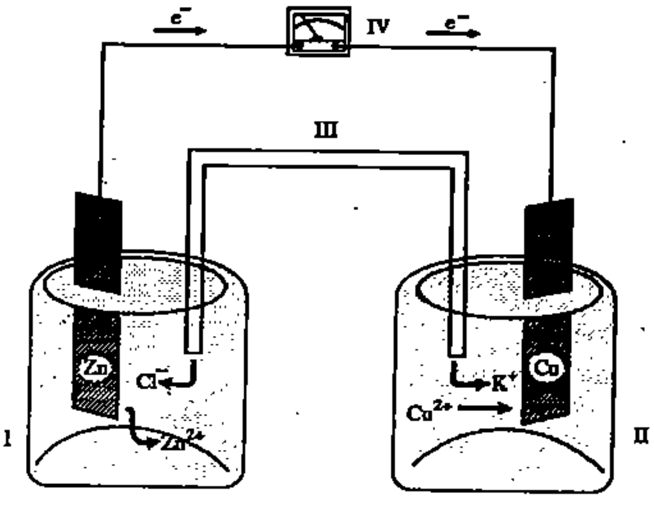


Fig. 3.8 : Daniell cell

I) anodic compartment, II) cathodic compartment, III) salt bridge, IV) voltmeter.

In Daniell cell, zinc gets oxidised to Zn^{2+} ions. Two electrons are released per each zinc ion formed. These electrons travel towards the copper electrode and are used in the reduction of Cu^{2+} ions to Cu. These two reactions can be written as follows:

$$Zn(s) \longrightarrow Zn^{2+}(c_1) + 2e^- \qquad \text{Oxidation} \qquad \ldots (3.10)$$

$$Cu^{2+}(c_2) + 2e^- \longrightarrow Cu(s) \qquad \text{Reduction} \qquad \ldots (3.11)$$

An electrode dipping in an electrolyte constitutes a half-cell. For instance, zinc rod dipping in zinc sulphate solution of concentration c_1 constitutes a half-cell and copper rod dipping in copper sulphate solution of concentration c_2 constitutes another half-cell. Daniell cell is made by the combination of two half-cells. The cell reaction in Daniell cell is the combination of two half-cell reactions (given by Eqs. 3.10 and 3.11) and is represented below by Eq. 3.12.

$$Zn(s) + Cu^{2+}(c_2) \longrightarrow Zn^{2+}(c_1) + Cu(s) \qquad \ldots (3.12)$$

Knowing the type of reaction taking place in a cell, we can represent the cell on paper. For this, the following rules will be helpful.

1) The oxidation part must appear on the left side of the cell. The reduction part must appear on the right side of the cell. The stoichiometric numbers, the electrons and water molecules appearing in the half cell reaction (or cell reaction) must not find a place in the cell representation.

2) 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.

3) In case of gas electrodes, and many oxidation-reduction systems like quinone-hydroquinone, inert electrodes such as carbon rod or platinum wire are used for electrical contact.

4) The various materials present in the same half-cell in the same phase are written together separated by commas.

5) Double vertical lines are used to join the two half-cells; this means a salt bridge is used between the two half-cells. We shall shortly understand the use of salt bridge in galvanic cells.

6) Concentrations of ions, pressures of gases etc. are indicated in brackets and mentioned along with the substance.

In the light of these rules, you can understand the representation of Daniell cell which is given below:

$$Zn(s)\ |\ Zn^{2+}(c_1)\ |\ |\ Cu^{2+}(c_2)\ |\ Cu(s) \qquad \ldots (3.13)$$

3.4.2 Measurement of E.M.F.

The potential difference across an electrode-electrolyte interface is called electrode potential.

The cell potential of a galvanic cell (E_{cell}) is given by the difference between the two electrode potentials, E_1 and E_2, of the cathode and anode, respectively.

$$E_{cell} = E_1 - E_2 \qquad \ldots (3.14)$$

The junction potential developed at the liquid junction between the two half-cells also contributes to the cell potential. But this liquid junction potential can be minimised by having a salt bridge between the two electrodes.

A salt bridge serves to

- maintain electrical neutrality within the solutions in the two half-cells
- minimise the liquid junction potential
- complete the circuit.

Let us now study the construction of salt bridge.

Preparation of Salt Bridge

Agar-agar forms a dispersion of liquid in solid (i.e., a gel) which becomes a thick mass. It prevents the free flow of KCl/KNO_3 into the two half-cells.

Bend a glass tube in U-shape on a burner. Prepare the agar-agar solution as follows: 0.3–0.5 g of powdered agar-agar is dissolved in 10 cm^3 of saturated solution of KCl/KNO_3 at 100°C on a steam bath (add agar-agar powder in small quantities so that solution does not froth). Keep the solution at 100°C until all the agar-agar has passed into the solution. Then add 1–1.5 g of KCl/KNO_3 to produce excess of the solid. Now connect the side arm of the bent U–tube to a rubber tubing and suck the hot solution from the other end of the ruber tubing. On cooling, the agar-agar solidifies and this acts as a salt bridge.

Instead of a salt bridge, a filter paper strip soaked in a saturated solution of KCl or KNO_3 can also be used across the two half-cells.

Let us now discuss the measurement of cell potential. If a current is drawn from a cell in the course of the measurement of cell potential, the cell reactio proceeds and the concentrations of the solutions change in the two half-cells. Hence, it is important to measure the cell potential without allowing current to flow. The cell potential measured nearly under zero or negligible current flow is called electromotive force (e.m.f.) of the cell. We shall be using low-cost mV/pH meter for measurement of e.m.f. and pH.

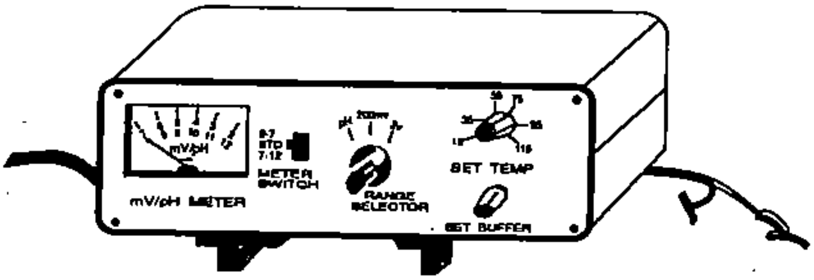


Fig. 3.9 : Low-cost mV/pH meter

The low-cost mV/pH meter (Fig. 3.9) has a circuit based on operational amplifier. This instrument draws only negligible current and hence is quite useful in the measurement of cell e.m.f. Another advantage is that it uses carbon electrodes for pH measurement. A carbon rod extracted from used dry batteries works as the electrode. This electrode is available almost at zero cost. Two carbon electrodes are provided with each low-cost mV/pH meter.

The two half-cells constituting a galvanic cell are known as the indicator half-cell and the reference half-cell. The reference half-cell potential is maintained constant and the indicator half-cell potential is allowed to vary in an experiment.

When we use mV/pH meter for the measurement of concentration of a species (such as in the measurement of pH of buffers or determination of solubility product of a salt), the concerned species must be made the electrolyte in the indicator half-cell. Before studying the various controls of the mV/pH meter, we should familiarise ourselves with Nernst equation.

3.4.3 Nernst Equation

The relationship between e.m.f. of a cell (or half-cell potential) and the concentration of species involved in cell reaction (or half-cell reaction) is given by Nernst equation. Let us consider the following cell reaction.

$$aA + bB \rightleftharpoons cC + dD \qquad \ldots (3.15)$$

Nernst equation applicable to this reaction is given below:

$$E_{\text{cell}} = E^0_{\text{cell}} + \frac{2.303RT}{nF} \log \frac{[A]^a [B]^b}{[C]^c [D]^d} \qquad \ldots (3.16)$$

where

- A and B are reactants and C and D are products in the cell reaction
- a, b, c and d are stoichiometric coefficients.
- $E^0_{\text{cell}} = E^0_{\text{RHE}} - E^0_{\text{LHE}}$; E^0_{RHE} and E^0_{LHE} are the standard electrode potentials of the electrodes at the right hand and left hand sides. The standard electrode potentials of some electrodes are given in Table 3.3. The standard electrode potential is the potential at the electrode when the species at the electrode are in

As per IUPAC convention, the standard electrode potential is mentioned for the reduction of a specified species at the electrode.

their standard states at 1 bar (= 10^5 Pa ≈ 1 atm) pressure at any specified temperature and at unit concentration. The temperature usually chosen is 298 K.

- *n* is the number of electrons involved in the cell reaction
- *F* is equal to 96500 coulombs
- *T* is temperature
- [A], [B], [C] and [D] are the concentrations of the concerned reactants and products.

Table 3.3: Standard Electrode Potentials

Half-cell reactions	E^o/V
$Li^+ + e^- \longrightarrow Li$	−3.05
$K^+ + e^- \longrightarrow K$	−2.93
$Ca^{2+} + 2e^- \longrightarrow Ca$	−2.87
$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.36
$Al^{3+} + 3e^- \longrightarrow Al$	−1.66
$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.76
$Fe^{2+} + 2e^- \longrightarrow Fe$	−0.44
$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.14
$Pb^{2+} + 2e^- \longrightarrow Pb$	−0.13
$Fe^{3+} + 3e^- \longrightarrow Fe$	−0.04
$2H^+ + 2e^- \longrightarrow H_2$	0.00
$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
$Cu^+ + e^- \longrightarrow Cu$	+0.52
$I_2 + 2e^- \longrightarrow 2I^-$	+0.54
$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$	+0.59
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.77
$Ag^+ + e^- \longrightarrow Ag$	+0.80
$Br_2 + 2e^- \longrightarrow 2Br^-$	+1.09
$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+1.33
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+1.36
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+1.49
$F_2 + 2H^+ + 2e^- \longrightarrow 2HF$	+2.87

For the calculation of electrode potentials when the concentration of the species at the electrode is not equal to unity, we have to use the following modified forms of Eqs. 3.15 and 3.16.

$$\text{Half-cell reaction: } A^{n+}(c) + ne^- \longrightarrow A(s, l \text{ or } g) \qquad \ldots (3.17)$$

$$\text{Nernst equation: } E = E^0 + \frac{2.303\,RT}{nF} \log c \qquad \ldots (3.18)$$

Where E and E^0 are the electrode potential and standard electrode potential respectively and c is the concentration of the solution in contact with the electrode.

We shall next discuss the types of electrode systems.

3.4.4 Types of Electrodes

A large number of electrodes are known. For convenience, the electrode systems are divided into various types. We shall discuss the following three types:

i) Metal-metal ion type

A metal is in equilibrium with its ions in solution. We shall study the following three examples under this type.

1) zinc-zinc sulphate solution
2) copper-copper sulphate solution
3) silver-silver nitrate solution

ii) Metal-insoluble salt type

A metal is in contact with a saturated solution of its sparingly soluble salt and another soluble salt having common anion.
We shall study the following example:

Silver-silver chloride-potassium chloride solution

iii) Redox electrodes

These electrode systems have species in solution in two different oxidation states. We shall discuss the following example:

Carbon–quinone–hydroquinone

The carbon rod is an inert electrode and is used for electrical contact: Some other familiar examples of redox electrodes are given below; we will not be discussing them in detail.

Platinum–ferric ion–ferrous ion
Platinum–permanganate ion–manganous ion

These two are used in acid medium.

Let us discuss in detail some of the half-cells coming under the above types of electrodes.

I) Zinc-zinc sulphate half-cell

The half-cell representation for zinc electrode is,

$$Zn(s) \mid ZnSO_4(c)$$

Where c is the concentration of zinc sulphate solution,
The half-cell reaction is,

$$Zn^{2+}(c) + 2e \longrightarrow Zn(s) \qquad \ldots (3.19)$$

This electrode is reversible with respect to Zn^{2+} ion.

The electrode is said to be reversible with respect to such ion or ions which take(s) part in the half-cell reaction.

The standard reduction potential for zinc ($E^0_{Zn^{2+}/Zn}$) is –0.76 V. The relationship useful in calculating the electrode potential of zinc electrode ($E^0_{Zn^{2+}/Zn}$) dipped in a solution of zinc sulphate of concentration c can be written using Eq. 3.18 as follows:

$$E_{Zn^{2+}/Zn} = E^0_{Zn^{2+}/Zn} + \frac{2.303RT}{2F}\log[Zn^{2+}] \qquad \ldots (3.20)$$

$$= E^0_{Zn^{2+}/Zn} + \frac{2.303RT}{2F}\log c$$

Construction of Zinc Electrode

A can is a container vessel.

Take a zinc rod and dip it in zinc sulphate solution of known concentration. If the zinc rod is not available, then use the can of a used dry battery. The can should be cleaned with a sand paper and the connecting wire is to be soldered.

2) Copper-copper sulphate half-cell

The half-cell representation for copper electrode is

$Cu(s) \mid CuSO_4(c)$

Where c is the concentration of copper sulphate solution.

The half-cell reaction is,

$$Cu^{2+}(c) + 2e^- \longrightarrow Cu(s) \qquad \ldots (3.21)$$

This electrode is reversible with respect to Cu^{2+} ion. The standard reduction potential for copper ($E^0_{Cu^{2+}/Cu}$) is +0.34 V. The electrode potential of copper electrode is related to the concentration of Cu^{2+} ions as per Eq. 3.22 which is written similar to Eq. 3.18.

$$E_{Cu^{2+}/Cu} = E^0_{Cu^2+/Cu} + \frac{2.303RT}{2F}\log[Cu^{2+}] \qquad \ldots (3.22)$$

$$= E_{Cu^{+}/Cu} + \frac{2.303RT}{2F}\log c$$

Construction of Copper Electrode

Take a copper rod and dip it in a solution of copper sulphate of known concentration kept in a beaker. If the rod is not available, then use a connecting copper wire.

3) Silver-silver nitrate half-cell

Silver wire can be used in the construction of

i) silver-silver nitrate half-cell which is reversible with respect to Ag^+ ions or

ii) silver-silver chloride half-cell which is reversible with respect to chloride ions. We shall discuss the former type now.

For silver-silver nitrate half-cell, the representation is

$Ag(s) \mid AgNO_3(c)$

where c is the concentration of silver nitrate solution.

The half-cell reaction is,

$$Ag^+(c) + e^- \longrightarrow Ag(s) \qquad \ldots (3.23)$$

Hence this electrode is reversible with respect to Ag^+ ion.

The standard reduction potential for Ag^+–Ag system is $(E^0_{Ag^+/Ag})$ is +0.80 V. The electrode potential of silver-silver ion electrode is related to the concentration of Ag^+ ions as per the equation,

$$E_{Ag^+/Ag} = E^0_{Ag^+/Ag} + \frac{2.303RT}{F}\log[Ag^+]$$

$$= E^0_{Ag^+/Ag} + \frac{2.303RT}{F}\log c \qquad \ldots (3.24)$$

Construction of Silver-Silver Nitrate Half-Cell

Solder a connecting wire to a small piece of silver wire and insert it from the top of a glass tube. Use araldite at the tip of the tube and keep it overnight for drying. Dip the silver wire in a solution of silver nitrate of known concentration.

We shall be using this half-cell in the determination of the solubility product of silver chloride in Experiment 9 of Block 3 of this course.

4) Silver–Silver Chloride Half–Cell

The representation for silver-silver chloride half-cell is,

$Ag(s) \mid AgCl(s) \mid KCl(c)$

where c is the concentration of potassium chloride solution.

The half-cell reaction is,

$$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(c) \qquad \ldots (3.25)$$

Hence this electrode is reversible with respect to Cl^- ion.

The standard reduction potential for this half-cell (E^0_{AgCl/Cl^-}) is 0.2223 V.

Nernst equation for this half-cell is given below:

$$E_{AgCl/Cl^-} = E^0_{AgCl/Cl^-} + \frac{2.303RT}{F}\log\frac{1}{[Cl^-]}$$

$$E_{AgCl/Cl^-} = E^0_{AgCl/Cl^-} + \frac{2.303RT}{F}\log\frac{1}{c} \qquad \ldots (3.26)$$

Construction of Silver-Silver Chloride Half-Cell

Solder a connecting wire to a small piece of silver wire and insert it from the top of a jet type glass tube. Use araldite at the tip of the tube and keep it overnight for drying. Keep the silver wire in contact with 0.1 M hydrochloric acid overnight. A fine coating of AgCl is obtained over silver wire. This can be used as Ag/AgCl electrode.

5) Quinhydrone Half-Cell

Quinhydrone is a 1:1 mixture of quinone $[C_6H_4O_2]$ represented by the symbol Q and. hydroquinone $[C_6H_4(OH)_2]$ represented by the symbol H_2Q. Quinhydrone electrode is an example of oxidation–reduction electrode. It consists of an inert electrode (carbon rod or platinum wire) dipped in a solution containing a mixture of oxidised (Q) and reduced (H_2Q) forms of a substance. The half-cell representation for quinhydrone electrode is

$C(s) \mid Q\text{–}H_2Q\,(s) \mid H^+\,(c)$

where c is the concentration of H^+ ions in solution.

The half-cell reaction is,

$$\underset{(Q)}{C_6H_4O_2(s)} + 2H^+(c) + 2e^- \longrightarrow \underset{(H_2Q)}{C_6H_4(OH)_2(s)} \qquad \ldots (3.27)$$

The standard reduction potential for quinhydrone electrode is 0.699 V. The relationship useful in calculating the electrode potential (E_{Q/H_2Q}) of quinhydrone electrode in a solution of H^+ concentration c can be written using Eq. 3.18 as follows:

$$E_{Q/H_2Q} = E^0_{Q/H_2Q} + \frac{2.303RT}{2F}\log[H^+]^2$$

$$= E^0_{Q/H_2Q} + \frac{2.303RT \times 2}{2F}\log[H^+]$$

$$= E^0_{Q/H_2Q} + \frac{2.303RT}{F}\log[H^+] \qquad \ldots (3.28)$$

$$= E^0_{Q/H_2Q} + \frac{2.303RT}{F}\log c \qquad \ldots (3.29)$$

$$= E^0_{Q/H_2Q} - \frac{2.303RT}{F}\,\text{pH} \qquad \ldots (3.30)$$

[since $-\log[H^+] = \text{pH}$]

As per Eq. 3.27, you can understand that quinhydrone electrode is reversible with respect to H^+ ions. As per Eqs. 3.28 and 3.30, the quinhydrone electrode can be employed for the calculation of $[H^+]$ and pH. In Experiment 8 of Block 3 of this course, we shall see the use of quinhydrone electrode in the determination of pH of buffer solutions. In CHE-03(L) course, quinhydrone electrode has been used in the potentiometric titration of vinegar under Experiment 2 of Block 1.

Construction of Quinhydrone Electrode

You are provided with two carbon rods to be used as electrodes. Use one of these carbon rods and dip it in a solution containing H^+ ions. Add a pinch of quinhydrone. This is quinhydrone electrode.

With this brief introduction to the elementary concepts of potentiometry, let us now take up the functions of the various controls of a mV/pH meter and the method of operation.

3.4.5 Various Controls of the Low-Cost mV/pH Meter

Power Switch : This is located on the back panel of the instrument. This is used to turn the instrument OFF/ON. After connecting the instrument to the mains, if this switch is turned on, the LED on the front panel will glow.

Range selector : This switch on the front panel of the instrument may be put on three positions marked pH, 200 mV and 2V. This brings into the circuit the pH scale, the 200 mV scale or 2 V scale. When the switch indicates pH, the meter reads between pH 2 and 7 or between 7 and 12; at 200 mV, the meter reads between 0 and 200 mV; and at 2 V, the meter reads between 0 and 2 V.

Meter switch	:	This is a sliding switch with three positions on the front panel. The middle position serves as a standby position (i.e., "off" position) when the meter is not in circuit. This switch is used to reverse the polarity of connections to the meter for measurements in the pH range 2–7 or 7–12.
Set temperature	:	This knob on the front panel has a scale marked in degree celsius. You must adjust it to read the temperature of the test solution.
Set Zero	:	This knob on the front panel is used for calibrating the instrument. While calibrating for e.m.f. measurement, this knob is used to bring the meter reading to zero. When the meter is being calibrated for reading pH, this knob is used to set the meter at the pH of the indicator cell solution.
Set slope	:	There are two knobs located on the back panel; the lower knob is used during e.m.f. calibration and the upper one is used for the pH calibration.
Cell Connection		There are two arrangements for connecting the cells to the instrument. For cells using carbon electrodes, two lead wires with black and red crocodile clips are provided. The black goes to the reference half-cell and the red to the indicator half-cell. The other arrangement has a socket on the back panel for plugging a commercial glass electrode; a terminal is provided nearby for a reference electrode, e.g., calomel electrode.

3.4.6 Method of Operation

Before using the pH meter, it is necessary to calibrate it. Check the mechanical zero of the meter before turning it on. If the needle is not showing zero, then adjust it inserting a small screw driver into the hole under the meter. The calibration for e.m.f. measurement is given below. The calibration for pH measurement will be done in Experiment 8 of Block 3 of this course.

Calibration of the instrument for e.m.f. measurement

1) Connect the instrument to the mains and switch it on. The LED on the front panel should glow.

2) Short the two input leads. Shift the meter switch to 2–7 or 7–12 position. If the meter does not read zero, adjust the set zero knob until it does. Do not disturb this knob.

3) Use a calibrated voltage source, such as the AVO source to obtain 200 mV. Keep the meter switch at STANDBY position. Connect the voltage source to the mV/pH meter at the cell connection terminals — positive lead of the voltage source to the red terminals. Shift the meter switch to 2–7 position and the selector switch to the 200 mV range.

4) Adjust the lower knob of the set slope until the meter reads full scale. With this adjustment, the meter is calibrated to read between 0 and 200 mV.

After this, the lower set slope knob is not to be disturbed for the rest of the experiment.

5) This calibrates the 2 V range also. You can check that by shifting the selector switch to the 2 V range and, by including a 2 V calibrated input at the cell connection terminals. Once the instrument is calibrated, you can connect any cell for which e.m.f. is to be measured at the cell connection terminals and, read the e.m.f. Each division is equal to 4 mV in the 200 mV range and 40 mV in the 2 V range.

To explain the construction of a galvanic cell and the use of mV/pH meter in e.m.f. measurement, the following demonstration experiment is given.

3.4.7 Demonstration Experiment 3: Construction of Daniell Cell and Measurement of E.M.F.

We shall illustrate the way of construction of a galvanic cell and measuring the e.m.f. For this, we shall construct Daniell cell. This experiment will help you in performing experiments 8 and 9 of Block 3 of this course.

We shall construct Daniell cell using 0.01 M $ZnSO_4$ and 0.1 M $CuSO_4$. The cell can be represented as follows:

$$\mathrm{Zn}(s)\ |\ \mathrm{Zn^{2+}}(0.01\ \mathrm{M})\ ||\ \mathrm{Cu^{2+}}(0.1\ \mathrm{M})\ |\ \mathrm{Cu}(s)$$

The cell reaction for Daniell cell can be written as follows:

$$\mathrm{Zn}(s) + \mathrm{Cu^{2+}}\ (0.01\ \mathrm{M}) \longrightarrow \mathrm{Zn^{2+}}(0.01\ \mathrm{M}) + \mathrm{Cu}(s) \qquad \ldots (3.31)$$

You can see that this equation is obtained by subtracting Eq. 3.19 from Eq. 3.21 since, Zn gets oxidised to Zn^{2+} and Cu^{2+} gets reduced to Cu. You know that Eqs. 3.19 and 3.21 are written for the reduction of the concerned species only. Again Nernst equation applicable to Eq. 3.31 is obtained as follows by subtracting Eq. 3.20 from Eq. 3.22.

$$E = E^0_{\mathrm{Cu^{2+}/Cu}} + \frac{2.303RT}{2F}\log[\mathrm{Cu^{2+}}] - \left(E^0_{\mathrm{Zn^{2+}/Zn}} + \frac{2.303RT}{2F}\log[\mathrm{Zn^{2+}}]\right)$$

$$= \left(E^0_{\mathrm{Cu^{2+}/Cu}} - E^0_{\mathrm{Zn^{2+}/Zn}}\right) + \frac{2.303RT}{2F}\log\frac{[\mathrm{Cu^{2+}}]}{[\mathrm{Zn^{2+}}]} \qquad \ldots (3.32)$$

$$E = \left(1.1 + \frac{2.303RT}{2F}\log\frac{[\mathrm{Cu^{2+}}]}{[\mathrm{Zn^{2+}}]}\right)\mathrm{V} \qquad \ldots (3.33)$$

Aim

i) To construct Daniell cell

ii) To find the e.m.f. of Daniell cell

Requirements

Apparatus

Copper rod
Zinc rod
Salt bridge or filter paper strip
Beaker (100 cm^3)
mV/pH meter
Connecting wires

Chemicals

0.1 M copper sulphate solution

0.01 M zinc sulphate solution

Saturated potassium nitrate solution.

Procedure

First mV/pH meter has to be calibrated as per the instruction given under "calibration of the instrument for e.m.f. measurement".

Next the zinc rod is dipped in a solution of 0.01 M zinc sulphate. The copper rod is dipped in 0.1 M copper sulphate solution. The zinc half-cell is connected to the indicator terminal of the mV/pH meter. The copper half-cell is connected to the reference terminal of the instrument. The two half-cells are connected by means of a potassium nitrate salt bridge or by means of a filter paper soaked in saturated potassium nitrate solution.

The diagram of Daniell cell is given in Fig. 3.8.

The e.m.f. of the cell is measured. The measurement is made at least two more times and the average e.m.f. value is taken. The result is entered as follows:

Temperature = ... K

The e.m.f. of Daniell cell containing 0.1 M $CuSO_4$ solution and 0.01 M $ZnSO_4$ solution measured using mV/pH meter:

i) first measurement = ... V

ii) second measurement = ... V

iii) third measurement = ... V

Average e.m.f. = ... /3 V

= V

The calculated value of e.m.f. of the above Daniell cell using Eq. 3.33 = 1.295 V

SAQ 3

Calculate the e.m.f. of the following cell at 298 K:

$$Zn(s) \mid ZnSO_4\,(5.0\times10^{-3}M) \parallel CuSO_4\,(5.0\times10^{-1}\,M) \mid Cu(s)$$

Hints: (i) Use Eq. 3.33 (ii) Since $E^0_{Cu^{2+}/Cu}$ and $E^0_{Zn^{2+}/Zn}$ are quantities defined by standard state, $E^0_{Cu^{2+}/Cu}$, $E^0_{Zn^{2+}/Zn}$ and $E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn}$ (which is equal to 1.1 V) are considered to be exact quantities. Hence '1.1' is supported to have infinite significant figures. (iii) $\frac{2.303RT}{F} = 0.059$ V

. . . .

. . . .

. . . .

3.5 SUMMARY

In this unit, we have discussed the principles of colorimetery, conductometry and potentiometry. We have explained the use of low-cost instruments in measuring absorbance, conductance and e.m.f. We have described three demonstration experiments to illustrate the use of the low-cost instruments.

3.6 ANSWERS

1) According to Eq. 3.1, $c = \frac{A}{\varepsilon l}$

$$= \frac{0.1250}{245 \times 1.00 \times 10^{-2}} \text{ mol m}^{-3}$$

$$= \frac{0.1250 \times 10^{-3}}{245 \times 1.00 \times 10^{-2}} \text{ mol dm}^{-3}$$

$$= 5.10 \times 10^{-5} \text{ M.}$$

2) Using Eq. 3.9, $\Lambda_m = \frac{\kappa}{c} = 11.67 \text{ S m}^2 \text{ mol}^{-1}$

3) $[Cu^{2+}] = 5.0 \times 10^{-1}$ M

$[Zn^{2+}] = 5.0 \times 10^{-3}$ M

Using these values in Eq. 3.33,

$$E = \left(1.1 + \frac{0.059}{2} \log \frac{5.0 \times 10^{-1}}{5.0 \times 10^{-3}}\right) \text{ V}$$

$$= \left(1.1 + \frac{0.059}{2} \times 2.00\right) \text{V}$$

$$= (1.1 + 0.0590) \text{ V}$$

$$= 1.1590 \text{ V}$$

FURTHER READING

1. Senior Practical Physical Chemistry, B.D. Khosla, A. Gulati and V.C. Garg, R. Chand & Co., New Delhi, 4th ed., 1985.

2. Practical Chemistry, S. Giri, D.N. Bajpai and O.P. Pandey, S. Chand & Company Ltd., New Delhi, 7th ed., 1993.

Utter Pradesh
Rajarshi Tandon Open University

UGCHE-L4

Chemistry Lab. IV

lock

2

ROPERTIES OF LIQUIDS AND THERMOCHEMISTRY

NIT 4
urface Tension 5

NIT 5
iscosity of Liquids 17

NIT 6
hermochemistry 27

NIT 7
etermination of Enthalpy of Neutralisation and Ionisation 39

BLOCK 2 PROPERTIES OF LIQUIDS AND THERMOCHEMISTRY

Introduction

In Block 1 of this course, you studied about some basic laboratory skills and techniques. By now, you must have understood how to carry out simple laboratory operations like

- weighing a solute
- using a thermometer
- tabulating your observations, plotting a graph and maintaining your laboratory record.

You are now welcomed to the laboratory for performing actual experiments. You are advised to go through this block and understand the concepts explained before starting the experiments. This block contains 4 units. The first two units of this block, viz., Units 4 and 5 are based on the study of properties of liquids while the other two units, i.e., Units 6 and 7 are devoted to the thermochemical measurements.

In Unit 4, you will study about the measurement of surface tension of aqueous solutions of common household detergents.

Unit 5 deals with the measurement of another property of liquids, i.e., viscosity.

Unit 6 discusses the determination of the enthalpy of solution of a solute. It also describes the determination of the heat capacity of a calorimeter.

Unit 7 explains how to determine the enthalpies of neutralisation of
(i) a strong acid with a strong base and
(ii) a weak acid with a strong base.
This data will be used for the determination of enthalpy of ionisation of the weak acid.

Keeping the above objectives in mind, we have designed six experiments. The details of these experiments have been explained in the units mentioned above. So, start studying the contents.

Wishing you all good luck in these experiments.

Objectives

After studying this block and performing the experiments, you should be able to:

- explain the concept of surface tension and various phenomena associated with it,
- state the factors affecting the surface tension,
- define the coefficient of viscosity and write its units (both in SI and c.g.s. systems),
- discuss the variation of viscosity with temperature,
- describe the first law of thermodynamics,
- state the principle of calorimetry,
- define the enthalpy of solution, enthalpy of neutralisation and enthalpy of ionisation and explain the method of their determination.

UNIT 4 SURFACE TENSION

Structure

4.1 Introduction
4.2 Surface Tension
  Surface Free Energy
  Interfacial Tension
  Capillary Action
4.3 Factors Affecting Surface Tension
  Effect of Surfactants
  Effect of Temperature
4.4 Measurement of Surface Tension
4.5 Experiment 1 : (i) Determination of Surface Tension of an Aqueous Solution of a Detergent
  (ii) The Study of Variation of Surface Tension with the Concentration of a Detergent (Optional)
    Principle
    Requirements
    Procedure
    Observations
    Calculations
    Result
4.6 Answers

4.1 INTRODUCTION

You already know that matter can exist in three possible states–solid, liquid or gas. In gases, the kinetic energy of the particles is sufficiently high to overcome the intermolecular forces of attraction. As a result of this, the gaseous molecules are free to move randomly in straight lines. In solids, the forces of attraction exceed the net kinetic energy of the molecules. The result is that the molecules become strongly packed together, giving them a shape rather fixed and restricted.

The properties of liquids are in between those of the gases and solids. In liquids, relatively short range forces of attraction are at work which hold their molecules at moderate distances. Though, the speed of the molecules in liquids is relatively slower than molecules in gases, their motion is still rapid enough to prevent them from being confined in definite positions. Hence, liquids have no specific shape and their molecules easily slide pass each other permitting them to take any possible shape allowed by the container.

Thus, not only the particular state of the substances but also their subsequent physical properties can be regarded as a result of the net balance between the kinetic energy of the molecules, which tend to keep them apart, and the intermolecular forces of attraction which tend to keep the molecules together. Here, in this unit you are going to study about the measurement of one such important property of liquids, namely, the Surface Tension.

Objectives

After going through this unit and performing Experiment 1, you should be able to:

- define surface tension and surface free energy, and give their units,
- express clearly the correlation between the molecular forces of attraction and the phenomenon of surface tension in liquids,
- explain interfacial tension and capillary action,
- comment on various methods of measuring surface tension and the principle involved therein,
- discuss how the surface tension varies with temperature and provide possible reasons for this variation, and
- explain why the surface tension of an aqueous solution should decrease in the presence of surface active agents.

4.2 SURFACE TENSION

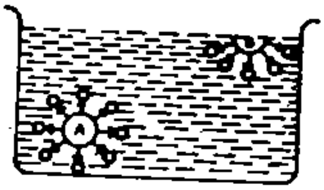


Fig. 4.1 : Forces of attraction at the surface and in the interior of a liquid.

Fig. 4.1 shows that a molecule **in the interior** of a liquid is completely surrounded by the other molecules, and experiences the force of attraction equally in all directions. On the other hand, a molecule at **the surface** experiences the attractive forces *only from downward direction*, and this results in a net inward pull. Thus, under the influence of the molecular forces of attraction from within, a liquid develops a tendency to contract its surface such that it acquires the smallest possible area for a given volume. That is why drops of a liquid and bubbles of a gas in a liquid tend to acquire a spherical shape. As a result of this contraction, a liquid surface eventually comes under the **state of stretch or tension**, and the force (stretching) acting equally at every point in all directions along the surface, is known as the **Surface Tension**.

Quantitatively, the surface tension denoted as γ, may be defined in SI units as the force in newtons (N) acting at right angle to any line of one metre length along the surface of the liquid. Since, the force in newtons acts along a distance of one metre, the unit of surface tension is expressed as N m^{-1}.

The surface tension may also be defined in c.g.s. system as the force in dynes acting at right angle to any line of one centimetre length along the liquid surface. In this case, the force in dynes acts along a distances of one centimetre, so the surface tension is expressed in dynes cm^{-1}.

In other words, we can also say that dynes $cm^{-1} \times 10^{-3} = N\ m^{-1}$

Related to the surface tension is the property of surface free energy. Let us now understand what do we mean by this term.

4.2.1 Surface Free Energy

The **surface free energy**, as such, is a characteristic property of the surface and arises due to surface tension. The surface tension acts inwards allowing a minimum surface area for a given volume of liquid. Therefore, extension of a surface against the force of surface tension requires some work to be done which results in an increase in the energy of the surface by the same amount. The work required to increase the surface area by one unit by moving the molecules from interior of the liquid to surface, is called the surface free energy. The SI units of surface free energy are joule metre^{-2}. The two quantities, the surface free energy (J m^{-2}) and the surface tension (N m^{-1}) and are mathematically equivalent. The surface tension for some substances is given in Table 4.1.

The c.g.s. units of surface free energy are ergs cm^{-2}.

$$1\ J = 1\ N\ m$$

$$1\ J\ m^{-2} = 1\ N\ m\ m^{-2} = 1\ N\ m^{-1}$$

Table 4.1: Surface Tension of Some Substances

Substance	Temperature/°C	$(10^3\gamma/\mathrm{N\,m^{-1}})$
Platinum	2273	1900
Copper	1404	1100
Aluminium	700	840
Lead	350	453
Mercury	20	472
Acetone	20	23.7
Benzene	20	28.88
Chloroform	20	27.14
Ethanol	20	22.8
Methanol	20	22.6
Water	20	72.88
Oxygen	–203	18.3
Nitrogen	–203	10.5

Surface tension is measured for liquids. You can see high temperatures being used for the first four entries mentioned in Table 4.1 which are required for reaching their melting point.

4.2.2 Interfacial Tension

The surface of a liquid is, infact, a surface of separation or an *interface* between the liquid and its vapour phase, and the value of the surface tension is the force acting per unit length along this liquid/vapour interface.

In general, the force acting per unit length along the surface of separation or interface is known as the **interfacial tension**. This is also expressed in Newton metre^{-1} (N m^{-1}) units.

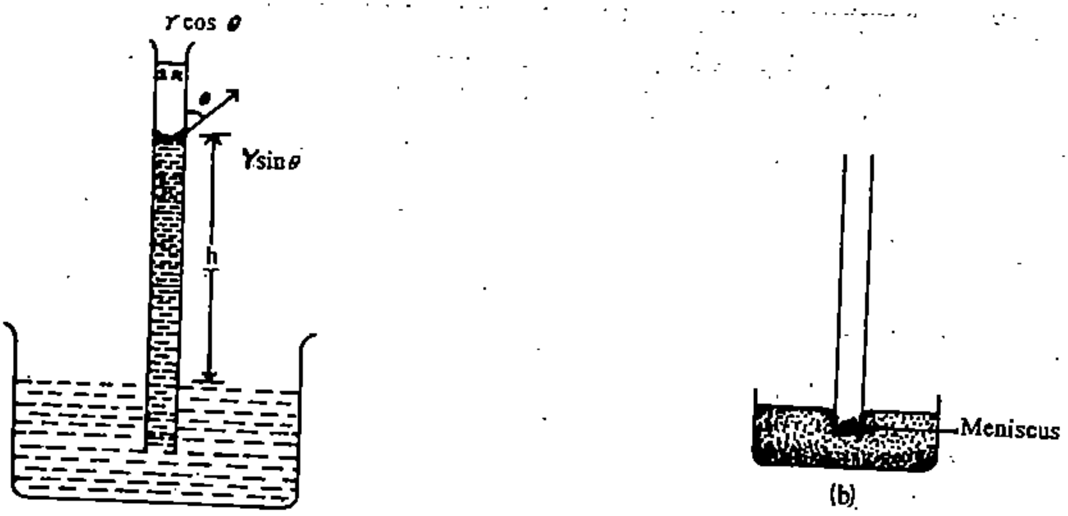
When a system contains more than one phase, the region where the phases meet, is called the **interface** or **interfacial region**. The common example of the interface being the surface of separation between two immiscible or partially miscible liquids.

Having understood the term interfacial tension, let us turn to the phenomenon of *capillary action*. You must be familiar with the fact that water rises in a capillary tube. Also you must have seen that mercury shows a depression of level in a capillary tube. The rise or fall (depression) of liquid level in a capillary tube is known as **capillary action**. Can you guess what is responsible for this phenomenon? It is the **surface tension** which is responsible for rise (or fall) of a liquid in the capillary. Let us now study it in more detail.

4.2.3 Capillary Action

Water in a capillary tube is pulled upwards due to the force of surface tension and is pulled downwards due to the force of gravity. Water continues to rise in the capillary till a balance between the two forces is reached. Such a rise is depicted in Fig. 4.2 (a).

This can be more clearly understood if we take into account the forces operating at the molecular level. Two types of forces operate when a glass capillary is dipped in water viz. **cohesive** and **adhesive** forces. **Cohesive forces** are the **intermolecular** forces among the molecules of water whereas **adhesive forces** operate between the molecules of water and the molecules of the glass which constitutes the capillary walls. The adhesive forces pull water upwards and lead to the wetting of glass (capillary walls). On the other hand, cohesive forces act downwards. The height of the resulting column of water in the capillary is determined by the balance of adhesive and cohesive forces.



(a)

(b)

Fig. 4.2: Capillary action: (a) Rise of water in a capillary.
(b) Depression of mercury level in a capillary.

You must have also noticed the shape of the meniscus when water rises in a glass capillary. The shape is **concave** indicating that the adhesive forces between water and glass are **stronger than** the cohesive forces between water molecules. In some cases, e.g., in case of mercury, the shape of the meniscus is **convex** and there is a depression in the level of mercury inside the capillary, see Fig. 4.2 (b). This is due to stronger cohesive forces as compared to adhesive forces.

Let us now derive an expression which relates the above forces with the surface tension.

A force vector (e.g. γ) can be resolved into two rectangular components : $\gamma \cos \theta$ and $\gamma \sin \theta$ as shown below :

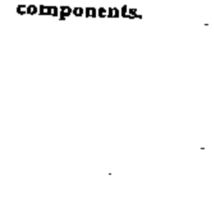


Fig. 4.3 : Resolution of a Vector into components.

The force in the downward direction, F_d, i.e. cohesive force is given by mass of the liquid column (m) above the flat surface of liquid multiplied by the acceleration due to gravity (g). Again mass of the liquid is equal to the product of volume (V) and density (d) of the liquid. Considering the particular bit of liquid portion as cylindrical, the volume can be given by the formula $\pi r^2 h$.

$$F_d = mg = V \cdot d \cdot g = \pi r^2 h d g \qquad \text{... (4.1)}$$

where r is the radius of the capillary and h is the height of the liquid column.

The upward force, F_u i.e. the adhesive force is equal to the vertical component (See Fig. 4.3) of the surface tension ($= \gamma \cos \theta$) multiplied by the circumference of the capillary ($2\pi r$). Therefore F_u, can be represented as given below

$$F_u = 2\pi r \gamma \cos \theta \qquad \text{...(4.2)}$$

where θ is the contact angle as shown in Fig 4.2. At equilibrium, $F_d = F_u$. Hence, we can write from Eqs. 4.1 and 4.2 that

$$\pi r^2 h d g = 2\pi r \gamma \cos \theta$$

$$\text{or} \qquad \gamma = \frac{r h d g}{2 \cos \theta} \qquad \text{... (4.3)}$$

We can use Eq. 4.3 for the determination of surface tension (γ).

Having understood the above discussion, answer the following SAQ.

SAQ 1

i) Why do the tiny drops of a liquid look spherical in shape?

....

....

ii) Surface tension of a liquid is .... in newton at right angles to a line of one meter length along the .... of the liquid.

ii) What is the surface free energy?

....

....

v) The unit of interfacial tension is .... and that of surface free energy is ....

.3 FACTORS AFFECTING SURFACE TENSION

Ve will now focus our attention on some of the factors affecting the surface ension. We will first explain the effect of surfactants and then discuss the effect of emperature.

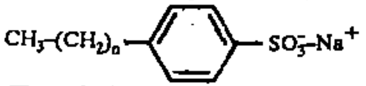
.3.1 Effect of Surfactants

urfactants are surface active materials and they generally consist of molecules ontaining polar and nonpolar parts. These parts have a strong tendency to orient emselves at the interfaces of two immiscible or partially miscible liquids. The ndency of the surfactant molecules to align at an interface favours its expansion. his expansion must be balanced against the tendency of the interface to contract nder surface tension forces. Hence, the presence of a surfactant in aqueous lutions lowers the surface tension.

$$\gamma = \gamma_o - \pi \qquad \text{.... (4.4)}$$

here, π is the expanding pressure or **surface pressure** due to absorbed layer of rfactant and γ_o is the surface tension of the liquid in the absence of the rfactant.

The common examples of surfactants are soaps and detergents. Soaps are salts of long-chain fatty acids. The detergents are of two types — anionic and cationic. The anionic detergents are sodium salts of linear alkylbenzene (LAB) sulphonic acids. Their general structure can be represented as,



The cationic detergents are generally the quaternary ammonium salts of the following type

$(CH_3)_3RN^+Cl^-$

where R is alkyl chain having 12-18 carbon atoms.

By lowering the surface tension, the surfactants help the grease or dirt (non-polar in nature) to dissolve in water. This solubilised grease is then washed away with water. This forms the basis for the **cleansing action** of soaps and detergents.

3.2 Effect of Temperature

s the temperature increases, the kinetic energy of the molecules increases. This uses a decrease in their intermolecular forces of attraction. This results in a crease in the surface tension of the liquid. For the majority of compounds the mperature dependence of the surface tension can be given as,

$$\gamma = A - B\,T \qquad \text{.... (4.5)}$$

ere, A and B are the constants and T is the temperature in degree celsius. The lues of A and B for various compounds are available due to the research work ne so far. After studying this section, answer the following SAQ.

SAQ 2

i) Addition of a detergent to water will .... its surface tension.

ii) At higher temperature, the surface tension of a liquid .... because .... decreases.

4.4 MEASUREMENT OF SURFACE TENSION

There are various methods for determining the surface tension of a liquid. The names of such methods are given below:

i) Capillary rise method

ii) Torsion balance method

iii) Maximum bubble pressure method

iv) Stalagmometer method

Here, we will be discussing the stalagmometer method only because this method you will be using in the determination of the surface tension in Experiment 1.

4.5 EXPERIMENT 1 : I) DETERMINATION OF SURFACE TENSION OF AN AQUEOUS SOLUTION OF A DETERGENT II) THE STUDY OF VARIATION OF SURFACE TENSION WITH THE CONCENTRATION OF A DETERGENT (OPTIONAL)

Here, in this experiment you are going to use a stalagmometer. This is shown in Fig. 4.4 and is called Traube's Stalagmometer. It is a simple apparatus and is frequently employed when the values of surface tension of two or more different liquids are to be compared.

Fig. 4.4 : Traube's Stalagmometer.

It consists of a bulbed capillary tube, the end of which is flattened and grounded carefully so that there is a large dropping surface. There are two marks, A and B, on it which are arbitrarily etched; one of them is above the bulb and the other is below the bulb. A liquid is sucked up to the level A and then allowed to flow at a slower rate drop by drop until it reaches the level B. The speed of the drop formation can be adjusted by attaching a piece of rubber tube with a screw pinch cock at the upper end of the tube. Before going to the actual details of the procedure, you should understand the principle involved in this method, which is explained below.

4.5.1 Principle

When a liquid is allowed to flow through a capillary tube, a drop begins to form at its lower end, and increases in size to a certain extent, and then falls off. The size of the drop will depend on the radius of the capillary and the surface tension of the liquid. The total surface tension supporting the drop is $2\pi r . \gamma$, where r is the outer radius of the capillary tube, see Fig. 4.5. The drop will fall when its weight w, just exceeds the force of surface tension acting along the circumference. Therefore,

$$w = 2\pi r \gamma \qquad \text{..... (4.6)}$$

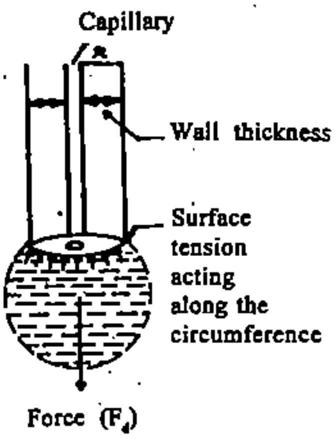


Fig. 4.5 : Formation of a drop at the end of the capillary.

where w, is the weight of the drop and $2\pi r$ is the outer circumference of the capillary tube.

From the above expression, it is clear that the surface tension of a liquid can be determined if the weight of a single drop w and the outer-radius of the dropping tube, r are known.

If, we have two liquids, such that

$$w_1 = 2\pi r \gamma_1,$$

and $$w_2 = 2\pi r \gamma_2$$

then, we can say that

$$\frac{w_1}{w_2} = \frac{\gamma_1}{\gamma_2} \qquad \text{.... (4.7)}$$

If γ_1 for one of the liquids is known, γ_2 for other liquid can be determined without needing a measurement of r, the outer radius of the dropping end of the capillary, provided the weights of the individual drops of two liquids are known. This method of determination is also known as **Drop Weight Method**. Alternatively, the surface tension can also be determined using the **Drop Number** method as given below.

Drop Number Method

Instead of finding the weights of individual drops, it is easier to count the number of drops formed by equal volumes of two liquids. With two different liquids, the weights of equal volumes are proportional to their densities. If n_1 and n_2 are the number of drops formed by the same volume V of the two liquids, then; v_1, the volume of a single drop of first liquid (i.e., liquid one) $= V/n_1$.

Thus,

weight of the single drop of the first liquid $= w_1 = V/n_1 \times d_1 \times g$ for first liquid, where d_1 is the density of the first liquid.

and

weight of the single drop of the second liquid $= w_2 = V/n_2 \times d_2 \times g$ for second liquid, where d_2 is the density of the second liquid.

Substituting the above values of w_1 and w_2 in Eq. 4.7, we get

Weight of an object is the force experienced by it due to gravitation when it is freely suspended (as in spring balance). Therefore,

weight = mass × acceleration due to gravity

or $w = m \times g$

$w_1 = m_1 \times g$

and $w_2 = m_2 \times g$

Thus, $\frac{w_1}{w_2} = \frac{m_1 \times g}{m_2 \times g} = \frac{m_1}{m_2}$

We get,

$$\frac{\gamma_1}{\gamma_2} = \frac{(V/n_1) \times d_1 \times g}{(V/n_2) \times d_2 \times g} = \frac{d_1/n_1}{d_2/n_2} = \frac{n_2 d_1}{n_1 d_2} \quad \text{.... (4.8)}$$

where, γ_1 and γ_2 are the surface tensions of two individual liquids, and d_1 and d_2 are their densities, respectively. Thus, for the determination of surface tension of any liquid, the number of drops produced from equal volume of two liquids and their densities must be known, in addition to the surface tension of the reference liquid (e.g. water).

You can also check your understanding about the Eq. 4.8 involved in the determination of surface tension by answering the following SAQ.

SAQ 3

Calculate the ratio of number of drops of water to those of mercury if the values of density for mercury and water are 13.6 kg dm^{-3} and 1.00 kg dm^{-3}, respectively. Use the values of surface tension of the two liquids as given in Table 4.1.

....

....

....

Let us now focus our attention on the actual procedure and requirements for the experiment.

4.5.2 Requirements

Traube's Stalagmometer	1
Weighing bottle/conical flask (50 ml)/ Outer jacket of transition temperature of C.S.T. apparatus	1
Rubber stopper	1
Rubber tube (small piece)	1
Pinch cock	1
Clamp stand	1
Specific gravity bottle	1
Thermometer (110°)– $\frac{1}{10}$ degree	1
Large beaker or glass trough	1

In addition, you will be provided with different solutions (upto 3 or 4 in numbers) of household detergents (with varying concentrations) and also a bottle of distilled water.

Chromic acid is prepared by dissolving potassium dichromate ($K_2Cr_2O_7$) in conc. H_2SO_4.

4.5.3 Procedure

Before starting the experiment, the stalagmometer should be cleaned by chromic acid solution to remove oil, grease etc. sticking on the inner capillary surface and then washed with distilled water and finally with acetone or alcohol, and dried by passing air. Now take a weighing bottle, tightly fitted with a rubber stopper having two holes. Insert the stalagmometer through one of the holes. Through the other hole, pass a glass tube for air ventillation (see Fig. 4.6). Attach a small rubber tubing with a screw pinch cock to the upper end of the stalagmometer. Take out the stalagmometer from the bottle, and fill it with distilled water by sucking it up to the mark A. Close the pinch cock and insert the stalagmometer into the weighing bottle. Now, clamp the stalagmometer in a thermostat and allow it to acquire the temperature of the bath. Now, open the pinch cock gently such that the liquid flows out slowly. Adjust the air inflow so that the number of drops formed should not exceed 15 drops per minute. Count the number of drops obtained when a fixed volume of water flows between the marks A and B, i.e., count the number of drops when the water level changes from A to B.

Refill the stalagmometer and repeat the counting of drops thrice, and record it in the observation table, shown as Table 4.2.

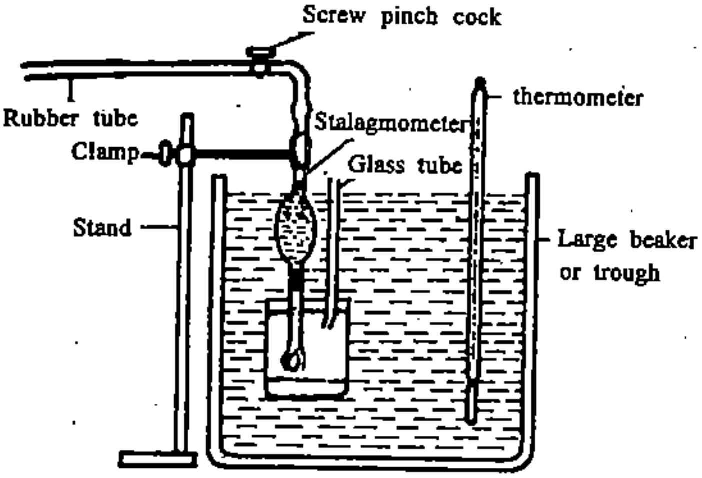


Fig. 4.6 : Apparatus for the determination of surface tension.

Now remove the stalagmometer from the weighing bottle, wash it thoroughly and dry it. Fill it with the given detergent solution and reset the stalagmometer in the weighing bottle. Count the number of drops fallen for the same volume of the detergent solution between the marks A and B. Repeat the counting process thrice and record in the observation table.

While doing the experiment, the following precautions should be taken.

Precautions

- The stalagmometer should be cleaned and dried before use.
- While sucking the liquid into the stalagmometer, no air bubble should be formed.
- Stalagmometer should be held in a vertical position throughout the drop counting process.
- Drop formation should be adjusted at a slower rate and should not exceed fifteen drops per minute.

ou can record your observations in the space given below:

5.4 Observations

emperature, t = ... °C

ensity of water at t°C = d_w = ... kg dm^{-3}

urface tension of water at t°C = γ_w = ... N m^{-1}

(use from Table 4.3)

Table 4.2

Number of drops formed from equal volume of liquids (between marks A and B)					
Sl. No.	Water	Detergent Solutions			
		s_1	s_2	s_3	s_4
i	.....	.....	.....	.....	.....
ii	.....	.....	.....	.....	.....
iii	.....	.....	.....	.....	.....
Average	..... n_w	..... n_{s_1}	..... n_{s_2}	..... n_{s_3}	..... n_{s_4}

mass of empty specific gravity bottle $= w_1 = ... g$

mass of specific gravity bottle + detergent solution $= w_2 = ... g$

mass of specific gravity bottle + Water $= w_3 = ... g$

The calculations to be done are also explained below:

4.5.5 Calculations

Density of the detergent solution 1 =

$$d_{S_1} = \frac{\text{Mass of the detergent solution}}{\text{Mass of water}} \times \text{density of water}$$

$$= \frac{w_2 - w_1}{w_3 - w_1} \times d_w$$

Relative surface tension of the detergent solution (s_1) =

$$\frac{\gamma_s}{\gamma_w} = \frac{d_{s_1} \times n_w}{d_w \times n_{s_1}}$$

Absolute surface tension of the detergent solution (s_1) =

$$\gamma_{s_1} = \gamma_w \times \frac{d_{s_1} \times n_w}{d_w \times n_s} = \text{.........} \ \mathrm{N\,m^{-1}}$$

Likewise repeat the determination of density and calculations of surface tension for other solutions and get $\gamma_{s_2}, \gamma_{s_3}$ etc.

....

....

....

....

....

....

....

....

Specific gravity is a term sometimes used in place of density. Specific Gravity is the ratio of density of a substance to that of water. Since it is a ratio of two densities, it is expressed without units.

Specific Gravity =

$$\frac{\text{density of solution (in kg dm}^{-3})}{\text{density of water (in kg dm}^{-3})}$$

The density of water is 1 kg $\mathrm{dm^{-3}}$; therefore, specific gravity of a liquid or solution is its density expressed without units.

From the following steps, you can verify the relationship between the density of a solution and density of water as given by specific gravity measurement.

Specific gravity of a solution =

$$\frac{\text{Density of a solution}}{\text{Density of water}} =$$

$$\frac{\text{Mass of solution/Volume of solution}}{\text{Mass of water/(same) Volume of water}}$$

= Mass of solution/Mass of water

Since we use same specific gravity bottle for measuring the masses of water and solution, volume is same in both the cases.

Hence Density of a solution =

$$\frac{\text{Mass of solution}}{\text{Mass of water}} \times \text{Density of water}$$

This relationship holds only if masses of water and solution are measured using same specific gravity bottle.

The surface tension of water γ_w at different temperatures is given in Table 4.3 for your reference.

Table 4.3 : Surface Tension of water at different temperatures

Temperature/°C	Surface Tension ($10^3\gamma$ /N m^{-1})
0	75.83
5	75.09
10	74.36
15	73.62
20	72.88
21	72.73
22	72.58
23	72.43
24	72.29
25	72.14
26	71.99
27	71.84
28	71.69
29	71.55
30	71.70
35	70.66
40	69.92
45	69.18
50	68.45
55	67.71
60	66.97
100	61.80

The result obtained can be reported as shown below:

4.5.6 Result

i) The absolute surface tension of the detergent solutions (s_1, s_2, s_3, s_4) at temperature .....°C are as follows:

γ_{s_1} = ... N m^{-1}
γ_{s_2} = ... N m^{-1}
γ_{s_3} = ... N m^{-1}
γ_{s_4} = ... N m^{-1}

ii) Similarly, you can determine the surface tension values for solutions of the same detergent having different concentrations and plot a graph of surface tension Vs concentration values (c_1, c_2, c_3 etc.). Discuss this graph with your counsellor and find the possible reasons for the variation of surface tension with concentration of the detergent solution.

4.6 ANSWERS

Self Assessment Questions

1 i) Because of surface tension, a liquid develops a tendency to acquire smallest possible area for a given volume. A sphere has the smallest surface area for a given volume.

ii) force, surface

iii) Work required to be done in order to expand the surface area by one unit.

iv) N m^{-1}, J m^{-2}

2 i) reduce

ii) decreases, intermolecular forces

3 Let subscript 2 represent water and subscript 1 represent mercury. Then Eq. 4.8 becomes,

$$\frac{\gamma_{\mathrm{Hg}}}{\gamma_{\mathrm{w}}} = \frac{n_{\mathrm{w}}\, d_{\mathrm{Hg}}}{n_{\mathrm{Hg}}\, d_{\mathrm{w}}}$$

or

$$\frac{n_{\mathrm{w}}}{n_{\mathrm{Hg}}} = \frac{\gamma_{\mathrm{Hg}}}{\gamma_{\mathrm{w}}} \times \frac{d_{\mathrm{w}}}{d_{\mathrm{Hg}}} = \frac{0.472}{0.07288} \times \frac{13.6}{1.00} = 88.1$$

(rounded to three significant figures)

UNIT 5 VISCOSITY OF LIQUIDS

Structure

5.1 Introduction
    Objectives
5.2 Viscosity of Liquids
    The Coefficient of Viscosity
    Units
5.3 Effect of Temperature
5.4 Measurement of the Coefficient of Viscosity
    Ostwald Viscometer Technique
5.5 Experiment 2 : Determination of the Coefficient of Viscosity of 30% Cane Sugar Solution By Ostwald Viscometer
    Principle
    Requirements
    Procedure
    Observations
    Calculations
    Result
5.6 Answers

5.1 INTRODUCTION

In the previous unit, you studied about the surface tension- a property which arises due to intermolecular forces of attraction operating between the molecules of the liquid. In this unit, in the light of the intermolecular forces, you will study another important property of liquids i.e. the **viscosity**. Viscosity is a property of fluids, i.e., both gases and liquids have viscosity; but here we will focus our attention only on the liquids. As you know the liquids are mobile and have general property to flow, known as **fluidity**. When the molecules of a liquid move forward, the surrounding molecules due to intermolecular forces of attraction develop a relative tendency to oppose this movement. Such internal resisting forces that restrain the molecules of a liquid from flowing past each other are, indeed, responsible for what is known as the **viscosity** of liquids. In this unit, you will study about the measurement of the coefficient of viscosity of aqueous solution of cane sugar.

Objectives

After studying this unit and performing the experiments, you should be able to:

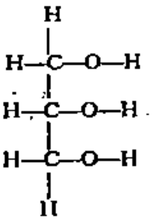
- distinguish between the fluidity and the viscosity of liquids and correlate them,
- define the coefficient of viscosity of a liquid,
- derive the units of coefficient of viscosity,
- predict the effect of temperature and the molecular forces of attraction on the coefficient of viscosity of a liquid, and
- explain the principles involved in the measurement of the coefficient of viscosity of a liquid.

5.2 VISCOSITY OF LIQUIDS

Coefficient of viscosity is represented by the Greek letter η (eta).

Liquids, in general, have an inherent tendency to flow. But this tendency to flow is not always the same for all liquids. It is a common experience that water flows more easily than honey. Therefore, water is said to have lower fluidity. On the other hand, honey is said to have lower fluidity. Those liquids which have lower fluidity are said to be viscous. The examples being honey, caster oil and glycerol. The **viscosity, therefore, measures the resistance of a liquid to flow, while the fluidity measures the ease with which a liquid can flow.** The two quantities, the viscosity and the fluidity, are essentially reciprocal to each other. Thus, we can say that

$\eta = \frac{1}{\phi}$, where η is the coefficient of viscosity and ϕ is the fluidity.



Glycerol

The viscosity is very much influenced by the shape, size and the chemical nature of the liquid molecules. The greater the size of the molecules and the higher the molar mass, the higher will be the viscosity because the greater will be the intermolecular interactions. The hydrogen bonds also enhance the coefficient of viscosity to a large extent. It is, indeed, the presence of a network of hydrogen bonds which accounts for the very high viscosity of glycerol. Incidentally, the larger the number of hydroxyl groups in a molecule, the more complex will be the network of hydrogen bonds and the greater will be the resistance of a liquid to flow. In long chain hydrocarbons or polymeric compounds the viscosity increases with the increase in the length of the molecular chain. Due to this reason, heavy hydrocarbon oil and grease (which are used as lubricants) have fairly high viscosity values. Similar to the surface tension, you would expect the viscosity to decrease with the increase in temperature. This is due to the decrease in intermolecular forces of attraction with increase in temperature. At higher temperature, the number of hydrogen bonds in a liquid also diminishes and the viscosity is expected to decrease.

5.2.1 The Coefficient of Viscosity

Parallel concentric cylindrical layers: cylindrical layers of liquids which have common central axis as shown in Fig. 5.1(a).

To define the coefficient of viscosity, let us consider a liquid flowing through a narrow circular tube. The flowing liquid can be viewed as being composed of parallel concentric cylindrical layers, See Fig. 5.1*(a)*. It is assumed that the layer of liquid in contact of the wall is stationary and each successive layer starting from the wall towards the centre, moves faster than the previous one. In other words, the velocity increases to a maximum at the middle of the tube. Such a flow in which one layer slides smoothly relative to another, with regular gradation of velocity is called **laminar flow** and is shown in Fig. 5.1. *(b)*.

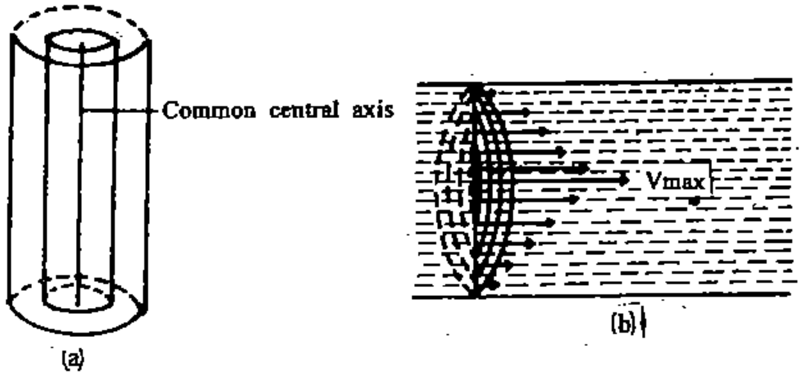


Fig. 5.1: (a) Parallel concentric cylindrical layers (b) Laminar Flow.

For such flow, if, at a given temperature dv (m s^{-1}) is the velocity difference between two successive layers each of area A(m^2) which are at a distance dx (m), then the net resisting force F operating between two successive layers will be directly proportional to the area A and velocity difference dv, and inversely proportional to the distance dx, such that

$$F \alpha A \cdot \frac{dv}{dx}$$

or

$$F = \eta \cdot A \cdot \frac{dv}{dx} \qquad \text{... (5.1)}$$

where, η is the proportionality constant and is also called the coefficient of viscosity of the liquid at the given temperature. Therefore, from Eq. 5.1, we can write

$$\eta = \frac{F}{A \cdot \frac{dv}{dx}} \qquad \text{... (5.2)}$$

$\frac{dv}{dx}$ is called the velocity gradient.

Unit of $\frac{dv}{dx} = \frac{ms^{-1}}{m}$

$= s^{-1}$

If A is $1m^2$ and $\frac{dv}{dx}$ is $1s^{-1}$, then $\eta = F$.

Thus, the coefficient of viscosity of a liquid, η, at a given temperature may be defined as, **the force per unit area required to maintain a unit difference of velocity between two parallel layers at unit distance apart.** This is also obvious from the Eq. 5.2. For convenience, at times, the coefficient of viscosity is often called the viscosity of liquids. Having defined the coefficient of viscosity, let us now study its units.

5.2.2 Units

In SI system, from Eq. 5.2, we can say that

$$\text{Unit of } \eta = \frac{\text{Unit of } F}{\text{Unit of } \left(A \cdot \frac{dv}{dx}\right)} = \frac{N}{\frac{m^2 \cdot \cancel{m} s^{-1}}{\cancel{m}}} = N\,m^{-2}\,s$$

Since N m^{-2} = Pa (Pascal, unit of pressure)

$$\eta = \text{Pa s}$$

1N = 1 kg m s^{-2}

Hence, 1 Pa s = 1 N m^{-2} s

= 1 (kg m s^{-2}) m^{-2} s

= 1 kg m^{-1} s^{-1}

In c.g.s. system, the unit of coefficient of viscosity is **poise**. A liquid has a coefficient of viscosity of one poise if a force of 1 dyne (1 g cm s^{-2}) is required to move a plane of 1 cm^2 at a velocity of 1 cm s^{-1} with respect to a plane 1 cm away and parallel with it.

A liquid has a viscosity of 1 Pa s if a force of IN is required to move a plane of 1 m^2 at a velocity of 1 m s^{-1} with respect to a plane surface 1 m away and parallel with it.

$$\begin{aligned}\text{Unit of } \eta &= \frac{\text{Unit of } F}{\text{Unit of } \left(A \cdot \frac{dv}{dx}\right)} \\ &= \frac{\text{dyne}}{cm^2 \cdot \frac{\cancel{cm} s^{-1}}{\cancel{cm}}} \\ &= \frac{g\,cm\,s^{-2}}{cm^2\,s^{-1}} \\ &= g\,cm^{-1}\,s^{-1} \\ &= \text{poise}\end{aligned}$$

In other words, 1 poise = 1 g cm^{-1} s^{-1}

If you are interested in knowing the conversion from c.g.s. to SI units, go through the following steps:

$$\begin{aligned}1 \text{ poise} = 1\ g\ cm^{-1}\ s^{-1} &= 1(10^{-3}\ kg)\ (10^{-2}\ m)^{-1}\ s^{-1} \\ &= 10^{-3}\ kg \times 10^{2}\ m^{-1}\ s^{-1} \\ &= 10^{-1}\ kg\ m^{-1}\ s^{-1} \\ &= 10^{-1} \quad \text{Pa. s}\end{aligned}$$

Hence, 10 poise = 1 Pa. s

At this stage, it will be beneficial for you to answer the SAQ given below:

SAQ 1

i) How are the viscosity and the fluidity of a liquid related to each other?

. . . .

ii) What does the viscosity of a liquid measure?

. . . .

iii) Fill in the blanks with correct words.
Liquids having high . . . . are said to have . . . .
. . . . viscosity and the liquids with the high . . . .
. . . . are said to have low . . . .

iv) What are the units of the coefficient of viscosity in the c.g.s. and SI systems?

. . . .

Let us now study the effect of temperature on viscosity.

5.3 EFFECT OF TEMPERATURE

In liquids, as the temperature rises, the kinetic energy of the molecules increases and the intermolecular forces of attraction become weak, resulting in the subsequent decrease in the viscosity. **The value of the coefficient of viscosity appreciably drops as the temperature of liquid increases** such that for each degree rise in temperature there is about two percent decrease in the viscosity. The viscosity and temperature are related to each other by the following expression:

$$\log \eta = \frac{A}{T} + B \qquad \text{... (5.3)}$$

where A and B are constants for a given liquid and T is the absolute temperature.

The plot of $\log \eta$ against $\frac{1}{T}$, therefore, gives a straight line, demonstrating the fact that the viscosity of a liquid rapidly decreases with the rise in temperature, see Fig. 5.2. (a).

On the other hand, if we plot a graph between coefficient of viscosity and temperature, we get a curve as shown in Fig. 5.2 (b)

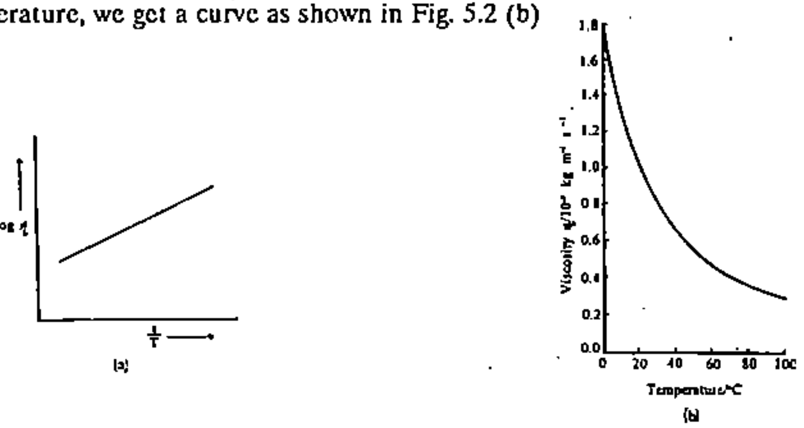


Fig. 5.2 : Temperature dependence of viscosity of water.

The viscosities of some liquids are shown in Table 5.1:

Table 5.1 : Coefficient of Viscosity of different substances

Substance	Temperature °C	Coefficient of Viscosity ($\eta/10^{-3}$ Pa s)
Acetic acid	20	1.314
Acetone	20	0.337
Chloroform	15	0.596
Methanol	25	0.544
Mercury	20	1.552

Now answer the following SAQ.

SAQ 2

Fill in the blanks with correct words.

i) With the .... in temperature, the viscosity of a liquid ....

ii) The viscosity of those liquids which have hydrogen bonds in their molecular structure, generally .... with the .... in temperature.

iii) The plot of log η against $1/T$ gives a ....

5.4 MEASUREMENT OF THE COEFFICIENT OF VISCOSITY

The coefficient of viscosity of liquids is generally determined by using the following two methods:

i) **Ostwald Viscometer technique**

ii) **Falling Sphere Technique**

We will discuss here the principles involved in the first method because in the laboratory, you will be measuring the coefficient of viscosity by this technique.

5.4.1 Ostwald Viscometer Technique

For the measurement of coefficient of viscosity of liquids having a laminar or streamlined flow, Poiseuille derived an expression, known as **Poiseuille's equation.** This expression is given below.

$$\eta = \frac{\pi p r^4 t}{8Vl} \qquad .... (5.4)$$

where η = coefficient of viscosity of the liquid

V = volume of the liquid flowing out of the tube

t = time in which the volume V flows

r = radius of the tube

l = length of the tube

p = driving pressure necessary to maintain uniform rate of flow of volume V, of the liquid.

The flow of liquid through a pipe or tube of radius r, is associated with Reynolds Number (R) which is given by the following expression,

$$R = \frac{2rvd}{\eta}$$

where v is the average velocity of the liquid, d is the density and η is the coefficient of viscosity. If the value of R is less than 2100, the flow of liquid is said to be laminar or streamlined, and if R is greater than 4000, the flow is termed as turbulent.

This involves the use of Ostwald Viscometer in which a fixed volume of a liquid is allowed to fall under its own weight or the force of gravity, and the time required for a given volume of the liquid to flow is noted. Obviously the driving pressure p is replaced by $h.d.g$, where h is the height of the liquid and d is its density and g is the acceleration due to gravity. Therefore,

$$p = h.d.g$$

substituting $h.d.g.$ for p in Poiseuille's Equation (Eq. 5.4), we get,

$$\eta = \frac{\pi r^4.h.d.g.t}{8Vl} \qquad .... (5.5)$$

The relationship, $p = hdg$ can be derived as follows:

$$p = \frac{\text{Force}}{\text{Area}}$$

$$= \frac{\text{mass} \times \text{acceleration due to gravity}}{\text{Area}}$$

$$= \frac{mg}{\pi r^2} \quad \text{(cross-sectional area of a cylindrical layer is } \pi r^2\text{)}$$

$$= \frac{Vdg}{\pi r^2} \quad \text{(since mass = volume} \times \text{density)}$$

$$= \frac{\pi . r^2 . h . d . g}{\pi r^2}$$

$$= h.d.g$$

During the flow of the liquid, as the height (h) (level) of the liquid changes, there is a change in the pressure difference (p). But, for every position of the meniscus, p is proportional to density (d).

Thus, $p_1 \propto d_1$

and $p_2 \propto d_2$

or $\frac{p_1}{p_2} = \frac{d_1}{d_2}$

As a result of the change in driving pressure (p) the rate of flow of the liquid also changes all the time the flow is taking place. The rate of flow, i.e., the volume of liquid flowing per second (V) is inversely proportional to time. Thus, for the liquids, 1 and 2, we can say that

$$\frac{V_2}{V_1} = \frac{t_1}{t_2}$$

If equal volumes of the two liquids (1 and 2) are allowed to fall through the same capillary tube under identical conditions of temperature and pressure then, from Eq. 5.5 by comparison, we have

$$\frac{\eta_1}{\eta_2} = \frac{d_1 \cdot t_1}{d_2 \cdot t_2} \qquad ...(5.6)$$

where η_1, d_1 and t_1 are, respectively, the coefficient of viscosity, density and time of flow for the liquid 1 under examination and η_2, d_2 and t_2 the corresponding values for the reference liquid (liquid 2). Thus, by knowing η_2, d_2, t_2 and d_1 and t_1 the coefficient of viscosity of first liquid, η_1 could be determined.

Let us now study about the experiment which you will be performing.

5.5 EXPERIMENT 2: DETERMINATION OF THE COEFFICIENT OF VISCOSITY OF 30% CANE SUGAR SOLUTION BY OSTWALD VISCOMETER

5.5.1 Principle

In this experiment, you will make use of the Ostwald viscometer. This is usually employed in the laboratory for the determination of the coefficient of viscosity of liquids. Ostwald viscometer is a simple apparatus and is shown in Fig. 5.2. It consists of a bulb A, with a mark (X) above and as mark (Y) below, attached to a capillary tube B and a storage bulb C.

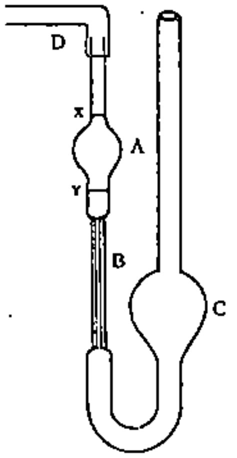


Fig. 5.3 : Ostwald Viscometer. (b)

A definite volume of a liquid say, 10 ml is introduced into bulb C. The liquid is then sucked into the bulb A through a rubber tube attached to the end, D. The liquid is allowed to flow freely from the mark X to the mark Y. Then the time t is observed for this flow of liquid. This method is very successful for comparing the viscosity coefficients of two or more liquids or liquid solutions.

In Ostwald viscometer, when a liquid is allowed to flow through the capillary under the influence of gravity, then the instant driving pressure is equal to $h.d.g$, where h is the difference in heights between the levels of the liquid in the two arms, which is constant for a particular set of the observations and g, acceleration due to gravity, is also constant. Obviously, the driving pressure is directly proportional to the density, d, of the liquid.

Since the same capillary is employed, and the same volume V of the liquid flows through it in each case, the values of r, l, V become all constant. Therefore, the Eq. 5.5 when applied to two liquids can be written as:

$$\frac{\eta_1}{\eta_0} = \frac{d_1 t_1}{d_0 t_0}$$

where, the subscripts, 1 and 0, denote the unknown and the reference liquids. Thus, if we divide the viscosity of the unknown liquid (η_1) with the viscosity of the reference liquid η_0, (say water), we can get the relative viscosity of the second liquid with respect to that of water.

Hence, the relative viscosity of second liquid $= \eta_{rel} = \frac{\eta_1}{\eta_0} = \frac{d_1 t_1}{d_0 t_0}$

To get the absolute viscosity of the liquid, multiply this relative viscosity by the absolute viscosity of the reference liquid. Thus, for absolute viscosity, the expression will be

$$\eta_{1(abs.)} = \frac{\eta_0 d_1 t_1}{d_0 t_0}$$

Now, answer the following SAQ to check your understanding of the above discussion.

SAQ 3

i) Name the two methods which can be used for the measurement of the coefficient of viscosity of liquids.

....

ii) The vertical flow of a liquid through a capillary is proportional to the .... of the liquid.

5.5.2 Requirements

Ostwald Viscometer (small)	1
Stop watch	1
Thermostat	1
Specific gravity bottle	1
10 cm^3 pippete	1
Distilled water	
30% Cane sugar solution	50 to 100 cm^3
Rubber tubing	small piece
Thermometer (110°C)	1

5.5.3 Procedure

Before use, the Ostwald Viscometer should be first cleaned with chromic acid solution ($K_2Cr_2O_7$ + Conc . H_2SO_4), and then with distilled water (twice), alcohol or acetone, respectively. Finally, it should be dried by passing the current of dust free air. Make sure that the capillary of the viscometer does not contain any dust particle or greasy material inside to pose any obstruction to the flowing liquid.

Now, introduce a definite volume of the 30% cane sugar solution (10 cm^3) into the bulb C, and suck the liquid up into the bulb A with the help of the rubber tube attached to the end D somewhere above the mark X. Make sure there is no air bubble inside the liquid. Now, allow the liquid to flow freely through the capillary upto the mark X. Start a stop watch and note the time t_1 for the flow of the liquid from mark X to mark Y. Repeat this process twice or thrice by sucking the liquid into the bulb A upto the mark X and noting the time t_1 for the flow of the liquid from mark X to mark Y. These values should be concordant. Fill the liquid again and repeat the same for second filling.

Remove the first liquid and clean and dry the viscometer again. Repeat the experiment by taking an exactly the same volume of water in bulb C and note the values of time, t_0, taken for water to flow from mark X to mark Y. Suck the water up, twice or thrice to obtain other values of t_0, as done above. Repeat the same for second filling. Determine the density of the cane sugar solution with the help of specific gravity bottle. This can be done by taking a definite volume of liquid (say, 5 cm^3) in the specific gravity bottle and determining its mass. Also note down the temperature at which the experiment was performed.

Do not forget to observe the following precautions while doing the experiment;

Precautions

1) The volume of the liquids taken in bulb C should be so much that when sucked up to mark X, it should fill the bulb A and a little should still remain in the bulb C.

2) The viscometer should be held in a vertical position during the flow of the liquids.

3) While sucking the liquids, no air bubble should be formed inside the capillary tube.

You can record your observations in the following manner.

5.5.4 Observations

Temperature of measurement = ... = t°C

Density of water at t °C = ... = d_0 (see from reference tables in the appendix)

Viscosity of water at t °C = ... = η_0 (see from Table 5.2)

Table 5.2 : Coefficient of viscosity of water at different temperatures

Temperature °C	Coefficient of Viscosity ($\eta/10^{-3}$ Pa s)
0	1.7702
5	1.5108
10	1.3039
15	1.1374
20	1.0019
21	0.9764
22	0.9532
23	0.9310
24	0.9100
25	0.8903
26	0.8703
27	0.8512
28	0.8328
29	0.8145

contd....

30	0.7973
35	0.7190
40	0.6526
45	0.5972
50	0.5468
55	0.5042
60	0.4669
65	0.4341
70	0.4050
100	0.2840

Table 5.3

Liquid	Time of flow		
	First Filling	Second Filling	
30% Cane sugar solution	(i) . . . . (ii) . . . . (iii) . . . . Average t_1=	(i) . . . . (ii) . . . . (iii) . . . . Average t_1=	Average t_1=. . . .s
Water	(i) . . . . (ii) . . . . (iii) . . . . Average t_0=	(i) . . . . (ii) . . . . (iii) . . . . Average t_0=	Average t_0=. . . .s

Weight of empty specific gravity bottle = ... = w_1 g

Weight of bottle + 30% cane sugar solution = ... = w_2 g

Weight of bottle + Same volume of water = ... = w_3 g

5.5.5 Calculations

Density of 30% cane sugar solution $= d_1 = \frac{w_2 - w_1}{w_3 - w_1} \times d_0$

Relative viscosity of 30% cane sugar solution $= \frac{\eta_1}{\eta_0} = \frac{d_1 \cdot t_1}{d_0 \cdot t_0}$

Absolute viscosity of 30% cane sugar solution, $\eta_{1(abs.)} = \frac{\eta_0 \cdot d_1 \cdot t_1}{d_0 \cdot t_0}$

5.5.6 Result

The relative viscosity of the given solution is . . . . Pa s

The absolute viscosity of the given solution is . . . . Pa s

Similarly, you can determine the coefficient of viscosity for various solutions such as that of NaCl or copper sulphate provided to you.

5.6 ANSWERS

Self Assessment Questions

1 i) They are reciprocal to each other.

ii) Viscosity of a liquid measures its resistance to flow.

iii) Fluidity, low, viscosity, fluidity

iv) Poise, Pa s

2 i) Rise, decrease

ii) Decreases, increases/rise

iii) Straight line

3 i) Ostwald technique, Falling sphere technique

ii) Density

UNIT 6 THERMOCHEMISTRY

Structure

6.1 Introduction
  Objectives

6.2 Some Fundamental Concepts

6.3 The First Law of Thermodynamics

6.4 The Enthalpy of a Reaction

6.5 Determination of the Enthalpy of Solution

  Experiment 3 : Determination of the Heat Capacity of the Calorimeter
    Heat Exchange Method
    Principle
    Requirements
    Procedure
    Observations
    Calculations
    Result

  Experiment 4 : Determination of the Integral Enthalpy of Solution of Ammonium Chloride
    Principle
    Requirements
    Procedure
    Observations
    Calculations
    Result

6.6 Answers

6.1 INTRODUCTION

In Units 4 and 5 of this block, you studied about the measurement of surface tension and viscosity. In this unit and in the next unit. i.e., Unit 7, you will study about the heat changes associated with chemical reactions. Chemical reactions are accompanied by **either the absorption or the evolution of heat.** The study of heat absorbed or evolved in a chemical reaction is called **thermochemistry.** In this unit, we will be dealing with the determination of heat of solution.

We will be first explaining some fundamental concepts of thermodynamics because this kind of study may be new to you. After that we shall discuss the actual determination of heat of solution.

Objectives

After studying this unit and having the experiments performed, you should be able to:

- state the first law of thermodynamics,
- define the enthalpy of a reaction,
- explain the integral and differential enthalpies of solution,
- explain how to determine the heat capacity of a calorimeter, and
- describe the determination of integral heat of solution of a given solute.

A reaction in an open beaker is an example of an **open system** as both matter and energy transactions are possible with the surroundings.

A reaction in a closed flask is an example of a **closed system** because the exchange of matter is not allowed with the surroundings. In this system only energy transactions with the surroundings are allowed.

A reaction inside a closed thermos flask is an example of an **isolated system**. Both matter and energy transactions with the surroundings are not allowed.

A **phase** is defined as a region of uniformity in a system.

6.2 SOME FUNDAMENTAL CONCEPTS

Let us first understand some of the concepts and terms which are often used in thermochemical studies.

Systems and Surroundings

A **system** is any part of the universe which is under study and is separated from the rest of the universe by a **boundary**. The rest of the universe is considered as the **surroundings** for that system. Further, a system can be **homogeneous, heterogeneous, open, closed** or **isolated** as explained below.

A system is said to be **homogeneous** or having a **single phase**, if the physical properties and chemical composition are identical throughout the system.

On the other hand, a **heterogeneous system** has two or more phases which are separated by boundaries.

An **open system** is a system which allows the exchange of **both** matter and energy with its surroundings. A **closed system** only allows the exchange of energy with the surroundings and **not** that of matter. An **isolated system** is the one which exchanges neither energy **nor** matter with its surroundings.

State and State Variables

A system is said to be in a **definite state** when each of its properties such as pressure, volume, temperature, composition, density etc. have definite values. These properties are also called **state** or **thermodynamic variables**. It is important here to note that a state variable is independent of the way the state has been reached.

Extensive and Intensive Variables

A property is said to be **extensive** if it is dependent on the amount of the substance, e.g., volume, mass etc. On the other hand, properties such as temperature and pressure which do not depend on the amount of a substance are called **intensive** variables.

Having understood the above terms, let us also study the first Law of Thermodynamics because the experiments which you will be performing in this unit and next unit are based on it.

6.3 THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics deals with the **conservation of energy**. It says that the energy can neither be created nor be destroyed but it can be changed from one form to another. Thus, if a system is left undisturbed, its energy will not change.

The internal energy, U, of a system is the total energy of the atoms and molecules which constitute the system. It is a state variable and is an extensive property. Since it is a state variable, the change in internal energy (ΔU) depends only on the initial and final states and not on the way how the system has changed from one state to another.

The internal energy of a system can be changed by two agencies, viz., heat (q) and work (w). By convention, when heat is absorbed by the system, the heat change (dq) is said to be **positive** leading to an increase in the internal energy of the system. Also, the loss of heat from the system indicates a **negative** dq and a decrease in internal energy of the system.

Similarly, if the work (dw) is done on the system, it is said to be **positive** because it ncreases the internal energy of the system. When work is done by the system, dw is aid to be **negative** because it is done at the cost of its internal energy leading to a decrease in the internal energy of the system. Thus, the change in the internal energy of a system (dU), when it absorbs dq amount of heat and a work dw is done on it, can be given as,

$$dU = dq + dw \text{ (for infinitesimal changes)} \qquad \ldots (6.1)$$

For larger changes, we can say,

$$U = q + w \qquad \ldots (6.2)$$

Let us now focus our attention on another property associated with a system, called the **enthalpy**. In the later sections of this unit, you will be studying about the determination of the **change in enthalpy** associated with the dissolution of a solute nto a solvent to give a solution.

6.4 THE ENTHALPY OF A REACTION

When a chemical reaction takes place in a system, generally, its temperature after the reaction (T_2) is different from the temperature before the reaction (T_1). Let us consider the following general reaction:

$$\underset{T_1}{\mathrm{R}} \longrightarrow \underset{T_2}{\mathrm{P}} \qquad \ldots (6.3)$$

To restore the system to its initial temperature (T_1), heat must flow either o or *from* the surroundings. If the system is hotter after the reaction than before ($T_2 > T_1$), heat must flow to the surroundings to restore the system to its initial emperature (T_1). In this case, the reaction is called **exothermic** and by convention flow of heat is negative (q is -ve). If the system is colder after the reaction ($T_2 < T_1$), heat must flow from the surroundings to restore the system to its initial state of emperature. This reaction is **endothermic** and flow of heat is positive (q = +ve).

The chemical reactions are performed under the conditions of constant volume or constant pressure. If no work is done on or by the system, then from Eq. 6.2 heat ransfer at constant volume is equal to the change of internal energy, ΔU. Similarly, heat transfer at constant pressure is identified as the change of enthalpy, ΔH. Thus, we can write,

$$\underset{T_1,V}{\mathrm{R}} \longrightarrow \underset{T_2,V}{\mathrm{P}} \qquad q_v = \Delta U \qquad \ldots (6.4)$$

$$\underset{T_1,\,p}{\mathrm{R}} \longrightarrow \underset{T_2,\,p}{\mathrm{P}} \qquad q_p = \Delta H \qquad \ldots (6.5)$$

In the general laboratory conditions, the chemical reactions are carried out at constant pressure. When q_p is the heat absorbed by the system and pdv is the work done by it, then according to Eq. 6.2 the change in internal energy can be written as follows :

$$\Delta U = q_p + (-pdV) \qquad (6.6)$$

where q_p is the heat absorbed at constant pressure and $-pdV$ is the amount of work done.

Let U_2 be the final internal energy and U_1, the initial internal energy; also let V_2 be the final volume and V_1, the initial volume. Then Eq. 6.6 can be written as

$$\begin{aligned} U_2 - U_1 &= q_p - p(V_2 - V_I) \\ &= q_p - pV_2 + pV_1 \end{aligned}$$

Rearranging, we get,

$$q_p = (U_2 + PV_2) - (U_1 + PV_1) \quad \text{. . . (6.7)}$$

At this stage, we can represent $U + PV$ by H, the enthalpy. We can rewrite Eq. 6.7 as,

$$q_p = H_2 - H_1 = \Delta H \quad \text{. . . (6.8)}$$

Since U, P and V are state variables, H is also a state variable. Thus, by Eq. 6.8, we are able to express heat absorbed (which is not a state variable) as a difference of enthalpy which is a state variable. Thus, the heat change (q_p) can be taken as the change in enthalpy (ΔH) provided the only work done is pressure volume work.

The heat of a reaction or more precisely, the **enthalpy of a reaction** (ΔH_r) is the enthalpy change in the transformation of reactants at a certain temperature (T_1) and pressure (p) to products at the same initial temperature (T_1) and pressure (p):

$$\underset{T_1, P}{\mathrm{R}} \longrightarrow \underset{T_1, P}{\mathrm{P}} \qquad \Delta H_r \quad \text{. . . (6.9)}$$

Work could be of various varieties: mechanical, volume-expansion, compression, surface increase, electrical, gravitational etc.

When heat is supplied to a system, its temperature rises. If dq is the amount of heat absorbed by the system and dT is the increase in temperature, then the quantity of heat required to raise the temperature by 1°C is called the **heat capacity**. The symbol for heat capacity is C and it can be expressed by the following relation :

$$C = \frac{dq}{dT} \quad \text{. . . (6.10)}$$

When the volume of the system is **constant**, heat capacity is denoted by C_v. On the other hand, when the pressure of the system is kept constant, heat capacity is represented as C_p.

From Eq. 6.8, you know that heat absorbed at constant pressure is equal to change in enthalpy. Then, substituting dq in Eq. 6.10 by ΔH, we get,

$$C_p = \frac{\Delta H}{dT} \quad \text{or} \quad \Delta H = C_p dT \quad \text{. . . (6.11)}$$

Having understood the above concepts, you can now proceed to the next section which explains the determination of enthalpy of solution.

6.5 DETERMINATION OF THE ENTHALPY OF SOLUTION

Let us first understand what do we mean by enthalpy of solution. The dissolution of a solute in a solvent is often accompanied by either evolution or absorption of heat. The amount of heat evolved or absorbed depends on the nature of the solute and the solvent and also on the composition of the solution. Thus, the enthalpy change accompanying the complete dissolution of one mole of solute in a definite amount of the solvent to give a solution of a specified concentration is known as the **integral enthalpy (or heat) of solution.** For example, the dissolution of one mole of ammonium chloride in 100 moles of water is represented by the following reaction with ΔH_1 as the enthalpy of solution:

$$\mathrm{NH_4Cl + 100\,H_2O \longrightarrow NH_4Cl \cdot 100\,H_2O} \quad \Delta H_1 \quad \text{. . . (6.12)}$$

he integral enthalpy of solution is found to be dependent upon the amount the solvent added: for example, the addition of 200 moles of water to the me 1 mole of ammonium chloride will yield a different enthalpy of solution, H_2.

$$NH_4Cl + 200\,H_2O \longrightarrow NH_4Cl \cdot 200H_2O \quad \Delta H_2 \qquad \ldots (6.13)$$

has also been observed that the integral enthalpy of solution approaches a miting value when more and more solvent is used. The difference of the above quations can be written as follows:

$$NH_4Cl \cdot 100\,H_2O + 100\,H_2O \xrightarrow[\Delta H = \Delta H_2 - \Delta H_1]{} NH_4Cl \cdot 200\,H_2O \qquad \ldots (6.14)$$

he enthalpy change in the above reaction (Eq. 6.14) is termed as the **enthalpy or eat of dilution.** The enthalpy of dilution depends upon original concentration of ie solution and on the amount of the solvent added.

ı addition to the integral enthalpy of solution, we can define another type of nthalpy, called the **differential enthalpy of solution**. This is defined as the nthalpy change when 1 mol of solute is dissolved in a sufficiently large volume f a solution of concentration, *c*, so that the final concentration remains almost nchanged.

special case of enthalpy of solution is the enthalpy change which occurs when a ıfficiently large amount of solvent is used so that further dilution does not ield any heat changes. This is called the **enthalpy of solution at infinite ilution.**

o determine the enthalpy changes associated with reactions, we use the following **rinciple of calorimetry.**

leat lost by one part of the system = Heat gained by the other part of the system

Jsing this principle, you will be performing thermochemical experiments by using n isolated system (such as a calorimeter kept in a thermos flask.)

he experimental determination of the integral enthalpy of solution involves the ıeasurement of rise or fall in temperature during the reaction (or the process) sing a container called **calorimeter** as mentioned above. A calorimeter, when kept ı a thermos flask is insulated from outside so that no heat is lost to or gained from ıe surroundings.

he calorimeter could be made of stainless steel or copper plated with gold. For ıost practical purposes, glass beakers are used as calorimeters. In case of glass alorimeters, due to the poor thermal conductivity of glass, heat capacity actually aries with the area of the glass in contact with the liquid content. It is, therefore, ssential to calibrate the calorimeter with the volume of water that is to be used in ubsequent experiments.

he following two methods are generally adopted for determining the heat capacity f the calorimeter: (1) Dilution method, (2) Heat exchange method. Here, we will iscuss the second method in detail because you will be actually using this for xperimental determination.

6.5.1 EXPERIMENT 3 : DETERMINATION OF THE HEAT CAPACITY OF A CALORIMETER

Heat Exchange Method

In this method, a definite volume, *V*, of the cold water is taken in the calorimeter. To this, the same volume of hot water is mixed. The temperatures of the cold water (T_c), hot water (T_h) and the mixture (T_m) are noted. In this case, the heat will be lost by hot water which will be gained by both the cold water and the calorimeter. According to the principle of calorimetry,

Heat gained by (cold water + calorimeter) = Heat lost by hot water,

i.e.,
Enthalpy change for (cold water + calorimeter) = Enthalpy change for hot water.

From Eq. 6.11, the heat or the enthalpy change is equal to $C_p.dT$. Substituting this formula for the individual components into the above equation, we get the following expression:

$$\left[C_p\,(\text{cold water}) + C_p\,(\text{calorimeter})\right]\left[T_m - T_c\right] = C_p\,(\text{hot water})\left[T_h - T_m\right] \quad \ldots (6.15)$$

The left hand side of Eq. 6.15 is obtained from Eq. 6.11 using the fact that the temperature change ($dT = T_m - T_c$) is the same both for the calorimeter and the cold water. In order to use Eq. 6.15, for the determination of heat-capacity of the calorimeter we shall see yet another definition for the term heat capacity. The heat capacity of a substance is equal to the product of its mass and specific heat.

Heat capacity of a substance=mass × specific heat

Specific heat(s) is the heat required to raise the temperature of 1g (0.001 kg) of a substance through 1°C.

For a calorimeter, the product of the two quantities, viz., the mass and its specific heat ($m \times s$) is also known as its water equivalent, *W*.

We use this relationship only to denote C_p (cold water) and C_p (hot water) but not for C_p (calorimeter). It is our aim to find out C_p (calorimeter) by performing this experiment ! Using this relation, the above equation can be modified as:

$$\left[m \times s\,(\text{cold water}) + C_p\,(\text{calorimeter})\right]\left[T_m - T_c\right] = \left[m \times s\,(\text{hot water})\right]\left[T_h - T_m\right] \quad \ldots (6.16)$$

We assume that,

$$s\,(\text{cold water}) = s\,(\text{hot water}) = s(\text{say})$$

In other words, specific heat of water is taken to be a constant irrespective of the temperature.

Hence, Eq. 6.16 becomes,

$$\left[(ms + C_p\,(\text{calorimeter})\right]\left[T_m - T_c\right] = ms\,(T_h - T_m) \quad \ldots (6.17)$$

$$\therefore \quad ms + C_p\,(\text{calorimeter}) = ms\,\frac{(T_h - T_m)}{(T_m - T_c)}$$

$$C_p\,(\text{calorimeter}) = ms\,\frac{(T_h - T_m)}{(T_m - T_c)} - ms$$

$$= ms\left[\frac{(T_h - T_m)}{(T_m - T_c)} - 1\right] \quad \ldots (6.18)$$

We shall now discuss the values of *m* and *s* individually.

Value of m

We know that mass of a substance = volume × density. The density of water is 1 kg dm^{-3}. You will be measuring the volume in cm^3 units. But you should express the volume in dm^3 units for compatibility of units.

You can understand the unit conversion for density of water as follows :

$$1\ g\ cm^{-3} = 1(10^{-3}\ kg)(10^{-1}\ dm)^{-3} = 1 \times 10^{-3}\ kg \times 10^{3}\ dm^{-3} = 1\ kg\ dm^{-3}$$

In other words, the magnitude of density is same in both the units expressed above.

$$1\ cm = 10^{-1}\ dm$$

$$(1\ cm)^3 = (10^{-1}\ dm)^3 = 10^{-3}\ dm^3$$

Note that,

$$\text{Volume in } dm^3 \text{ units} = \frac{\text{volume in } cm^3 \text{ units}}{10^3}$$

Since the volumes of cold water and hot water are equal, we can say that

$$\text{Volume of cold water} = \text{Volume of hot water} = V\ cm^3 = \frac{V}{10^3}\ dm^3$$

Hence, mass of cold water (m)

$$= \text{mass of hot water } (m) = \text{Volume} \times \text{density} = \frac{V}{10^3}\ dm^3 \times d_w\ \ kg\ dm^{-3}$$

$$\text{i.e.,} \qquad m = \frac{V}{10^3}\ d_w\ kg \qquad \ldots (6.19)$$

Note that the value of density d_w is to be used as given in the table in Appendix of this Block. Magnitude wise the density is same both in g cm^{-3} and kg dm^{-3} units.

Note that now you have got mass in terms of volume you are measuring experimentally. You simply substitute the **magnitude of volume you measure in the** place of V above. Mass so obtained is in kg units.

Value of s

The SI units of specific heat are J K^{-1} kg^{-1}. The specific heat of water in SI units is 4.185×10^3 J $K^{-1} kg^{-1}$, i.e.,

$$s = 4.185 \times 10^3\ J\ K^{-1}\ kg^{-1} \qquad \ldots (6.20)$$

Substituting Eqs. 6.19 and 6.20 in Eq. 6.18, we get,

$$C_p(\text{calorimeter}) = \frac{V \cdot d_w}{10^3}\ kg \times 4.185 \times 10^3\ J\ K^{-1}\ kg^{-1} \left[\frac{T_h - T_m}{T_m - T_c} - 1\right]$$

$$C_p\ (\text{calorimeter}) = 4.185 V\ d_w \left[\frac{T_h - T_m}{T_m - T_c} - 1\right]\ J\ K^{-1} \qquad \ldots (6.21)$$

Having measured the volume in cm^3 units, you substitute it as such in Eq. 6.21 without attempting any unit conversion. By substituting the values of T_h, T_m and T_c, you will get the value of C_p in J K^{-1} units.

Requirements

Apparatus			Chemicals
Thermos flask	—	1	Only water is needed
Glass Stirrer	—	1	
Thermometer −110°C (1/10°C)	—	1	
Stop watch or stop clock	—	1	
Beaker 250/400 cm^3	—	2	
Measuring cylinder 100 cm^3	—	1	

Procedure

Take a thermos flask with a lid having two holes. Through one of these holes insert the thermometer and through the other insert the stirrer. Take 100 cm^3 of distilled water into a 250/400 cm^3 beaker. Keep this beaker in the thermos flask. Note down the temperature of water after every half a minute for about 4 minutes. Take 100 cm^3 of water in another beaker and increase its temperature by 20 degrees more than the room temperature. Remove the burner and note down the temperature at an interval of half a minute for another 4 minutes. Then quickly pour this hot water into the calorimeter, stir the contents and note down the temperature after every half minute for about 4 minutes.

Temperature–time curves are also known as cooling curves.

Plot the temperature-time curves for the cold water, hot water and the mixture on a graph paper. You will get curves similar to those shown in Fig. 6.1. Calculate the temperature of the cold water (T_c), hot water (T_h) and the mixture (T_m) at the time of mixing from the graph. Then find out the heat capacity of the calorimeter by substituting the above values in Eq. 6.21.

Repeat the experiment to get reproducible results.

How to plot temperature-time curve

Take a graph paper. Draw with a pencil, X and Y axes. Represent temperature on Y axis and Time on X axis. Put points corresponding to temperature recorded for the cold water with respect to time. Suppose you have recorded the temperature for cold water for 4 minutes. Then do similarly for the hot water (i.e., plot the temperature recorded for hot water for another 4 minutes). At the time when hot water is mixed with cold water (i.e., at $8\frac{1}{2}$ minutes), draw a line as mixing line. Start plotting the temperature of the mixture from next reading of time (i.e., at 9 minutes). Extrapolate the three lines and get T_c, T_h and T_m as shown in Fig.6.1.

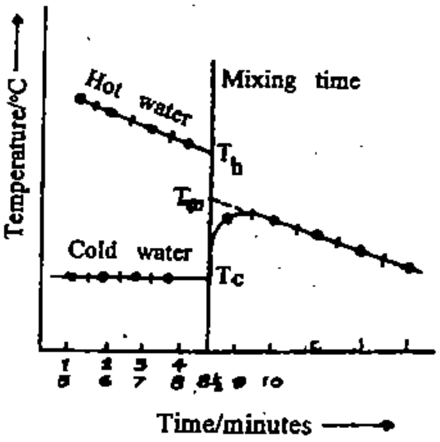


Fig. 6.1: Temperature–time curve.

Observations

SET I

Volume of cold water, $V = 100\ cm^3 = 0.1\ dm^3$
Volume of hot water, $V = 100\ cm^3 = 0.1\ dm^3$
Temperature - time data for cold, hot water and the mixture:

Time/s	Temperature/°C		Time/s	Temperature/°C Mixture
	Cold Water	Hot Water		
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....

Time of mixing =........ s

SET II : Similar observations as reported above.

Time/s	Temperature/°C		Time/s	Temperature/°C (Mixture)
	Cold Water	Hot Water		
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
			Time of mixing	=........s

You can do the calculations as shown below:

Calculations

Plot a graph of temperature versus time for cold water, hot water and for the mixture on a single graph paper. Find the temperature of cold water (T_c), hot water (T_h) and for the mixture (T_m) from the curves. Put these values in Eq. 6.21 and calculate the heat capacity of the calorimeter, C_p. Similarly calculate C_p with the help of the data of the second set of observations. Then take the average value if the results are not very far from each other; otherwise repeat the experiment.

Report your result as follows.

Result :

The heat capacity of the given calorimeter is =..... J K^{-1}

SAQ 1

Explain how the unit of heat capacity is J K^{-1}.

....

....

....

Having determined the heat capacity (or the water equivalent) of the calorimeter, you can now proceed to the determination of integral enthalpy of solution.

6.5.2 EXPERIMENT 4 : DETERMINATION OF THE INTEGRAL ENTHALPY OF SOLUTION OF AMMONIUM CHLORIDE

Principle

In the laboratory, the integral enthalpy of solution is determined by observing the initial temperature, T_1 of a known volume of water (if water is used as the solvent, and the final temperature, T_2 of the contents when a known mass of the solute is completely dissolved in it. The enthalpy of solution of ammonium chloride can be calculated by taking into account the heat capacity of the calorimeter in the following manner.

Heat change = [(Heat capacity of the calorimeter+Heat capacity of the products) × (temperature change)]

$$q_p = [C_p(P) + C_p(c)](T_2 - T_1) \qquad \ldots (6.22)$$

Where $C_p(P)$ and $C_p(c)$ are the heat capacities of the products and the calorimeter, respectively. The latter can be determined as discussed in Experiment 3. The heat capacity of the products can be calculated presuming the solution to be quite dilute. In other words, considering the heat capacity component of the solute as negligible, we can assume that $C_p(P)$ is equal to the heat capacity of the water taken, i.e.,

$$\begin{aligned} C_p(P) &= \text{Mass of water } (m_w) \times \text{ specific heat of water } (s) \\ &= m_w\, s \qquad \ldots (6.23) \\ &= m_w \times 4.185 \text{ J K}^{-1} \qquad \ldots (6.24) \end{aligned}$$

The enthalpy of solution for one mole of the solute can thus be calculated as:

$$\Delta H_{sol} = q_p/n \qquad \ldots (6.25)$$

where n is the amount (number of moles) of the solute added, i.e.

$$n = \frac{\text{mass of solute/g}}{\text{molar mass of solute/g mol}^{-1}} = \frac{m_2}{M} \ldots \text{ mol} \qquad \ldots (6.26)$$

Using Eqs. 6.22 to 6.26, we can say,

$$\Delta H_{sol} = \frac{q_p}{n} = [m_1 s + C_p(c)](T_2 - T_1)\frac{M}{m_2} \qquad \ldots (6.27)$$

Note that $s = 4.185 \text{ J K}^{-1} \text{ kg}^{-1}$

Therefore, this ΔH value is the integral enthalpy of the solution of a solute in a specific mole ratio of the solute to the solvent.

1 mol of NH_4Cl
= 14+4+35.5 = 53.5 g
molar mass of
NH_4Cl=0.0535 kg

The calculation of the mass of ammonium chloride required for preparing a solution with a specific solute-solvent mole ratio of 1:100 in 200 cm^3 of water can be done as follows:

100 mol of water is required for 1 mol of NH_4Cl
100 × 0.018 kg (18 g) of water is required for 0.0535 kg (53.5 g) of NH_4Cl
Mass of 200 cm^3 of water= 200 g =0.200 kg

$$0.200 \text{ kg of water requires } \frac{0.0535 \times 0.200}{1.8} = 0.0059445 \text{ kg of } NH_4Cl$$
$$= 5.9445 \text{ g of } NH_4Cl$$

Requirements

Apparatus

Thermos flask	—	1
Glass Stirrer	—	1
Thermometer 110 °C (1/10 °C)	—	1
Stop watch or stop clock	—	1
Beaker 250/400 cm^3	—	1
Measuring cylinder 100 cm^3	---	1
Weighing bottle	—	1
Funnel	—	1

Chemicals

solid Ammonium Chloride
Water

Procedure

(1) Weigh the appropriate mass of ammonium chloride on a glazed paper or in a weighing bottle, i.e. 0.0059445 kg (5.9445 g) for 1:100 solute–solvent mole ratio for 0.200 kg or 200 cm^3 water.

(2) Take 200 cm^3 of distilled water (solvent) in a beaker. Use the beaker (calorimeter) for which the heat capacity has already been determined in the previous experiment. Place it in a thermos flast. Insert the thermometer and the stirrer into the holes of the lid. Note down the temperature of water for about 4 minutes at an interval of half-a-minute.

(3) Add ammonium chloride (solute) to the water. Stir the solution well with the help of the stirrer already placed in the beaker. Note down the time of mixing and the temperature readings after every half a minute for another 4 minutes.

(4) Repeat the experiment for reproducible results.

(5) Plot temperature-time curve on a graph paper and find out the initial and final temperature from it. Then calculate the enthalpy of solution for this mass of solute using Eq. 6.22 and consequently the enthalpy of solution for the dissolution of one mole of solute using Eq. 6.27.

You can record your observations as shown below:

Observations

SET I

Mass of empty weighing bottle = m_1 =..... g

Mass of weighing bottle+NH_4Cl = m_2 =..... g

Mass of weighing bottle after transferring of salt = m_3 =..... g

Mass of salt transferred (m) = m_2–m_3 =..... g

Volume of water in calorimeter = V =..... cm^3

Mass of water = m_w =..... g = $\frac{......}{1000}$ kg

Temperature-time data for pure water and for solution :

Time/s	Temperature/°C of water	Time/s	Temperature/°C of solution
....	....	....	....
....	....	....	....
....	....	....	....
....	....	....	....
....	....	....	....
....	....	....	....
....	....	....	....
....	....	....	....
....	....	....	....
....	....	....	....
		Time of mixing	=........ s

SET II: Similarly present the data for the second set also.

Mass of empty weighing bottle =m_1 =.... g

Mass of weighing bottle+NH_4Cl =m_2 =.... g

Mass of weighing bottle after transferring of salt =m_3 =.... g

Mass of salt transferred(m) =m_2–m_3 =.... g

Volume of water in calorimeter =V =.... cm^3

Mass of water =m_w =.... g = $\frac{......}{1000}$ kg

Temperature-time data for pure water and for solution :

Time/s	Temperature/°C of water	Time/s	Temperature/°C of solution
....	....	....	....
....	....	....	....
....	....	....	....
....	....	....	....
....	....	....	....
....	....	....	....
....	....	....	....
....	....	....	....
....	....	....	....
....	....	....	....
		Time of mixing = ... s	

Calculations

Plot the graph of temperature-time curve on a graph paper and find out the value of T_1, the constant temperature of water and T_2, the temperature of the solution at the time of mixing. Calculate the enthalpy change for dissolving the specific mass of ammonium chloride in the above mentioned salt-water ratio.

The same procedure is adopted to calculate the value of ΔH for the second set. Calculate the average value of enthalpy of solution from the two sets of values.

Result

The integral enthalpy of solution of ammonium chloride was found to be .... J mol^{-1}.

6.8 ANSWERS

Self Assessment Question

1 Heat capacity is given by the expression *ms*.

Thus, the units of heat capacity $= \text{kg J K}^{-1}\,\text{kg}^{-1}$

$= \text{J K}^{-1}$.

UNIT 7 DETERMINATION OF ENTHALPY OF NEUTRALISATION AND IONISATION

Structure

7.1 Introduction
    Objectives
7.2 The Enthalpy of Neutralisation
    Experiment 5: Determination of the Enthalpy of Neutralisation of Hydrochloric Acid with Sodium Hydroxide
        Principle
        Requirements
        Procedure
        Observations
        Calculations
        Results
    Experiment 6: Determination of the Enthalpies of Neutralisation and Ionisation of Acetic Acid
        Principle
        Requirements
        Procedure
        Observations
        Calculations
        Results
7.3 Answers

7.1 INTRODUCTION

In the last unit, you have studied about the determination of the integral enthalpy of solution. There are other kinds of enthalpies which are named according to the type of transformation or reaction they are associated with. The examples of some such enthalpies include **enthalpy of combustion, enthalpy of fusion, enthalpy of formation, enthalpy of hydration, enthalpy of neutralisation, enthalpy of ionisation**, etc. In this unit, we will be discussing the determination of

(i) the enthalpy of neutralisation and

(ii) the enthalpy of ionisation, using the enthalpy of neutralisation.

Objectives

After studying this unit and having the experiments performed, you should be able to:

- define the enthalpy (heat) of neutralisation,
- give reason for the constant value of ΔH_{neut} for the neutralisation of a strong acid with a strong base, and
- explain how to calculate the enthalpy of ionisation of a weak acid or a weak base from the enthalpy of its neutralisation.

7.2 THE ENTHALPY OF NEUTRALISATION

The **enthalpy of neutralisation** (ΔH_{neut}) of an acid can be defined as the enthalpy change associated with the complete neutralisation of its dilute aqueous solution containing one mole of H^+ ions by a dilute aqueous solution of a base containing one mole of OH^- ions. Let us consider the example of neutralisation of hydrochloric acid with sodium hydroxide. You are aware that hydrochloric acid is a strong acid and sodium hydroxide is a strong base. This means that both hydrochloric acid and sodium hydroxide are completely dissociated in aqueous solution. Therefore, we can write

$$HCl\,(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

and $$NaOH\,(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$

The neutralisation reaction can be represented as

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow Na^+(aq) + Cl^-(aq) + H_2O$$

or $$HCl\,(aq) + NaOH(aq) \longrightarrow NaCl\,(aq) + H_2O$$

$$\Delta H_{neut} = -57.3 \text{ kJ mol}^{-1}$$

Thus, the neutralisation of a strong acid with a strong base can be considered as the combination or reaction of H^+ (aq) ions with OH^-(aq) ions and can be represented as

$$H^+(aq)^+ + OH^-(aq) \longrightarrow H_2O$$

because Na^+ and Cl^- remain unchanged in the reaction.

In other words, the enthalpy of neutralisation of strong acids and strong bases is the enthalpy of formation of 1 mole of water from one mole each of H^+ and OH^- ions.

You must then also expect that the enthalpy of neutralisation of the strong acids with strong bases to be of a constant value irrespective of the strong acid or the strong base used.

Let us now focus our attention on the actual determination of the enthalpy of neutralisation.

7.2.1 EXPERIMENT 5 : DETERMINATION OF THE ENTHALPY OF NEUTRALISATION OF HYDROCHLORIC ACID WITH SODIUM HYDROXIDE

Requirements

Apparatus		
Thermos Flask	—	1
Glass Stirrer	—	1
Thermometer 110° (1/10°C)	—	1
Stop Watch or Stop Clock	—	1
Beaker 250/400 cm^3 (1 as calorimeter)	—	2
Measuring Cylinder 100 cm^3	—	1

Chemicals

Sodium hydroxide

Hydrochloric acid

Solutions Provided

0.50 mol dm^{-3} NaOH

0.50 mol dm^{-3} HCl

Procedure

Measure 100 cm^3 of HCl in a beaker for which heat capacity has already been determined in Experiment 3. Place it in a thermos flask. Insert the stirrer and the thermometer through the two holes and cover the thermos flask with the lid. Stir the contents with the stirrer and note down the temperature of the acid after every half a minute for 5 minutes. Take 100 cm^3 of NaOH in another beaker (preferably in a flask) and note down its temperature after every half a minute for five minutes. Pour the NaOH solution in the acid already placed in the thermos flask and note down the exact time of mixing. Close the lid and keep on stirring the solution and note down temperature after every half minute for another 5 minutes. Repeat the experiment for second set of readings.

You can record your observations as given below:

Observations

Neutralisation of HCl with NaOH:

SET I

Volume of HCl in the calorimeter, $V_{\text{acid}} = 100\ \text{cm}^3$
Volume of NaOH in the beaker, $V_{\text{base}} = 100\ \text{cm}^3$.

Temperature–time data for acid, base and for mixture :

Time/s	Temperature/°C		Time/s	Temperature/°C Mixture
	HCl	NaOH		
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
			Time of mixing =.........s	

SET II: Take observations in a similar way and record them in the same manner as given above for Set I.

Volume of HCl in the calorimeter, $V_{\text{acid}} = 100\ \text{cm}^3$
Volume of NaOH in the beaker, $V_{\text{base}} = 100\ \text{cm}^3$

Temperature–time data for acid, base and for mixture :

Time/s	Temperature/°C		Time/s	Temperature/°C Mixture
	HCl	NaOH		
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
			Time of mixing = ... s	

Calculations

(1) Plot temperature — time curve for the neutralisation of HCl with NaOH data. You will get a plot as given in Fig. 7.1. From the graph, calculate T_b and T_a (the temperature of the reactants: base and acid, respectively) and T_m, the temperature of the products.

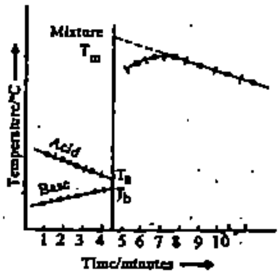


Fig. 7.1 : Temperature-time curve for neutralisation.

(2) The heat evolved during neutralisation will raise the temperature of the solution and that of the beaker (calorimeter). In other words, the enthalpy change for the neutralisation of the given amount of the acid with the given amount of the base is equal in magnitude but opposite in sign to the heat gained by the calorimeter and its contents. That is why there is a negative sign in the right hand side of Eq. 7.1 as given below:

$$\Delta H = -[\text{Heat gained by the calorimeter} + \text{Heat gained by the solution}] \qquad \ldots (7.1)$$

$$= -[(\text{Heat capacity of the calorimeter} \times \text{Rise in temperature of the calorimeter}) + (\text{Mass of base} \times \text{Specific heat of base} \times \text{Rise in temperature of base}) + (\text{Mass of acid} \times \text{Specific heat of acid} \times \text{Rise in temperature of acid})]$$

$$= -[\{C_p\,(\text{c}) \text{ as obtained in the earlier experiment} \times (T_m - T_a)\} + \{V_{\text{base}} \times \text{sp. heat of base} \times (T_m - T_b)\} + \{V_{\text{acid}} \times \text{sp. heat of acid} \times (T_m - T_a)\}] \qquad \ldots (7.2)$$

For dilute solutions of acids and bases, mass can be assumed to be equal to volume because density could be taken as 1 kg dm^{-3} for them.

Using Eq. 7.3,

$$\Delta H = -[C_p\,(\text{c})\,(T_m - T_a) + V_{\text{base}}\,s(T_m - T_b) + V_{\text{acid}}\,s(T_m - T_a)] \qquad \ldots (7.4)$$

Calculate ΔH from Eq. 7.4 by substituting the values of T_m, T_a and T_b as obtained by the plot of temperature versus time curve and those of heat capacity of calorimeter [C_p(C) from Experiment 3] and specific heat (s = 4.185 J K^{-1}kg^{-1}). ΔH so obtained in the above equation is the enthalpy change for the neutralisation of 100 cm^3 of 0.5 M HCl with 100 cm^3 of 0.5 M NaOH. From this ΔH, you can now calculate the ΔH_{neut} as follows.

The specific heat of water is 4.185 J K^{-1} kg^{-1}. For a dilute solution of an acid and a base, the specific heats can be assumed to be equal to the specific heat of water. Let us denote the specific heat of water as s. Hence, specific heat of acid
= specific heat of base
= specific heat of water = s ...(7.3)

You know that the enthalpy of neutralisation is the enthalpy change per mole of the substance neutralised. Thus, we have to first calculate the amount (number of moles) of HCl present in the volume of solution taken for neutralisation in the experiment. As given in the procedure, when 100 cm^3 of 0.5 M HCl in neutralised using 100 cm^3 of 0.5 M NaOH, then, the amount (no. of moles) of HCl present in the 200 cm^3 solution (100 cm^3 acid + 100 cm^3 base) will be equal to 0.05 mole.

0.5 M HCl means 0.5 mole of HCl present in 1 dm^3 of the solution. Thus, amount (no. of moles) of HCl present in 100 cm^3 of HCl (or 200 cm^3 of the solution)

$$= \frac{0.5}{10} \text{ mole} = 0.05 \text{ mole}$$

Because $1 \text{ dm} = 10 \text{ cm}$
and $(1 \text{ dm})^3 = (10 \text{ cm})^3$

$1 \text{ dm}^3 = 1000 \text{ cm}^3$ or $100 \text{ cm}^3 = \frac{1}{10} \text{ dm}^3$.

Thus, to get the amount (number of moles) present in 100 cm^3 of 0.5 M HCl or 200 cm^3 of the solution from the molarity (or amount in no. of moles of substance present in 1 dm^3), we have to divide the molarity by 10 as done above.

To calculate the heat of neutralisation, we have to divide the ΔH obtained by Eq. 7.4 by amount (the number of moles) of hydrochloric acid, i.e.,

$$\Delta H_{\text{neut}} = \frac{\Delta H(\text{obtained from Eq. 7.4})}{\text{amount (No. of moles) of HCl}}$$

$$= \frac{\Delta H\ (\text{obtained from Eq. 7.4})}{0.05}$$

$$= \ldots\ldots \text{ J mol}^{-1}$$

Now report your result as given below:

Result

The heat of neutralisation of hydrochloric acid with sodium hydroxide is ..... J mol^{-1}

Let us now turn to a similar experiment using acetic acid instead of hydrochloric acid.

7.2.2 EXPERIMENT 6: DETERMINATION OF THE ENTHALPIES OF NEUTRALISATION AND IONISATION OF ACETIC ACID

Principle

The enthalpy of neutralisation of acetic acid can be determined by the similar method as done above for the hydrochloric acid. The acetic acid, in contrast to the hydrochloric acid, is a **weak acid** and is **not completely** dissociated in dilute aqueous solutions into H^+ and CH_3COO^- ions.

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+(aq)$$

When acetic acid is neutralised with a base (NaOH), some of the heat evolved during the neutralisation is used in the process of dissociating the acetic acid to allow the completion of neutralisation. Therefore, you can expect that the enthalpy change associated with the neutralisation of acetic acid (a weak acid) with a strong base to be lower than that of the enthalpy of neutralisation of a strong acid with a strong base (i.e., $-57.3\ \text{kJ mol}^{-1}$). Similarly, the value of enthalpy of neutralisation of a weak base with a strong acid will also be lower than that of the enthalpy of neutralisation of a strong base with a strong acid.

The difference in the enthalpy of neutralisation of a strong acid (HCl) with a strong base (NaOH) and enthalpy of neutralisation of weak acid (CH_3COOH) with strong base (NaOH) will give the enthalpy of ionisation of the weak acid (CH_3COOH).

Since the ionisation proceeds simultaneously with neutralisation, the enthalpy change observed is the sum of enthalpy of ionisation and enthalpy of neutralisation, i.e.,

$$\begin{aligned} \Delta H_{\text{ionis}} + \Delta H_{\text{neut}} &= \Delta H_{\text{observed}} \\ \Delta H_{\text{ionis}} &= \Delta H_{\text{obs}} - \Delta H_{\text{neut}} \\ &= \Delta H_{\text{obs}} - (-57.3\ \text{kJ mol}^{-1}) \\ \Delta H_{\text{ionis}} &= \Delta H_{\text{obs}} + 57.3\ \text{kJ mol}^{-1} \end{aligned}$$

Since the ΔH_{obs} has a negative sign and is smaller in value than 57.3, ΔH_{ionis} is positive. Thus, ionisation is endothermic.

Requirements

Apparatus

Thermos flask	—	1
Glass stirrer	—	1
Thermometer — 110°C 1/10th°C)	—	1
Stop Watch or Stop Clock	—	1
Beaker 250/400 cm^3	—	2
Measuring cylinder 100 cm^3	—	1

Chemicals

Acetic acid
Sodium Hydroxide

olutions Provided

0.50 mol dm^{-3} CH_3COOH
0.50 mol dm^{-3} NaOH

rocedure

o exactly in a similar way as done in the previous experiment using acetic acid stead of hydrochloric acid.

Record your observations in the following manner.

Observations

Neutralisation of CH_3COOH with NaOH

SET I

Volume of CH_3COOH in the calorimeter, $V_{acid} = 100\ cm^3$
Volume of NaOH, $V_{base} = 100\ cm^3$

Temperature-time data for the acid, the base and for the mixture:

Time/s	Temperature/°C		Time/s	Temperature/°C Mixture
	CH_3COOH	NaOH		
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
			Time of mixing =........s	

SET II

Repeat same observations as done above for Set I.

Volume of CH_3COOH in the calorimeter, $V_{acid} = 100\ cm^3$
Volume of NaOH, $V_{base} = 100\ cm^3$

Temperature-time data for the acid, the base and for the mixture:

Time/s	Temperature/°C		Time/s	Temperature/°C Mixture
	CH_3COOH	NaOH		
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
....	....	....	....	....
			Time of mixing =........s	

Calculations

From the observations that you have recorded, plot a graph of temperature versus time for the acid, the base and the mixture. You will get a similar plot as you got in the previous experiment. From this plot, note down the temperature of the acid (T_a), the base (T_b) and the mixture (T_m). Now, substitute the values of T_a, T_b and T_m in Eq. 7.4 and get the value of enthalpy change (ΔH) or heat evolved during the neutralisation of 100 cm^3 of 0.5 M CH_3COOH with 100cm^3 of 0.5 M NaOH. Then divide the above value of enthalpy change with the number of moles of acetic acid present in the amount of solution taken for neutralisation.

Remember ΔH_{neut} has a negative sign.

$$\Delta H_{neut} \text{ of acetic acid} = \frac{\Delta H \text{ (obtained above)}}{0.05 \text{ mol}}$$

$$= \text{......} \text{ kJ mol}^{-1}$$

Now calculate the enthalpy of ionisation of acetic acid as given below:

$$\Delta H_{ionis} = \Delta H_{neut} \text{ (strong acid with strong base)} -$$

$$\Delta H_{neut} \text{ (acetic acid with NaOH)}$$

$$= (57.3 \text{ kJ mol}^{-1}) + (\text{value of } \Delta H_{neut} \text{ as obtained above})$$

$$= \text{.........} \text{ kJ mol}^{-1}$$

Result

The enthalpy of neutralisation of acetic acid with sodium hydroxide is .... kJ mol^{-1} and the enthalpy of ionisation of acetic acid is .... kJ mol^{-1}.

SAQ 1

Calculate the mass of acetic acid present in 75.0 cm^3 of 0.150 molar solution.

....

....

....

....

7.3 ANSWERS

Self Assessment Questions

1 1000 cm^3 acetic acid solution contains 0.150 mol acetic acid

$$75.0 \text{ cm}^3 \text{ acetic acid solution will contain } \frac{0.150 \text{ mol} \times 75.0 \text{ cm}^3}{1000 \text{ cm}^3}$$

$$= 0.01125 \text{ mol}$$

$$= 0.01125 \text{ mol} \times 0.0600 \text{ kg mol}^{-1}$$

$$= 6.75 \times 10^{-4} \text{ kg}$$

The molar mass of acetic acid is 0.0600 kg mol^{-1}

Appendix

Density of water at different temperatures

Temperature/°C	Density/ g cm^{-3}
10	0.9997
15	0.9991
20	0.9982
21	0.9980
22	0.9978
23	0.9975
24	0.9973
25	0.9970
26	0.9968
27	0.9965
28	0.9962
29	0.9959
30	0.9956
31	0.9953
32	0.9950
33	0.9947
34	0.9944
35	0.9941
40	0.9922

NOTES

NOTES

Utter Pradesh
Rajarshi Tandon Open University

UGCHE-L4
Chemistry Lab-IV

Block

3

APPLICATIONS OF THERMODYNAMICS

UNIT 8

Depression of Freezing Point 5

UNIT 9

Applications of Emf Measurements 9

UNIT 10

Adsorption 19

UNIT 11

Phase Equilibria - I 28

UNIT 12

Phase Equilibria - II 36

BLOCK 3 APPLICATIONS OF THERMODYNAMICS

In Block 1 of this course, you were introduced to some basic laboratory skills and techniques, and three demonstration experiments based on colorimetry, conductometry and potentiometry. In Block 2, you studied some experiments based on properties of liquids and thermochemical measurements.

In this block, you will study some experiments which are based on the applications of thermodynamics. In Unit 8, you will study the determination of molecular mass of a non-volatile solute by Rast method. Unit 9 deals with the measurement of emf of cells for determining the pH of a solution and the solubility product of a sparingly soluble salt. In Unit 10, we describe an experiment for verifying adsorption isotherms for adsorption of oxalic acid on charcoal. Units 11 and 12 deal with experiments based on phase equilibria. In Unit 11, we describe an experiment for constructing phase diagram for a simple eutectic system. In Unit 12, you will study the determination of CST of phenol-water system and the effect of impurity on the CST of this system. In this unit you will also study the determination of distribution coefficient of iodine in carbon tetrachloride-water system, and of benzoic acid in toluene-water system.

Objectives

After studying this block and having performed the experiments described, you should be able to:

- determine molar mass of a solute by Rast method,
- determine pH of an acid solution by measuring emf of appropriate galvanic cells,
- determine the solubility product of a sparingly soluble salt by emf measurements,
- verify adsorption isotherms for adsorption of oxalic acid on charcoal,
- construct phase diagram for a simple eutectic system,
- determine CST of phenol-water system,
- determine concentration of unknown sodium chloride solution by CST method,
- determine the distribution coefficient of iodine in carbon tetrachloride-water system, and of benzoic acid in toluene-water system.

Study Guide

We are going to represent concentrations of solutions using scientific notation, since we would like to express the results maintaining the significant figures. For example, instead of 0.1 M, we prefer to write 1.000×10^{-1} M. This is because we are going to use four figure logarithms for calculation (although the weighing may be accurate upto 0.2 mg).

For the sake of convenience in calculations and plotting graphs, it is desirable to take solutions of certain concentrations for various experiments. However, in their place, you can also use other solutions of known concentrations. For example, in Experiment 11, you are advised to use a standardised solution of potassium permanganate of concentration, 2.000×10^{-2} M. It does not mean that you have to use only 2.000×10^{-2} M $KMnO_4$. In fact, you can use any standardised solution of $KMnO_4$ having concentration about 0.02 M.

UNIT 8 DEPRESSION OF FREEZING POINT

Structure

8.1 Introduction
  Objectives
8.2 Experiment 7 : Determination of Molar Mass by Rast Method
  Principle
  Requirements
  Procedure
  Observations
  Calculations
  Result
8.3 Summary
8.4 Terminal Questions
8.5 Answers

8.1 INTRODUCTION

In this unit, you will study how to determine the molar mass of a non-volatile solute by Rast Method. This method is based upon the measurement of depression of freezing point of a solvent by addition of a known amount of non-volatile solute. The depression of freezing point is a colligative property, since it depends on the number of non-volatile solute particles in solution. The only condition is that the solute should not associate or dissociate in solution. Osmotic pressure, relative lowering of vapour pressure and elevation of boiling point are some other examples of colligative properties, which you might have studied in detail in Unit 12 of the CHE-04 course.

After studying this unit and having performed the experiment described in the unit, you should be able to:

- explain what is meant by colligative property,
- give examples of colligative properties,
- state the relation between depression of freezing point and molality of the solution,
- define molal depression constant, and
- determine molar mass of a solute by measuring depression of freezing point.

8.2 EXPERIMENT 7 : DETERMINATION OF MOLAR MASS BY RAST METHOD

This method was devised by Rast in 1922. Rast method is actually a micro-method because only a few milligrams of the solute are required. This method can be used for determining the molar mass of those non-volatile solutes which dissolve in molten camphor and do not react with it or decompose at its melting point. The molal depression constant of camphor is very high, i.e., 40.00 K kg mol^{-1}. It means that when one mole of a solute is dissolved in one kilogram of camphor, the depression in freezing point is 40°C, which can be read using an ordinary thermometer. Thus, there is no need of using a costly Beckmann thermometer to measure the depression in freezing point. In this method, we actually measure the depression in melting point of camphor. But, the melting point of solid phase and the freezing point of liquid phase of any substance are the same. Therefore, it does not make any difference whether we measure depression in the melting point or depression in the freezing point.

8.2.1 Principle

When a non-volatile solute is added to a solvent, it lowers the freezing point of the solvent. The relationship between the molar mass of a non-volatile solute and the depression in freezing point of a solvent has been discussed in Unit 12 of the CHE-04 course. We shall use Eq. 12.37 from this Unit for this purpose of determining molar mass of a non-volatile solute by Rast method.

$$\Delta T_f = \frac{K_f w_2}{w_1 M_2} \qquad \text{... (12.37)}$$

where $K_f = \dfrac{RT^2 M_1}{\Delta H_{fus}}$ = molal depression constant

Eq. 12.37 can also be written as

$$M_2 = \frac{K_f w_2}{\Delta T_f w_1} \qquad \text{... (8.1)}$$

where w_1 and w_2 refer to the masses of the solute and solvent (camphor), respectively, M_2 stands for the molar mass of the solute and ΔT_f refers to the depression in melting point of the solvent.

ΔT_f = Depression in Melting point of the solvent
= (Melting point of the solvent) − (Melting point of the mixture)
= $T_0 - T_1$

In Eq. 8.1, w_1 and w_2 are in kg unit, M_2 is in kg mol^{-1} units and K_f is in K kg mol^{-1} units. The molal depression constant of camphor is 40.0 K kg mol^{-1}. w_1, w_2 and ΔT_f are experimental quantities. Thus, using Eq. 8.1, you can calculate the molar mass of the given solute.

If you want to study more about the depression of freezing point and other colligative properties, go through Unit 12 of the CHE- 04 (physical chemistry) course.

SAQ 1

The molal depression constants of water, acetic acid, cyclohexane and camphor are 1.85, 3.90, 20.20 and 40.00 K kg mol^{-1}, respectively. Which of the above four you would prefer for determining the molar mass of a non-volatile solute and why?

8.2.2 Requirements

Apparatus

1.	Beaker 100 cm^3	1
2.	Capillary tubes	5
3.	One-tenth degree thermometer	1
4.	Thiele's melting point tube	1
5.	Test tube	1

Chemicals

1. Camphor
2. Acetanilide, urea or thiourea
3. Liquid paraffin

8.2.3 Procedure

Prepare a homogeneous mixture of the solute and camphor. For this, take a clean and dry test tube and weigh it accurately on an analytical balance. Put about 200 mg of the solute in it and weigh it. Now add approximately 3 g of camphor to the test tube and note down its mass. Seal the open end of the tube on the flame by drawing a capillary. Melt the mixture by placing it in a beaker containing liquid paraffin. Continue heating till the mixture melts completely and the temperature of the bath is about 5° above the melting point of pure camphor i.e., 177°C. Mix the contents of the tube by rotating it. Now cool the tube quickly in a water bath. Repeat the process of heating and cooling the mixture two more times to ensure homogeneity. Cut off the sealed end of the tube, take out the solid and powder it with pestle and mortar. Fill it in a capillary tube after sealing its lower end. Stick it to a thermometer after wetting it with the bath liquid and set up the apparatus for determining melting point as shown in Fig. 1.9 of Unit 1 of this course.

Heat gently and determine the melting point of the mixture as described in Section 1.9. Watch the melting of crystals in the capillary and note the temperature on the thermometer when the last crystals have just melted. This gives the melting point of the mixture. Allow the bath liquid to cool so that the liquid in capillary freezes. Find the melting point of the mixture again. In this way, take three readings to confirm the results and calculate the average value.

Fill another capillary with pure camphor powder and in the same manner determine its melting point. Take three readings in this case also and determine the average value.

8.2.4 Observations

Record your observations as under:

i) Mass of the empty test tube = ... g

ii) Mass of the test tube + solute = ... g

iii) Mass of the test tube + solute + camphor = ... g

iv) Melting point of the mixture

a) .... b) .... c) ....

v) Melting point of pure camphor

a) .... b) .... c) ....

8.2.5 Calculations

Mass of the solute taken = w_2 = ii) – i) = ... g = ... kg

Mass of camphor taken = w_1 = iii) – ii) = ... g = ... kg

Average melting point of mixture = T_1 = ... °C = ... K

Average melting point of camphor = T_0 = ... °C = ... K

Depression in melting (freezing) point = $\Delta T_f = T_0 - T_1$

Molal depression constant of camphor = K_f = 40.00 K kg mol^{-1}

As w_1, w_2, K_f and ΔT_f are known, calculate the molar mass of the solute using Eq. 8.1.

$$M_2 = \frac{K_f\, w_2}{\Delta T_f\, w_1}$$

8.2.6 Result

The molar mass of the solute as determined by Rast method = ... kg mol^{-1}

Calculated molar mass of the solute = ... kg mol^{-1}

8.3 SUMMARY

In this unit you studied the determination of molar mass of a non-volatile solute by Rast method. This method is based upon the measurement of depression in freezing point of a solvent by addition of a known amount of the solute. Depression of freezing point is a colligative property as are elevation of boiling point, osmotic pressure and lowering of vapour pressure. Colligative properties depend on the number of solute particles present in solution, but not on their nature.

8.4 TERMINAL QUESTIONS

1. What is a colligative property?
2. For what type of solid compounds Rast method can be used?
3. What is molal depression constant?

8.5 ANSWERS

Self Assessment Question

1. The value of molal depression constant of camphor is the largest of the four solvents. Therefore, a given amount of solute will produce the largest depression in freezing point, if camphor is taken as a solvent. Thus, camphor would be the obvious choice provided that the solute dissolves in molten camphor and does not react with it or decompose at the melting point of camphor.

Terminal Questions

1. The property which depends only on the number of solute particles and not on their nature is called a colligative property.

2. Rast method can be used only for those compounds which dissolve in molten camphor, do not react with it and do not decompose at its melting temperature.

3. Depression in freezing point of the solvent when one mole of the solute is dissolved in one kg of the solvent is known as the molal depression constant.

UNIT 9 APPLICATIONS OF EMF MEASUREMENTS

Structure

9.1 Introduction
  Objectives
9.2 Experiment 8 : Determination of pH by EMF Method
  Principle
  Requirements
  Procedure
  Observations
  Calculations
  Result
9.3 Experiment 9 : Determination of Solubility Product of AgCl from EMF Measurements
  Principle
  Requirements
  Procedure
  Observations
  Calculations
  Result
9.4 Summary

9.1 INTRODUCTION

In Unit 3 you were introduced to elementary concepts of potentiometry such as types of electrodes, electrode potential, galvanic cell, cell potential, emf, Nernst equation, etc. We also described a demonstration experiment for construction of a Daniell cell and measurement of its emf. In this unit we shall describe two experiments which are based on the applications of emf measurements. In these experiments, you will measure the emf of appropriate galvanic cells using low cost potentiometer and then determine the pH of solutions and the solubility product of a sparingly soluble salt such as silver chloride.

After studying this unit and having performed the experiments described in this unit, you should be able to:

- explain the terms electrodes, electrode potential, galvanic cell, cell potential, emf, Nernst equation, pH and solubility product,
- state the relationship between emf of a cell (or half-cell potential) and the concentration of species involved in cell reaction (or half-cell reaction),
- describe the relationship between emf of a cell and the pH of the solution in the indicator half-cell,
- construct copper, silver and quinhydrone electrodes,
- measure emf of a cell using low cost potentiometer,
- determine pH of an acid solution and solubility product of a sparingly soluble salt by measuring emf with a low cost potentiometer.

9.2 EXPERIMENT 8 : DETERMINATION OF pH BY EMF METHOD

In Chemistry Lab - I, CHE-03(L), course, you performed an experiment based on low cost pH meter. You performed a pH metric titration and determined the amount of acetic acid in a commercial sample of vinegar. The low cost pH meter can also be used for measuring pH of solutions directly. But in this experiment, you will use the low cost pH meter as a potentiometer. You will measure the emf of a galvanic cell and then, calculate the pH of hydrochloric acid and acetic acid solution by making use of Nernst equation.

9.2.1 Principle

In Unit 3 of this course, you studied that the quinhydrone electrode is reversible with respect to the H^+ ions. You have also studied that the half-cell reaction of this electrode is

$$\underset{(Q)}{C_6H_4O_2(s)} + 2H^+(c) + 2e^- \longrightarrow \underset{(H_2Q)}{C_6H_4(OH)_2(s)} \qquad \text{..... (3.27)}$$

The expression for electrode potential of a quinhydrone electrode (E_{Q/H_2Q}) in a solution of H^+ ions can be written, by using Nernst equation (Eq.3.18), as follows :

$$E_{Q/H_2Q} = E^0_{Q/H_2Q} + \frac{2.303\,RT}{2F}\log[\,H^+]^2 \qquad \text{.... (3.18)}$$

$$= E^0_{Q/H_2Q} + \frac{2.303\,RT \times 2}{2F}\log[\,H^+]$$

$$= E^0_{Q/H_2Q} + \frac{2.303\,RT}{F}\,pH \qquad \text{.... (3.30)}$$

The standard reduction potential, E^0_{Q/H_2Q}, for quinhydrone electrode is 0.699 V. Therefore, from the above we get,

$$E_{Q/H_2Q} = 0.699 - \frac{2.303\,RT}{F}\,pH \qquad \text{.... (9.1)}$$

Thus, you can see that the electrode potential of a quinhydrone electrode is related to the pH of the solution with which it is in contact. Now if you set up a galvanic cell by connecting the quinhydrone indicator electrode to a saturated silver-silver chloride reference electrode, the quinhydrone electrode will act as a reduction electrode and the silver-silver chloride electrode will act as an oxidation electrode. The cell can be represented as follows:

$Ag(s)\,|\,AgCl(s), KCl(satd)\,||\,Q, H_2Q(s), H^+(c)\,|\,C(s)$

The half-cell reactions are :

$$Ag(s) + Cl^-(aq) \longrightarrow AgCl(s) + e^-, \text{ and}$$

$$Q(s) + 2H^+(c) + 2e^- \longrightarrow H_2Q(s)$$

Using Eq. 3.14 of Unit 3 of this course, the emf of the cell can be written as:

$$E_{cell} = E_{Q/H_2Q} - E_{AgCl/Cl^-}$$

But E_{AgCl/Cl^-} (as per literature value) = 0.222 V

As per literature value, $E_{AgCl/Cl^-} = 0.222$ V

Using this in Eq. 9.1, we get

$$E_{cell} = 0.699 - \frac{2.303\,RT}{F}\,pH - 0.222$$

$$\text{or} \quad E_{cell} = 0.477 - \frac{2.303\,RT}{F}\,pH$$

$$\text{or} \quad pH = \frac{(E_{cell} - 0.477)F}{2.303\,RT} \qquad \text{.... (9.2)}$$

Thus, by measuring the emf of the cell, the pH of the solution can be calculated.

9.2.2 Requirements

Apparatus		Chemicals
1. Low cost potentiometer	1 No.	1. Quinhydrone
2. Silver-silver chloride electrode	1 No.	2. Potassium chloride
3. Carbon electrode	1 No.	

4. Salt Bridge 1 No.
5. Beakers 100 cm^3 2 Nos.

Stock Solutions Provided

1. Hydrochloric acid (1.00×10^{-2} M)
2. Acetic acid - (1.00×10^{-2} M)

9.2.3 Procedure

Calibrate the low cost potentiometer by following the method given in Sub-section 3.4.6 of Block 1 of this course.

Set up a silver-silver chloride half-cell by taking 20-25 cm^3 of saturated solution of KCl in one 100 cm^3 beaker and by placing a silver-silver chloride electrode in it. Set up a quinhydrone half-cell by taking 20-25 cm^3 of 1.00×10^{-2} M hydrochloric acid in another 100 cm^3 beaker. Add a pinch of quinhydrone and insert a carbon electrode in this solution. Connect the two half-cells through a KCl salt bridge. If a salt bridge is not available, take a strip of filter paper, dip it in saturated KCl solution and use it in place of the salt bridge.

Connect the carbon electrode to the indicator terminal (through the red crocodile clip) and the silver-silver chloride electrode to the reference terminal (through the black crocodile clip) of the instrument.

Keep the range selector at 2 V and then measure the emf of the cell. Remember each division on the meter scale is equal to 0.04 V in the 2 V range. Take the measurements at least two more times for the same set-up, and record the values in Table 9.1.

Now set up the quinhydrone half-cell again, this time using acetic acid (1.00×10^{-2} M), and measure the emf value in the same manner. Repeat the measurement at least two more times and record the values in Table 9.1.

9.2.4 Observations

Room temperature, T = °C = K

Table 9.1 : Emf Values of Cells

Cell	Emf/V
$Ag(s) \mid AgCl(s), KCl(satd) \mid\mid Q, H_2Q(s), HCl(1.00 \times 10^{-2}\ M) \mid C(s)$	--------
	--------

Average value of emf of the cell	--------
$Ag(s) \mid AgCl(s), KCl(satd) \mid\mid Q, H_2Q(s), CH_3COOH(1.00 \times 10^{-2} M) \mid C(s)$	--------
	--------

Average value of emf of the cell	--------

9.2.5 Calculations

pH value of 1.00×10^{-2} M HCl

Average value of emf of the cell containing 1.00×10^{-2} M HCl = ... V

Temperature (T) = ... K

Gas constant (R) = 8.314 J K^{-1} mol^{-1}

Faraday constant (F) = 96500 C mol^{-1}

Using Eq. 9.2, pH of 1.00×10^{-2} M HCl = $\frac{(E_{cell} - 0.477)\,96500}{2.303 \times 8.314\,T}$

(You can compare this with the theoretical pH value of 2)

pH Value of 1.00×10^{-2} M CH_3COOH

Average value of emf of the
cell containing 1.00×10^{-2} M CH_3COOH = ... V

Again, using Eq. 9.2, pH of 1.00×10^{-2} M CH_3COOH = $\frac{(E_{cell} - 0.477)\,96500}{2.303 \times 8.314\,T}$

9.2.6 Result

The pH values of 1.00×10^{-2} M HCl and 1.00×10^{-2} M CH_3COOH are found to be --- and ---, respectively.

Give reason for the relative magnitudes of pH of 1.00×10^{-2} M HCl and 1.00×10^{-2} M CH_3COOH in the space given below:

. . . .

. . . .

. . . .

. . . .

. . . .

9.3 EXPERIMENT 9 : DETERMINATION OF SOLUBILITY PRODUCT OF AgCl FROM EMF MEASUREMENTS

In Experiment 8 you have made use of emf of a cell in determining the pH of a solution. In Unit 17 of the CHE-04 course, you had studied that the emf measurement can also be used in determining the solubility product of a sparingly soluble salt. In this experiment, you will determine the solubility product of a sparingly soluble salt, silver chloride, by measuring the emf of an appropriate galvanic cell.

9.3.1 Principle

You know that the silver chloride with a solubility of 1.37×10^{-5} mol dm^{-3} in water is a sparingly soluble salt. As a result, when silver chloride is placed in water, only a very small amount of it dissolves in water to give a saturated solution. You also know that all the sparingly soluble salts are strong electrolytes; therefore, AgCl that dissolves will be completely dissociated into Ag^+ and Cl^- ions. Thus, there will be an equilibrium between undissolved AgCl and its ions in solution:

$$AgCl(s) \quad \overset{H_2O}{\rightleftharpoons} \quad Ag^+(aq) + Cl^-(aq)$$

The equilibrium constant for this reaction, which is generally known as solubility product constant, K_{sp}, is given by

$$K_{sp} = [Ag^+(aq)][Cl^-(aq)] \qquad ..... (9.3)$$

where $[Ag^+(aq)]$ and $[Cl^-(aq)]$ represent the molar concentrations of respective ions. The potentiometric determination of K_{sp} is based on the following simple idea.

An aqueous solution of AgCl contains equal amounts of Ag^+ and Cl^- ions. However, if to this solution, a known excess of KCl is added, then $[Cl^-]$ is essentially determined by the concentration of KCl. The $[Ag^+]$ can be determined by setting up and then measuring the emf of the following galvanic cell:

$Cu(s)\,|\,Cu^{2+}(1.000 \times 10^{-1}\ M)\ ||\ Ag^+(x\ M),\ AgCl(s), KCl(1.000 \times 10^{-1}\ M)\,|\ Ag(s)$ ...(9.4)
Reference half-cell Indicator half-cell

The emf of the cell is given by

$$\begin{aligned} E_{cell} &= E_{Ag^+/Ag} - E_{Cu^{2+}/Cu} \\ &= \left(E^\circ_{Ag^+/Ag} + \frac{2.303\,RT}{F}\log[Ag^+]\right) - \left(E^\circ_{Cu^{2+}/Cu} + \frac{2.303\,RT}{F}\log[Cu^{2+}]\right) \\ &= E^\circ_{Ag^+/Ag} - E^\circ_{Cu^{2+}/Cu} - \frac{2.303\,RT}{2F}\log(1.000\times10^{-1}) + \frac{2.303\,RT}{F}\log[Ag^+] \\ &= \left(E^\circ_{Ag^+/Ag} - E^\circ_{Cu^{2+}/Cu} + \frac{2.303\,RT}{2F}\right) + \frac{2.303\,RT}{F}\log[Ag^+] \qquad \text{..... (9.5)} \end{aligned}$$

$$\begin{aligned} &-\frac{2.303\,RT}{2F}\log(1.000\times10^{-1}) \\ &= -\frac{2.303\,RT}{2F}(-1) \\ &= \frac{2.303\,RT}{2F} \end{aligned}$$

At a given temperature, the value of the term within brackets is constant. Thus, by measuring the emf of the cell, the value of $[Ag^+]$ can be calculated using Eq. 9.5. A more accurate method of obtaining $[Ag^+]$ in solutions of unknown concentration from E_{cell} values is to plot a calibration curve between $[Ag^+]$ values of silver nitrate solutions of known concentration and the corresponding E_{cell} values. This is explained below.

Plotting a calibration curve

For the purpose of drawing calibration curve, you shall use the following cell:

$Cu(s)\,|\ Cu^{2+}(1.000 \times 10^{-1}\ M)\ ||\ Ag^+(c)\,|\,Ag(s)$ ..... (9.6)

where $Ag^+(c)$ is the concentration of standard silver nitrate solution. You shall use $AgNO_3$ solutions of 5.000×10^{-2} M, 1.000×10^{-2} M, 5.000×10^{-3} M, 1.000×10^{-3} M, 5.000×10^{-4} M and 1.000×10^{-4} M concentration and measure E_{cell} every time and note down the values in Table 9.2.

You can note that Eq. 9.5 is applicable to both the cells set up as per Eq. 9.4 and 9.6 since
i) the reference electrode is the same in each case, and
ii) the indicator electrode in each case is reversible with respect to Ag^+ ions.

To understand this clearly, you are advised to go through Section 17.8 of Unit 17 of the CHE-04 course.

The actual plot as per Eq. 9.5 should be between E_{cell} and $\log[Ag^+]$. Since $[Ag^+]$ in various $AgNO_3$ solutions is much less than 1, $\log[Ag^+]$ will be a negative quantity in each case. But it will be easier to plot a graph using positive quantities. Hence, Eq. 9.5 is transformed into Eq. 9.7 by multiplying the last term in right hand side of Eq. 9.5 by (−1) twice.

$$E_{cell} = \left(E^\circ_{Ag^+/Ag} - E^\circ_{Cu^{2+}/Cu} + \frac{2.303RT}{2F}\right) - \frac{2.303\,RT}{F}\left(-\log[Ag^+]\right) \qquad \text{..... (9.7)}$$

You should use this equation for the purpose of obtaining the calibration curve. Using E_{cell} and $-\log[Ag^+]$ values from Table 9.2, plot the calibration curve. Shape of the curve should be as shown in Fig. 9.1.

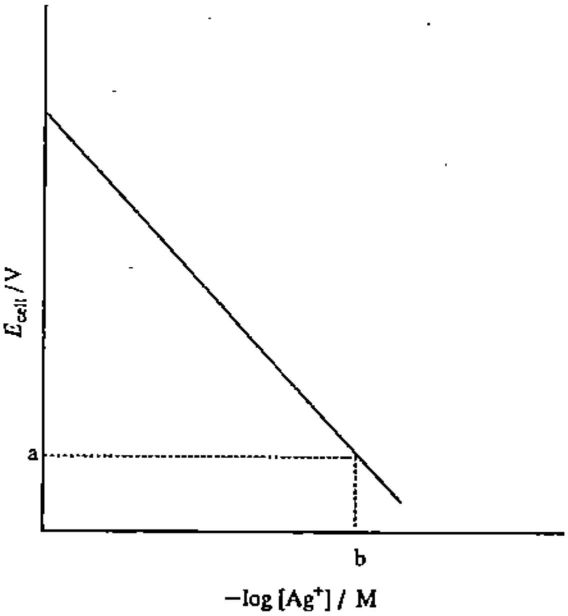


Fig. 9.1 : Calibration curve and $[Ag^+]$ by interpolation

Obtaining unknown $[Ag^+]$ from the calibration curve

The emf of the cell set up as per Eq. 9.4 is measured to obtain $[Ag^+]$ in a saturated solution of AgCl by interpolation method. You have studied the details of interpolation method in Section 2.6 of Unit 2 of this course. Following this method, find out the x-coordinate value (b) from the curve corresponding to the E_{cell} value (a) obtained for the cell mentioned in Eq. 9.4. Once the x-coordinate value (b) is known, $[Ag^+]$ in a saturated solution of AgCl can be calculated using the following relationship:

$$-\log [Ag^+] = b$$

Hence, $[Ag^+] = 10^{-b}$ M ..... (9.8)

(as shown in Example 8 discussed in Sub-section 2.3.2 of Unit 2 of Block 1 of this course).

Calculation of K_{sp}

$[Cl^-] = 3.333 \times 10^{-2}$ M as shown in the calculation part of this experiment.

Using $[Ag^+]$ value obtained above by interpolation method and $[Cl^-]$ as 3.333×10^{-2} M, we can calculate K_{sp} using Eq. 9.3.

K_{sp} = ($[Ag^+]$ as obtained by interpolation method) × ($[Cl^-]$ in the indicator half-cell)

or $K_{sp} = (10^{-b} \times 3.333 \times 10^{-2})$ ..... (9.9)

9.3.2 Requirements

Apparatus

1.	Low cost potentiometer	1 No.
2.	Copper electrode	1 No.
3.	Silver electrode	1 No.
4.	Salt bridge/KNO_3	1 No.
5.	Beaker 100 cm^3	4 No.
6.	Graduated pipette 20 cm^3	1 No.
7.	Graduated pipette 10 cm^3	1 No.

Stock Solutions Provided

1. 1.000×10^{-4} M, 5.000×10^{-4} M, 1.000×10^{-3} M, 5.000×10^{-3} M, 1.000×10^{-2} M, 5.000×10^{-2} M and 1.000×10^{-1} M $AgNO_3$ solutions
2. 1.000×10^{-1} M $CuSO_4$ solution
3. 1.000×10^{-1} M KCl solution

9.3.3 Procedure

1. Calibrate the low cost potentiometer as you did in Experiment 8 by following the method given in Sub-section 3.4.6 of Block 1 of this course.

2. Set up the following galvanic cell (as per Eq. 9.6) using 1.000×10^{-1} M $CuSO_4$ and 1.000×10^{-1} M $AgNO_3$ solutions, copper and silver electrodes, and KNO_3 salt bridge:

   $Cu(s) \mid Cu^{2+}(1.000 \times 10^{-1}\,M) \parallel Ag^+(1.000 \times 10^{-1}\,M) \mid Ag(s)$
   Reference half-cell Indicator half-cell

3. Connect the copper electrode to the reference terminal (through the black crocodile clip) and the silver electrode to the indicator terminal (through the red crocodile clip) of the instrument.

4. Keep the range selector at 2 V and then measure the emf of the cell. Remember each division on the meter scale is equal to 0.04 V in the 2 V range. Note down the measurement in Table 9.2 and remove the salt bridge as soon as possible.

5. Now take 5.000×10^{-4} M silver nitrate solution in the indicator half-cell. Connect the two half-cells through the salt bridge and note down the emf. Similarly measure the emf for the rest of the silver nitrate solutions (1.000×10^{-3} M, 5.000×10^{-3} M, 1.000×10^{-2}M and 5.000×10^{-2} M) and record the values in Table 9.2.

6. Prepare a system by mixing 10 cm^3 of 1.000×10^{-1} M $AgNO_3$ solution with 20 cm^3 of 1.000×10^{-1} M KCl solution. Shake the mixture well. Take this mixture in the indicator half- cell and set up a galvanic cell as shown in Eq. 9.4.

7. Measure the emf of the cell and record the value below Table 9.2.

8. Repeat the steps 6 and 7 once more and record the value of emf.

9.3.4 Observations

Room temperature = °C

Table 9.2 : Emf Values of Cells constructed as per Eq. 9.8

M stands for molarity unit

S.No.	$[Ag^+]$/M	E_{cell}/V	log $[Ag^+]$/M	−log $[Ag^+]$/M
1.	1.000×10^{-4}			
2.	5.000×10^{-4}			
3.	1.000×10^{-3}			
4.	5.000×10^{-3}			
5.	1.000×10^{-2}			
6.	5.000×10^{-2}			

Emf of the cell constructed as per Eq. 9.4 is measured twice and the values are recorded below.

(i) V
(ii) V

The average of the two measurements = ... V

We shall use this as *a*, for the purpose of interpolation.

9.3.5 Calculations

(i) Plotting of calibration curve

Plot a calibration curve between E_{cell} and -log $[Ag^+]$ as explained in Sub-section 9.3.1. For this purpose, use the values from Table 9.2. You will get a calibration curve as shown in Fig. 9.1.

(ii) Obtaining $[Ag^+]$ from the calibration curve

As explained in Sub-section 9.3.1, obtain *x*- coordinate (*b*) corresponding to the average E_{cell} value (*a*) of the cell constructed as per Eq. 9.4.

b = ...

Then using Eq. 9.8, $[Ag^+]$ = 10^{-b}M

= .... M

(iii) Calculation of $[Cl^-]$

Volume of 1.000×10^{-1} M KCl taken in the indicator half-cell = 20 cm^3

$$\text{Amount of KCl present} = \frac{1.000 \times 10^{-1} \times 20}{1000} = 2.000 \times 10^{-3} \text{ mol}$$

Volume of 1.000×10^{-1} M $AgNO_3$ taken = 10 cm^3

$$\text{Amount of } AgNO_3 \text{ present} = 1.000 \times 10^{-1} \times \frac{10}{1000} = 1.000 \times 10^{-3} \text{ mol}$$

Now, 1.000×10^{-3} mol of KCl will react with 1.000×10^{-3} mol of $AgNO_3$ to give 1.000×10^{-3} mol of AgCl and 1.000×10^{-3} mol of KNO_3.

Hence, amount of KCl left in the solution

$= 2.000 \times 10^{-3} \text{ mol} - 1.000 \times 10^{-3} \text{ mol}$

$= (2.000 - 1.000) \times 10^{-3} \text{ mol}$

$= 1.000 \times 10^{-3} \text{ mol}$

Volume of the solution = $(10 + 20)\ cm^3 = 30\ cm^3$

$$\text{Molar concentration of } Cl^- = \frac{1.000 \times 10^{-3}}{30} \times 1000 \text{ M}$$

or $[Cl^-] = 3.333 \times 10^{-2}$ M

(iv) Calculation of K_{sp}

Now using Eq. 9.3, we can calculate the solubility product of AgCl as shown below:

$$K_{sp} = [Ag^+][Cl^-] = (10^{-6} \times 3.333 \times 10^{-2})$$

= ....

9.3.6 Result

The solubility product of silver chloride at .... °C = ...

Literature value at 25°C = 1.5×10^{-10}

9.4 SUMMARY

In this unit, you had studied two experiments – one for determining the pH of solutions and the other for determining the solubility product of a sparingly soluble salt silver chloride. These experiments are based upon the applications of measurement of emf of galvanic cells.

APPENDIX - I

Hydrochloric acid : 1.00×10^{-2} M : Using a burette or a measuring cylinder, transfer in small lots 9 cm^3 of concentrated hydrochloric acid to a 500 cm^3 volumetric flask which contains about 250 cm^3 of deionised water. Shake the flask after the addition of each lot. Make up the solution to the mark with deionised water. Let this solution, say solution (A), is approximately 0.1 M. Now titrate this solution against 1.000×10^{-1} M sodium carbonate solution using methyl orange indicator. Calculate the molarity of HCl solution (A) by using the following formula:

1.000×10^{-1} M sodium carbonate solution can be prepared by dissolving 1.325 g of anhydrous sodium carbonate in minimum quantity of deionised water and making up to the mark in a 250 cm^3 volumetric flask.

$$2\, M_{Na_2CO_3} \cdot V_{Na_2CO_3} = M_{HCl} \cdot V_{HCl}$$

Let the molarity of the HCl solution (A) be x mol dm^{-3}.

Prepare HCl solution of 1.00×10^{-2} M concentration by diluting appropriate volume of HCl solution (A) with deionised water. Volume of solution (A) required can be calculated by using the formula,

$$M_1V_1 = M_2V_2$$

$$\text{or} \quad V_1 = \frac{M_2 V_2}{M_1}$$

Thus, volume of HCl solution (A) required to prepare 1 dm^3 of 1.00×10^{-2} M HCl

$$= \frac{1.00 \times 10^{-2}\ \text{M} \times 1000\ \text{cm}^3}{x\ \text{M}} = \frac{10}{x}\ \text{cm}^3$$

Therefore, take $10/x$ cm^3 of HCl solution (A) and dilute to 1 dm^3 with deionised water in a volumetric flask. The concentration of this HCl solution would be 1.00×10^{-2} M.

Acetic acid : 1.00×10^{-2} M : Using a burette, transfer 1.5 cm^3 of glacial acetic acid into a 250 cm^3 volumetric flask containing 100 cm^3 of deionised water and make up the solution to the mark. This solution say, acetic acid (A), is approximately 0.1 M. Find out the exact molarity of this solution by titrating against a standard solution of NaOH using phenolphthalein indicator. Let the exact molarity of acetic acid (A) be y mol dm^{-3}.

Details of preparation of standard NaOH solution are given in Appendix-II to Unit 12 of this Block.

Now prepare 1.00×10^{-2} M acetic acid by diluting appropriate volume of acetic acid (A) with deionised water. Volume of acetic acid (A) required can be calculated by using molarity equation $M_1V_1 = M_2V_2$. Thus, volume of acetic acid (A) required to prepare 1 dm^3 of 1.00×10^{-2} M acetic acid $= \frac{1.00 \times 10^{-2}\ \text{M} \times 1000\ \text{cm}^3}{y\ \text{M}}$

$$= \frac{10\ \text{cm}^3}{y}$$

Therefore, take $10/y$ cm^3 of acetic acid (A) and dilute with deionised water to 1 dm^3 in a volumetric flask. This would give an acetic acid solution of concentration 1.00×10^{-2} M.

APPENDIX - II

Copper sulphate : 1.000×10^{-1} M : Dissolve 12.484 g of A.R. $CuSO_4.5H_2O$ in deionised water and make up the volume to 500 cm^3 in a volumetric flask. Before making up the volume, add 5cm^3 of acetic acid to prevent hydrolysis.

Potassium chloride : 1.000×10^{-1} M : Dissolve 3.728 g of A.R. KCl in deionised water and make up the volume to 500 cm^3 in a volumetric flask.

Silver nitrate : 1.000×10^{-1} M : Dissolve 16.987 g of A.R. $AgNO_3$ in deionised water and make up the volume to 1 dm^3 in a volumetric flask.

Silver nitrate : 5.000×10^{-2} M : Dilute 250 cm^3 of 1.000×10^{-1} M $AgNO_3$ to 500 cm^3 with deionised water in a volumetric flask.

Silver nitrate : 1.000×10^{-2} M : Dilute 50 cm^3 of 1.000×10^{-1} M $AgNO_3$ to 500 cm^3 with deionised water in a volumetric flask.

Silver nitrate : 5.000×10^{-3} M : Dilute 25 cm^3 of 1.000×10^{-1} M $AgNO_3$ to 500 cm^3 with deionised water in a volumetric flask.

Silver nitrate : 1.000×10^{-3} M : Dilute 10 cm^3 of 5.000×10^{-2} M $AgNO_3$ to 500 cm^3 with deionised water in a volumetric flask.

Silver nitrate : 5.000×10^{-4} M : Dilute 25 cm^3 of 1.000×10^{-2} M $AgNO_3$ to 500 cm^3 with deionised water in a volumetric flask.

Silver nitrate : 1.000×10^{-4} M : Dilute 10 cm^3 of 5.000×10^{-3} M $AgNO_3$ to 500 cm^3 with deionised water in a volumetric flask.

UNIT 10 ADSORPTION

Structure

10.1 Introduction
  Objectives
10.2 Adsorption on Solids
  Physisorption
  Chemisorption
10.3 Adsorption Isotherms
10.4 Experiment 10 : Adsorption of Oxalic Acid from Solution on Activated Charcoal
  Principle
  Requirements
  Procedure
  Observations
  Calculations
  Result
10.5 Summary

10.1 INTRODUCTION

Adsorption is an important surface related phenomenon which has many practical applications. Use of activated charcoal in gas masks for removal of harmful gases from air, use of activated charcoal or Fuller's earth in decolorisation of solutions before crystallation, use of ion exchange resins in demineralisation of water, heterogeneous catalysis, concentration of ores by froth flotation process, etc. are only some of the examples which depict the applications of adsorption. In this unit, we shall discuss an experiment which is based on adsorption phenomenon.

After studying this unit and having performed the experiment described in the unit, you should be able to :

Objectives

- cite applications of adsorption,
- differentiate between adsorption and absorption,
- define physisorption and chemisorption,
- describe adsorption isotherms, and
- study adsorption isotherms for adsorption of oxalic acid on activated charcoal.

10.2 ADSORPTION ON SOLIDS

In Unit 4, you studied that the molecules on the surface of a liquid experience an inward pull. The liquid surface is thus in a state of unsaturation. The surface of a solid also behaves in a similar manner. In a solid, the ions or the molecules at the surface of a solid do not have all their valancies satisfied by union with other particles. Such forces also arise due to the fact that when a new surface is created by breaking a solid, some interatomic bonds are broken and some of the valancies of surface atoms are left unsatisfied. As a result of these residual forces, the surface of the solid has a tendency to attract and retain available molecules and particles towards itself; such a condition is helpful in decreasing the surface energy of a solid. The molecules so attracted are retained on the surface of the solid and do not go deeper into the bulk. Their concentration is more on the surface than in the bulk of the solid. This phenomenon of accumulation (higher concentration) of a substance on the surface of another substance is called **adsorption.** The substance that accumulates on the surface is the adsorbate and the underlying solid is the adsorbent. For example, charcoal adsorbs acetic acid when kept in contact with it; here, acetic acid is adsorbate and charcoal is adsorbent.

Adorption should be clearly differentiated from absorption. In absorption, the substance is not only retained on the surface but passes through the surface and is distributed throughout the bulk of the solid. Thus, anhydrons calcium chloride **absorbs** water to form a hydrate, while charcoal **adsorbs** acetic acid from its solution. Sometimes the term **'sorption'** is used when there is a doubt whether a process is true adsorption or absorption.

10.3 PHYSISORPTION AND CHEMISORPTION

Depending on the type of interaction between the adsorbate and the adsorbent, adsorption is of two types – physisorption (physical adsorption) and chemisorption (chemical adsorption).

10.3.1 Physisorption

If the adsorbate molecules are weakly bound to the adsorbent, it is classified as physisorption. It is also known as van der waals adsorption since the forces involved are of van der waals type. The forces are of the same magnitude as are involved in the liquefaction of gases. The enthalpy decrease ($-\Delta H$) associated with physisorption is much low (less than 40 kJ mol^{-1}) and is of the same order as the enthalpy of condensation of the adsorbate. Increase of temperature is not favourable to physisorption. Adsorption of gases by charcoal is an example of physisorption. Physisorption is generally independent of the chemical nature of the adsorbate. All gases exhibit physisorption.

10.3.2 Chemisorption

Chemisorption is very specific and can occur only if the adsorbate is capable of forming a chemical bond with an active centre on the surface. The enthalpy decrease associated with chemisorption is much high (between 40 kJ mol^{-1} and 400 kJ mol^{-1}) and is of the order of bond enthalpies. Many chemisorption processes involve activation energy as in a chemical reaction. In such cases, the rates of chemisorption and desorption increase with temperature in contrast with the rate of physisorption . Adsorption of nitrogen on iron surface at 770 K is an example of chemisorption. Chemisorption results in release of large amounts of energy and chemisorbed nitrogen is present as nitrogen atoms but not as molecules.

At room temperature, iron does not adsort nitrogen at all. But as temperature is lowered and brought near 80 K, the boiling point of liquid nitrogen, iron adsorbs nitrogen gas physically as N_2 molecules.

10.3 ADSORPTION ISOTHERMS

Adsorption on solids can be from gaseous phase as well as from liquid solution. Extent of adsorption in any case of adsorption is defined as the quantity of adsorbate held on a unit mass of the adsorbent. The extent of adsorption at equilibrium depends on a number of factors such as :

- temperature at equilibrium,
- the chemical nature and surface area of the adsorbent, and
- the chemical nature and the concentration (pressure in case of gases) of the adsorbate.

Of particular interest is the relationship between the extent of adsorption and the concentration (pressure) of the adsorbate at equilibrium. This relationship is studied at constant temperature and so is called adsorption isotherm. In general, experimental isotherms take a variety of forms. In Unit 21 of the CHE-04 course, you might have studied Freundlich and Langmuir adsorption isotherms for adsorption on solid surfaces. Here,we shall discuss an experiment to show that the adsorption of acetic acid from solution on activated charcoal follows Freundlich and Langmuir adsorption isotherm equations.

10.4 EXPERIMENT 10 : ADSORPTION OF OXALIC ACID FROM SOLUTION ON ACTIVATED CHARCOAL

Activated charcoal is a very good adsorbent. When activated charcoal is added to an aqueous solution of oxalic acid, and the contents are allowed to attain equilibrium, oxalic acid is adsorbed on charcoal. Objectives of this experiment are to show that

- the extent of adsorption of oxalic acid from solution on activated charcoal increases as equilibrium concentration of oxalic acid in solution increases, and
- the adsorption of oxalic acid from solution on activated charcoal follows Freundlich and Langmuir adsorption isotherms.

Activated charcoal can be obtained by heating wood charcoal between 625 K and 1275 K in vacuum, air, steam, chlorine or carbon dioxide. During heating, hydrocarbons and other impurities are removed from charcoal leading thereby to a large surface area for adsorption. The resulting substance is called activated charcoal.

10.4.1 Principle

For adsorption of a substance from a solution by a solid adsorbent, Freundlich gave an empirical equation, which is known as **Freundlich adsorption isotherm**. This equation, as shown below, gives the relationship between the amount of the adsorbate (x) adsorbed by a particular mass (m) of the adsorbent and the equilibrium concentrataion (c) of the adsorbate at a particular temperature, i.e.,

$$\frac{x}{m} = Kc^{1/n} \qquad \text{..... (10.1)}$$

where K and n are constants.

Taking logarithm of both the sides, we get

$$\log\frac{x}{m} = \log K + \frac{1}{n}\log c$$

If the plot of $\log\frac{x}{m}$ against $\log c$ is a straight line, it means that the adsorption follows Freundlich adsorption isotherm. The slope of this line will be equal to $1/n$ and the intercept will be equal to $\log K$. Since x/m and c are fractions (i.e., less than 1), $\log x/m$ and $\log c$ will be negative quantities.

Since it is easier to plot with positive quantities, we shall multiply both sides of the above equation by (-1) and write,

$$-\log x/m = -\log K - \frac{1}{n}\log c$$

$$\text{or } -\log x/m = -\log K + \frac{1}{n}(-\log c) \qquad \text{..... (10.2)}$$

Hence, make a plot of ($-\log x/m$) against ($-\log c$) to verify the observance of Freundlich isotherm. The slope should be a straight line. The slope of this line will be equal to $1/n$ and the intercept will be equal to $\log K$

Langmuir derived another relationship between the amount adsorbed and the equilibrium concentration of the solute by making certain basic assumptions. This you might have studied in Unit 21 of the CHE-04 course. This relationship can be written as:

$$\frac{x}{m} = \frac{\alpha c}{1+\beta c}$$

Taking inverse, $1/(x/m) = \dfrac{1+\beta c}{\alpha c}$

or $$\frac{c}{x/m} = \frac{1+\beta c}{\alpha}$$

or $$\frac{c}{x/m} = \frac{1}{\alpha} + \frac{\beta c}{\alpha} \qquad \text{..... (10.3)}$$

where α and β are constants.

This equation can be verified by plotting $c/(x/m)$ against c, which should result in a straight line. The slope of the line will give β/α and the intercept will give $1/\alpha$. Hence, the values of constants α and β can be evaluated experimentally.

In this experiment, a known mass (m) of activated charcoal is added to an aqueous solution of oxalic acid of known initial concentration (c_i). The contents are shaken for some time and allowed to attain equilibrium. Some oxalic acid is adsorbed on activated charcoal. Solution is filtered. The equilibrium concentration of oxalic acid (c) is determined by titrating the filtrate against a standard solution of potassium permanganate. For this purpose, Eq. 1.15 of Unit 1 of this course can be used:

$$2\, M_{H_2C_2O_4} \cdot V_{H_2C_2O_4} = 5\, M_{KMnO_4} \cdot V_{KMnO_4} \qquad \text{..... (1.15)}$$

The value of x (i.e., the amount of oxalic acid adsorbed) can be calculated from the change in concentration due to adsorption (i.e., $c_i - c$) and the initial volume of the solution (i.e., 100 cm^3) as follows.

You can recognise that the concentration of oxalic acid decreases due to adsorption on the activated charcoal. Hence, whatever amount of oxalic acid is adsorbed on the charcoal will be equal to the decrease in the amount of oxalic acid in the solution.

Decrease in the concentration of oxalic acid

= (Initial concentration of oxalic acid) – (equilibrium concentration of oxalic acid)

$$= c_i - c \qquad \text{..... (10.4)}$$

The amount of oxalic acid adsorbed (x)

= Decrease in the amount of oxalic acid in the solution

= Decrease in the concentration of oxalic acid × Volume of solution in dm^3
(as per Eq. 1.12 of Unit 1 of this course)

$$= (c_i - c) \times \frac{100}{1000} \qquad \text{..... (10.5)}$$

We intend to verify the observance of Freundlich isotherm and Langmuir isotherm by graphical method. For this, we need atleast five variations. So you have to perform the experiment with five oxalic acid solutions having different initial concentrations and each time determine x, c and m. You enter these values in Table 10.2. For the purpose of making the plot, the modified values are entered in Table 10.3. Finally, the following plots are made:

(i) $-\log x/m$ against $-\log c$ (to verify Freundlich isotherm)

(ii) $c/(x/m)$ against c (to verify Langmuir isotherm)

You must get a straight line in both the cases verifying the observance of both the isotherms.

10.4.2 Requirements

Apparatus

1.	Burette 50 cm^3	2 Nos.
2.	Pipettes 25, 20 and 10 cm^3	1 No. each
3.	Stoppered bottles or conical flasks with corks, capacity 250 cm^3	12 Nos.
4.	Funnel	6 Nos.
5.	Watch glasses	6 Nos.
6.	Large water trough	1 Nos.
7.	Thermometer 100°	1 No.
8.	Glazed paper 5 cm × 5 cm.	7 Nos.

Chemicals

1.	Activated charcoal	15 g

Stock Solutions Provided

1.	2.000×10^{-1} M Oxalic acid	200 cm^3
2.	2.000×10^{-2} M Potassium permanganate	500 cm^3
3.	2 M Sulphuric acid	200 cm^3

10.4.3 Procedure

Standard solutions are provided to you to save your time which you shall need for this rather long experiment. Strengths of oxalic acid solutions are estimated by titration against $KMnO_4$ solution using an excess of dilute sulphuric acid. Please carry out a blank titration of dilute sulphuric acid solution to confirm that it does not need any $KMnO_4$ solution. If it does, a correction must be made in all the titre values. The solution to be titrated will need to be warmed to 60°C before starting the titration. 60°C is a temperature which is very uncomfortable to bear on the reverse side of the hand. Over heating must be avoided. Reheating during the titration will not be necessary as the Mn^{2+} ions produced in the reaction catalyse the reaction. The reaction equation for the titration is:

$$2\,KMnO_4 + 3\,H_2SO_4 + 5\,(COOH)_2 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + 8\,H_2O$$

Set up two 50 cm^3 burettes, rinse one of them with 2.000×10^{-1} M oxalic acid and the other with distilled water.

Take six 250 cm^3 dry stoppered bottles or corked conical flasks. Label them as A, B, C, D, E and F. With the help of burettes measure into these, in order from A to E,

(i) 50 cm^3, 40 cm^3, 30 cm^3, 20 cm^3 and 10 cm^3 of 2.000×10^{-1} M oxalic acid, and then

(ii) 50 cm^3, 60 cm^3, 70 cm^3, 80 cm^3 and 90 cm^3 of distilled water, respectively,

so that the total volume in each case becomes 100 cm^3. Measure 100 cm^3 of distilled water into bottle F.

Place all the six bottles in a thermostat or water trough and set them aside to acquire the temperature of the bath. Measure the temperature of the bath.

Take seven glazed paper pieces which are of equal mass. Place one of these paper pieces on the left pan. Place a 2 gram weight over it. Place the other glazed paper pieces one by one on the right pan and each time weigh 2 gram of charcoal powder. Keep the weighed powder aside under watch glasses or funnels to avoid loss by air currents or spilling. When all the six powders have been thus made ready, our experiment begins. All the operations to follow will be carried out with the six bottles in the same sequence.

Carefully pour weighed charcoal powder into solutions of bottles A to F and close each of them. Shake each of the bottles for two minutes and place it back in the water trough. Do it repeatedly for about an hour and half. Long contact periods like keeping overnight should not affect the results. If they do, presence of reactive impurities in the charcoal powder can be suspected. Shorter intervals will not be enough for the adsorption equilibrium state to be reached due to the heterogeneous porosity of the charcoal powder.

Label the remaining six dry bottles A′, B′, C′, D′, E′, and F′ to correspond to the bottles A to F. Place one funnel on each bottle. In each funnel set one high quality small dry filter paper. When all this is set, shake the bottles A to F for the last time and allow the charcoal to settle. Record the temperature of water in the trough used for thermostating. In turn, take these bottles one by one in the order A to F and filter their contents into the corresponding bottles A′ to F′. Each funnel should be covered with a watch glass to prevent evaporation of solution during filtration. In each case reject about half a test-tube full of filtrate coming out initially (since initial filtrate will have a slightly reduced concentration of the acid due to adsorption of the acid by the dry filter paper used). After filtration, remove the funnels along with the watch glasses, filter papers and used charcoal. Stopper the bottles A′ to F′. Titrate the contents of each bottle (from A′ to F′) against the standardized $KMnO_4$ solution.

Keeping in view the varied concentrations of oxalic acid in bottles A′ to F′, the volumes of oxalic acid to be taken in each case for titration are indicated below:

(i) 10 cm^3 from A′ and B′

(ii) 20 cm^3 from C′ and D′

(iii) 25 cm^3 from E′ and

(iv) 40 cm^3 from F′.

The volume of oxalic acid is taken as above for carrying out the titrations conveniently.

For each titration add one test tube full of 2 M H_2SO_4 warmed to 60°C approximately to the flask and titrate against standard $KMnO_4$ solution from the burette. End point will be marked by the appearance of a light pink colour. In order to facilitate concordant titre values, you have been asked to do three titrations using solution from each bottle. The results of titrations are to be recorded in Table 10.1.

Observations :

Temperature of water in trough (i) Initial = ... °C

(ii) Final = ... °C

Total volume of oxalic acid solution in each bottle = 100 cm^3

Total mass of charcoal powder added to each bottle = 2 g

Molarity of stock solution of $KMnO_4$ = 2.000×10^{-2} M (standardized)

Table 10.1 : Titration data for Solutions A′ to F′

Sl. No.	Soln. No.	(Volume taken)/cm^3	Initial burette reading	Final burette reading	(Volume of $KMnO_4$ consumed)/cm^3
1.	A′	10			
2.	A′	10			
3.	A′	10			
4.	B′	10			
5.	B′	10			

6.	B′	10			
7.	C′	20			
8.	C′	20			
9.	C′	20			
10.	D′	20			
11.	D′	20			
12.	D′	20			
13.	E′	25			
14.	E′	25			
15.	E′	25			
16.	F′	40			
17.	F′	40			

If $KMnO_4$ solution required for the filtrate from bottle F′ is more than a few drops (say 3 drops), corresponding correction must be made in the titre values of the remaining bottles.

10.4.4 Calculations

Initial concentration (c_i)

You can calculate the initial concentrations (c_i) of solutions A to E as follows:

$$\text{Solution A}: \frac{50}{100} \times 2.000 \times 10^{-1}\,\text{M} = 1.000 \times 10^{-1}\,\text{M}$$

$$\text{Solution B}: \frac{40}{100} \times 2.000 \times 10^{-1}\,\text{M} = 8.000 \times 10^{-2}\,\text{M}$$

$$\text{Solution C}: \frac{30}{100} \times 2.000 \times 10^{-1}\,\text{M} = 6.000 \times 10^{-2}\,\text{M}$$

$$\text{Solution D}: \frac{20}{100} \times 2.000 \times 10^{-1}\,\text{M} = 4.000 \times 10^{-2}\,\text{M}$$

$$\text{Solution E}: \frac{10}{100} \times 2.000 \times 10^{-1}\,\text{M} = 2.000 \times 10^{-2}\,\text{M}$$

The values are entered in Table 10.2.

Equilibrium concentration (c)

Calculate the equilibrium concentrations (c) of solutions A to E i.e., the molarities of solutions A′ to E′ by using Eq. 1.15 given in Section 10.4.1. Enter the values in Table 10.2.

Amount of oxalic acid adsorbed

Calculate the amount of oxalic acid adsorbed (x) by using Eq. 10.5. Enter the values in Table 10.2.

Table 10.2: Data for Adsorption of Oxalic Acid on Charcoal

Soln. No.	c_i	(c/M)	x/mol	m/g	(x/m)/(mol/g)
A	1.000×10^{-1}				
B	8.000×10^{-2}				
C	6.000×10^{-2}				
D	4.000×10^{-2}				
E	2.000×10^{-2}				

Determine the values of log c, $-$log c, log (x/m), $-$log (x/m) and $c/(x/m)$. Enter these values in Table 10.3.

Table 10.3 : Data for Plotting Graphs

Soln. No.	c/M	log c/M	-log c/M	log (x/m.g/mol)	–log (x/m.g/mol)	(c/(x/m)) × (mol/g.M)
A						
B						
C						
D						
E						

Note that M, mol and g are units for concentration, amount and mass, respectively.

To verify that the adsorption of oxalic acid follows Freundlich and Langmuir adsorption isotherm equations, plot the following graphs:

For Freundlich isotherm : $-$log (x/m) versus $-$log c

For Langmuir isotherm : $c/(x/m)$ versus c

The graphs obtained should be straight lines.

10.4.1 Result

i) It is evident from the values of c and x/m that the extent of adsorption increases as the equilibrium concentration of oxalic acid increases.

ii) Graph plotted between $-$log (x/m) and $-$log c comes out to be a ....

ii) Graph plotted between $c/(x/m)$ and c comes out to be a............... ....

10.5 SUMMARY

In this unit you studied adsorption, physisorption, chemisorption, absorption and sorption. You were told how to study the adsorption of oxalic acid from aqueous solution on activated charcoal.

APPENDIX - I

Oxalic acid : 2.000×10^{-1} M : Dissolve 25.20 g of $(COOH)_2.2H_2O$ in deionised water and make up the volume to 1 dm^3.

Sulphuric acid : 2 M : Take 900 cm^3 of deionised water in a 2 dm^3 beaker. Carefully add to it, 112 cm^3 of conc. H_2SO_4 drop by drop with constant stirring. **Be careful, the reaction is highly exothermic.**

Potassium permanganate : 2.000×10^{-2} M : Dissolve 16 g of $KMnO_4$ in 5 dm^3 of distilled water. Standardise this solution by titrating against 2.000×10^{-1} M oxalic acid.

Fill up the burette with the $KMnO_4$ solution and mount the burette on a stand. Take 5 cm^3 of 2.000×10^{-1} M oxalic acid solution into a conical flask and add to it one test tube full of 2 M H_2SO_4 warmed to 60°C approximately. Add $KMnO_4$ solution drop by drop and shake the conical flask continuously. The end point will be marked by the appearance of a light pink colour. Note down the volume of $KMnO_4$ required for the titration. Repeat the titration till you get two concordant readings. Calculate the exact molarity of the $KMnO_4$ solution using Eq. 1.15 given in Unit 1 of this course (molarity of the solution would be around 0.02 M).

$$2\, M_{H_2C_2O_4} \cdot V_{H_2C_2O_4} = 5\, M_{KMnO_4} \cdot V_{KMnO_4} \qquad \text{... (1.15)}$$

Use the exact molarity of $KMnO_4$ solution in your calculations.

UNIT 11 PHASE EQUILIBRIA - I

Structure

11.1 Introduction
    Objectives
11.2 Definition of Terms
    Phase Rule
    Application of Phase Rule to Two Component Systems
11.3 Experiment 11 : To Construct a Phase Diagram for Naphthalene-Benzoic Acid System
    Principle
    Requirements
    Procedure
    Observations
    Result
11.4 Summary
11.5 Terminal Questions
11.6 Answers

11.1 INTRODUCTION

In Unit 13 of the CHE-04 course, you studied the phase rule and its applications to various one component and two component systems in equilibrium. The phase rule helps us in understanding the effect of various parameters such as pressure, temperature and composition on the phase equilibria of a system. It also helps us in understanding many metallurgical processes (e.g. Pattinsons process for the extraction of silver) of great practical value. In this unit, we will describe an experiment for constructing the phase diagram for a simple eutectic system consisting of two components.

After studying this unit and having performed the experiment described in it, you should be able to:

- define the terms phase, component and degrees of freedom,
- calculate the number of phases, components and degrees of freedom in a system,
- state the phase rule,
- apply the phase rule to the study of a two component system, and
- construct the phase diagram for a simple eutectic system.

11.2 DEFINITION OF TERMS

Before we proceed further, let us define some of the terms involved in phase equilibria.

Phase

Phase (P) is defined as a physically distinct and homogeneous part of the system that is mechanically separable from other parts of the system. The definition as suggested by Gibbs is that a phase is a state of matter that is uniform throughout, not only in chemical composition but also in physical state.

Let us discuss some examples for counting the number of phases in a system.

- A gas or a gaseous mixture is a single phase since there cannot be an interface between one gas and another. Air, for example, is in one phase only although it is a mixture of many gases.
- A system of totally miscible liquids will exist in one phase only as far as the liquid is concerned. But since each liquid has its vapour above, the total number of phases in a

system of miscible liquids is two, one for the liquid and the other for vapour. These two phases are separated by the surface of the solution in the liquid phase.

- A system of two immiscible liquids has a total of three phases, two being for the substances in the liquid state and another for the vapour phase containing vapours of both the liquids.
- A crystal is a single phase. Different solids having different crystal structures constitute different phases, irrespective of the fact whether they have same chemical composition or not. A mixture of graphite and diamond constitutes two phases although both are only allotropic modifications of carbon.

Next we take up the definition of the term, component.

Components

The number of components (C) in a system is the smallest number of substances in terms of which the composition of all the phases in the system can be described separately. The number of components may be smaller than the number of substances that are present in the system.

The definition is easy to apply when the species do not react, for then we simply count their number. For example, phase equilibria containing ice, water and its vapour is a one component system since the composition of each phase can be expressed in terms of the component, H_2O, only. A mixture of ethanol and water is a two component system.

If the species react chemically and are at equilibrium, we have to take into account the significance of the phrase' all the phases' in the above definition. Dissociation of calcium carbonate in a closed vessel is a two component system although at the first look it may appear to have three components, namely, $CaCO_3$, CaO and CO_2.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

You can see that the composition of any one species is related to the other two and the dissociation of calcium carbonate is, therefore, a two component system.

In the case of solid ammonium chloride being heated in a closed vessel, there is an equilibrium between the solid ammonium chloride and its vapour (which consists of ammonia and hydrogen chloride molecules). Since both the phases have the formal composition 'NH_4Cl', it is a one component system. However, if ammonia or hydrogen chloride is added to the system, the system has two components because now the relative amounts of hydrogen chloride and ammonia are not the same.

If there are 'S' substances (may be chemical compounds or ionic species) and 'R' relations (which include equations representing chemical equilibria or charge neutrality) among them, then the number of components (C) can be calculated using the equation,

$$C = S - R \qquad \text{..... (11.1)}$$

To illustrate this, we can consider two examples. If you consider a solution of glucose in water, there are two substances and hence $S = 2$.

But there is no relation between them and so $R = 0$, therefore, $C = 2$ and this is a two component system.

Let us reexamine the equilibrium of ammonium chloride with its vapour containing NH_3 and HCl molecules. Here $S = 3$ since there are three substances, NH_4Cl, NH_3 and HCl. But $R = 2$ since there are two relations as shown below:

(1) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

(2) Concentration of NH_3 = Concentration of HCl.

Therefore, $C = S - R = 3 - 2 = 1$. This is a one component system. If extra $HCl(g)$ is added, then the second relation given above no more holds. That is, $R = 1$ although $S = 3$. This is, therefore, a two component system, as $C = S - R = 3 - 1 = 2$.

Degrees of Freedom

The number of degrees of freedom (F) or variance of a system is the smallest number of intensive variables such as pressure, temperature and composition which are to be specified to describe the state of the system completely.

- If $F = 0$, the system is invariant and this means none of the intensive variables can be changed.
- In case $F = 1$, the system is univariant and one of the intensive variables can be changed.
- For a bivariant system F is equal to 2, and two of the intensive variables can be changed.

The phase rule relates the degrees of freedom to the number of phases and the components. Before studying phase rule, try the following SAQs.

SAQ 1

Calculate the number of phases in the following cases:

a) A closed beaker partially filled with toluene and water;

. . . .

. . . .

. . . .

b) A closed beaker partially filled with acetone and water.

. . . .

. . . .

. . . .

SAQ 2

Calculate the number of components in the following cases:

a) Dissociation of ammonia in a closed vessel;

. . . .

. . . .

. . . .

b) Dissociation of ammonia in a closed vessel containing nitrogen.

. . . .

. . . .

. . . .

11.2.1 Phase Rule

In 1876, Willard Gibbs deduced a simple relationship among the number of phases in equilibrium, the number of components and the number of intensive variables known as degrees of freedom. This relationship is known as **phase rule**. According to phase rule, in a heterogeneous equilibrium, not influenced by gravitational, electrical or magnetic forces, the number of degrees of freedom (F) of the system is defined by the number of components (C) and the number of phases (P) according to the equation,

$$F = C - P + 2 \qquad \text{..... (11.2)}$$

Once the values of C and P are known, F can be calculated.

Let us take up some examples to understand Eq. 11.2. In the vaporization equilibrium of water ($C = 1$), there are two phases (liquid and vapour) and hence, $F = C - P + 2 = 1 - 2 + 2 = 1$. That is, specifying pressure or temperature fixes the other. This is all the more understandable from the general statement that at a particular temperature, vapour pressure of a liquid is constant. If all the three phases, ice, water and its vapour, are to be in equilibrium, then $F = 1 - 3 + 2 = 0$; that is, the system is invariant and this means, all the three phases of water are in equilibrium only at a fixed temperature and pressure. Any effort to change pressure or temperature results in the disappearance of one of the phases.

If you are interested in knowing more about the phase rule, refer to Unit 13 of the CHE-04 course.

11.2.2 Application of Phase Rule to Two Component Systems

Two component systems are also known as binary systems. When a single phase is present in a two component system, phase rule states that $F = 2 - 1 + 2 = 3$. This requires three variables in order to specify a system. We must have a phase diagram in three coordinate axes to understand such a system. Since it is quite difficult to understand such a diagram, it is simplified as a two dimensional plot, keeping one of the three variables constant. In this case, each type of equilibria is studied separately. Thus the usual practice is to study liquid-gas, liquid-liquid, solid-liquid and solid-gas equilibria individually. We concentrate our attention on the solid-liquid equilibria in this section.

Phase Rule for the Condensed System

Solid-liquid equilibria are characterised generally by the absence of gas phase and are not much affected by small changes in pressure. Systems in which the gas phase is absent are called condensed systems. Measurements on solid-liquid equilibria in condensed systems are usually carried out at atmospheric pressure. Because of the relative insensitivity of such systems to small variations in pressure, the pressure may be considered constant. For such a system, the phase rule takes the form,

$$F = C - P + 1 \qquad \text{..... (11.3)}$$

Eq. 11.3 is known as condensed phase rule. For two component systems, Eq. 11.3 becomes,

$$F = 3 - P \qquad \text{..... (11.4)}$$

The solid-liquid equilibria are best represented using temperature-composition diagram. Let us now discuss a method suitable for studying solid-liquid equilibria.

Thermal Analysis

Thermal analysis is a convenient method to study solid-liquid equilibria. In this method, solids of different compositions are separately heated above their melting points. The resulting liquids are cooled slowly and the cooling curves are constructed by plotting temperature against time. A break in the cooling curve indicates the crystallisation of a solid, whereas a horizontal portion in the curve represents the separation of a second solid and temperature remains constant indicating the presence of three phases - two solids and a liquid. At this point, $F = 0$. Once solidification is complete, temperature falls gradually giving a smooth curve again. A typical cooling curve is shown in Fig. 11.1. The portion *ab* represents the gradual cooling of a liquid. The portion *bc*, with a different slope and a break at *b*, shows the crystallisation of a solid phase. The horizontal portion *cd* represents the separation of a second solid phase alongwith the first and, the temperature halt continues till *d* when the last drop of the liquid is solidified. The portion *de* represents the cooling of the solid mixture.

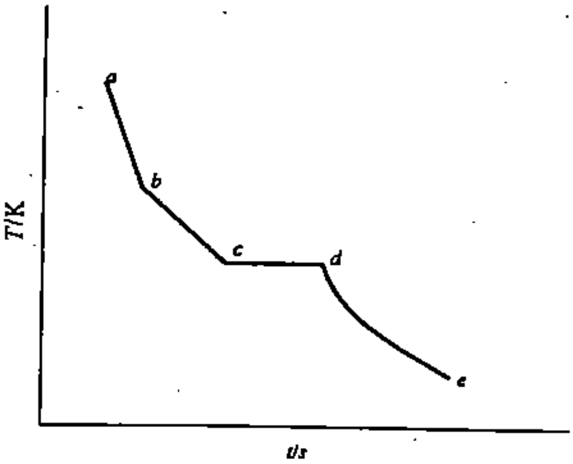


Fig. 11.1 : Cooling curve for two component systems: *b* denotes the break and *cd* the halt, *T* and *t* stand for temperature and time, respectively.

Using the temperatures corresponding to the break and the halt in the cooling curves, the solid-liquid phase diagrams are constructed.

Let us now discuss an experiment for studying phase diagram of a two component system involving solid-liquid equilibria wherein a simple eutectic is formed.

11.3 EXPERIMENT 11 : TO CONSTRUCT A PHASE DIAGRAM FOR NAPHTHALENE-BENZOIC ACID SYSTEM

In this experiment, you will construct a phase diagram for a binary system of naphthalene and benzoic acid, wherein a simple eutectic solid is formed. You know that the mixture of solids, which has the same overall composition as the liquid phase has, is called an **eutectic solid mixture**. The liquid phase of an identical composition and in equilibrium with an eutectic solid mixture, is called an **eutectic liquid mixture**. An eutectic liquid mixture has the lowest freezing point amongst other neighbouring liquid mixtures having more of either component.

When a liquid mixture of naphthalene and benzoic acid is allowed to cool, depending upon the composition of the liquid mixture, pure naphthalene or benzoic acid starts crystalling out from the mixture. The liquid mixture left behind has a different composition from the initial liquid phase. It will be poorer in the component separating out as solid. The remaining liquid will have a lower freezing point than the initial liquid and the freezing point will progressively decrease as more and more of the solid separates out. This happens up to a certain characteristic composition of the liquid phase, when whole of the liquid phase freezes without any further change in temperature. At this point, a temperature halt is observed. The solid separating out at this stage is called an eutectic solid, and the temperature and composition of the liquid mixture are called eutectic temperature and eutectic composition.

Liquid mixtures of naphthalene and benzoic acid of varying composition are allowed to cool. Freezing point (temperature at which the separation of solid phase just starts) and temperature halt for various mixtures are noted. You should note that the temperature halt will be the same for all the mixtures irrespective of their composition because the composition of the solid phase (eutectic) is same in all the cases. A graph is plotted between composition of the mixture and its freezing point. This is the phase diagram for this eutectic system.

11.3.2 Requirements

Apparatus			Chemicals
1.	Boiling tube	1 No.	1. Naphthalene
2.	Test tubes	11 Nos.	2. Benzoic acid

3.	Corks	2 Nos.
4.	Thermometer 360°	1 No.
5.	Stirrer	1 No.
6.	Iron stand	1 No.
7.	Bunsen burner	1 No.
8.	Wire gauze	1 No.
9.	Tripod stand	1 No.
10.	Stop watch	1 No.

3. Liquid paraffin

11.3.3 Procedure

1. You are provided with 11 samples. Two of these are pure naphthalene and pure benzoic acid (100%). The other nine samples have composition as indicated below:

Sample No.	1	2	3	4	5	6	7	8	9	10	11
% Naphthalene	100	90	80	70	60	50	40	30	20	10	0

The percentages indicated are mass by mass. For example, sample no. 2 is 90% naphthalene mass by mass. This means, 10 g of the mixture is prepared from 9 g of naphthalene and 1 g of benzoic acid.

2. Melt the first sample (i.e. pure naphthalene) by placing the test tube in the hot liquid paraffin bath. When all the crystals of the solid have melted and a homogeneous liquid phase is obtained, remove the test tube from the bath.

3. Wipe the test-tube clean and fix the thermometer and the stirrer into it through the cork. Now with the help of another cork, fix the test-tube into the boiling tube which provides an air jacket (Fig. 11.2)

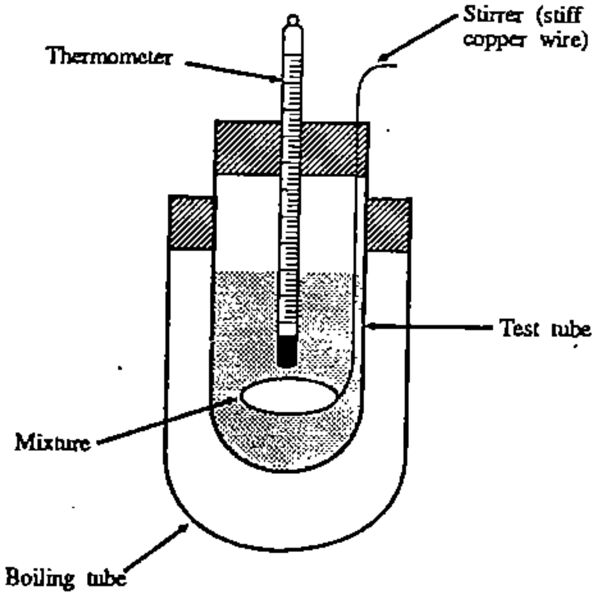


Fig. 11.2 : Determination of freezing point and temperature-halts.

4. Stir the mixture slowly with the stirrer and observe the temperature every half-minute. **Note the temperature at which first crystals of the solid** are formed (i.e., freezing point). Allow the cooling to continue and find out the temperature or temperatures at which the liquid-solid system shows temperature halts, before complete solidification. Lowest **temperature halt will be the eutectic temperature**. Enter the data in Table 11.2.

5. Proceed in a similar manner with the other samples. Record the freezing point and temperature halt for every sample. **When the experiment is over, remelt the samples and return them to bottles marked with respective compositions for re- use by other students.** You have to do this carefully.

6. Construct the phase diagram by plotting a graph between percent composition of naphthalene and freezing temperature by taking **percent** composition on x-axis and temperature on y-axis.

11.3.4 Observations

Table 11.1 : Percent Composition, Freezing Point and Temperature Halts for Various Samples

Sample No.	% Naphthalene	Freezing Point	Temperature halts
1	100		
2	90		
3	80		
4	70		
5	60		
6	50		
7	40		
8	30		
9	20		
10	10		
11	0		

11.3.5 Result

Phase diagram for the naphthalene-benzoic acid system is shown in graph.

11.4 SUMMARY

In this unit, we defined the terms phase, component, degrees of freedom, eutectic and the phase rule. Also, we described an experiment for constructing the phase diagram for a binary liquid-solid system having naphthalene and benzoic acid as components.

11.5 TERMINAL QUESTIONS

1. Fill in the blanks with appropriate word:

   a) The physically separable and homogeneous part of a system is called ________.

   b) The number of independently variable constituents by which the composition of each phase can be determined is called ____________.

   c) The reduced phase rule equation is ____________.

d) The lowest temperature at which any liquid mixture can exist is called ______ temperature.

e) The smallest number of independently variable factors which must be specified in order to define the system completely is called ______________.

2. What is phase rule equation?

3. What is a condensed system?

11.6 ANSWERS

Self-Assessment Questions

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

   b) Two (one liquid and one vapour phase, since acetone and water are miscible).

2. a) $C = 1$ as per Eq. 11.1, since $S = 3$ and $R = 2$

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

Terminal Questions

1. a) Phase

   b) Components

   c) $F = C - P + 1$

   d) Eutectic

   e) Degrees of freedom

2. $F = C - P + 2$

3. Heterogeneous system in which the gas phase is absent, is called a condensed system.

UNIT 12 PHASE EQUILIBRIA - II

Structure

12.1 Introduction
Objectives
12.2 Critical Solution Temperature
12.3 Experiment 12A : CST of Phenol-Water System
12.4 Experiment 12B : Effect of NaCl on CST of Phenol-Water System
12.5 Distribution Law
12.6 Experiment 13 : Distribution Coefficient of Iodine in Carbon tetrachloride-Water System
12.7 Experiment 14 : Distribution Coefficient of Benzoic Acid in Toluene-Water System
12.8 Summary
12.9 Terminal Questions
12.10 Answers

12.1 INTRODUCTION

In Unit 11 of the CHE-04 course, you were introduced to critical solution temperature (CST) of two partially miscible liquids and the distribution law. In this unit, we will describe four experiments which are based upon these two concepts. You studied that the presence of small amounts of impurity produces a very large change in critical solution temperature and the change in CST values is usually a linear function of concentration of impurity. Thus, the amount of impurity can be determined by measuring the CST values.

The distribution law can be used to study the state of association or dissociation of a solute in one or both of the liquid phases. It also helps us in selection of a solvent for extraction of a compound.

After studying this unit and having performed the experiments described in it, you should be able to:

- define critical solution temperature and state the distribution law,
- describe the effect of impurity on critical solution temperature,
- determine the CST of partially miscible liquid pairs such as phenol and water,
- determine the concentration of NaCl in a solution by the CST method,
- determine the distribution coefficient of iodine between water and carbon tetrachloride, and
- determine the distribution coefficient of benzoic acid between water and toluene.

12.2 CRITICAL SOLUTION TEMPERATURE (CST)

You studied in Unit 11 of the CHE-04 course that some liquid pairs do not give homogeneous solutions at all compositions. Such liquid pairs are said to be partially miscible liquids. However, due to increased solubility with increase or decrease of temperature, these may become completely miscible. We can explain such a system of liquids using phenol and water. When a very small amount of phenol is added to water at room temperature, it dissolves completely to give a single liquid phase. However, when the addition of phenol is continued, a point is reached when phenol does not dissolve any more. At this point, two phases, i.e., two liquid layers are formed - one consisting of water saturated with phenol and the other containing phenol saturated with water. Further addition of phenol causes water to shift from water-rich layer to phenol-rich layer. If the addition of phenol is continued, a point is reached when phenol acts as a solvent for all the water present and the two phases merge with each other to form a single phase, i.e., solution of water in phenol. Thus, on shaking equal volumes of phenol and water, two layers are formed - one of phenol in water and the other of water in phenol.

It has been experimentally found that at constant temperature, the composition of the two layers, although different from each other, remains constant as long as the two phases are present. Such solutions of different compositions coexisting with each other are termed as conjugate solutions. The addition of small amounts of phenol or water changes the volume of the two layers and not their compositions. As the temperature is increased, the behaviour remains the same except that the mutual solubility of the two phases increases. When the temperature reaches 338.8 K, the composition of the two layers becomes identical and thereafter the two liquids are completely miscible. Thus, at and above 338.8 K, phenol and water dissolve in each other in all proportions and yield only a single liquid layer on mixing. The variation of mutual solubility of water and phenol with temperature is shown in Fig. 12.1.

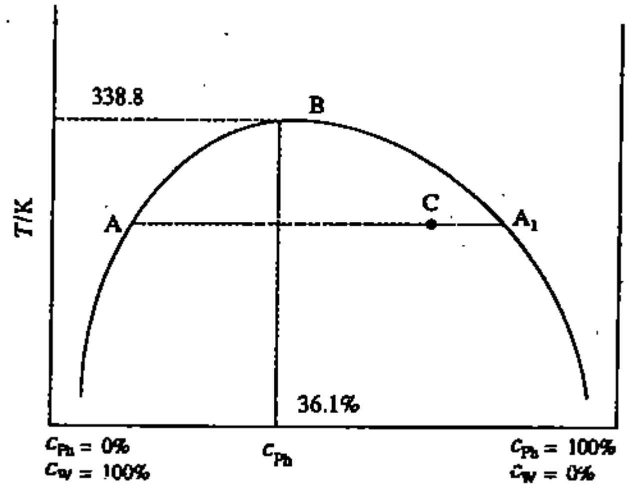


Fig. 12.1: Phenol-water system; c_{Ph} stands for composition of phenol and cw for composition of water.

At a particular temperature, say 325 K, point A represents the composition of water-rich layer and point A_1, represents the composition of phenol-rich layer in equilibrium with A. Between these compositions, all mixtures will yield two layers of compositions A and A_1. Outside these compositions, the two liquids are soluble mutually at 325 K. Similar behaviour is seen at other temperatures below 338.8 K. We can conclude that the dome-shaped area represents the range of existence of two liquid phases and the area outside the dome represents a single liquid phase. The temperature corresponding to the point B, i.e., the temperature at which the solubility becomes complete is called the **critical solution temperature** or the **consolute temperature**. Since the mutual solubility of phenol and water increases with rise in temperature, the critical solution temperature (CST) lies well above the room temperature. Hence, such liquid systems are said to possess an upper critical solution temperature or consolute temperature. Thus, the critical solution temperature, for phenol-water system is 338.8 K. At and above 338.8 K, phenol and water are completely miscible with each other in all proportions. At this temperature, the composition of the solution is 36.1% phenol and 63.9% water. At any point C, the relative weights of the two separate layers are given by the relationship,

$$\frac{\text{Mass of water rich layer}}{\text{Mass of phenol rich layer}} = \frac{A_1C}{AC} \qquad \text{..... (12.1)}$$

There are some liquid pairs (e.g., triethylamine-water) for which mutual solubilities decrease with rise in temperature. As the temperature is decreased, the mutual solubilities increase and below the consolute temperature, the two liquids become miscible in all proportions. Such systems possess lower consolute temperatures. The variation of mutual solubility of triethylamine and water with temperature is shown in Fig. 12.2. Above 291.5 K, on shaking triethylamine and water, two layers are formed; but below 291.5 K, triethylamine and water are completely miscible with each other in all proportions.

Some liquid pairs, e.g., nicotine and water, show both the upper and lower consolute temperatures. These liquid pairs are completely miscible above a certain temperature (upper consolute temperature) and below a certain temperature (lower consolute temperature). The variation of mutual solubilities of nicotine and water with temperature is shown in Fig. 12.3. Within the enclosed area, the liquids are only partially miscible, while

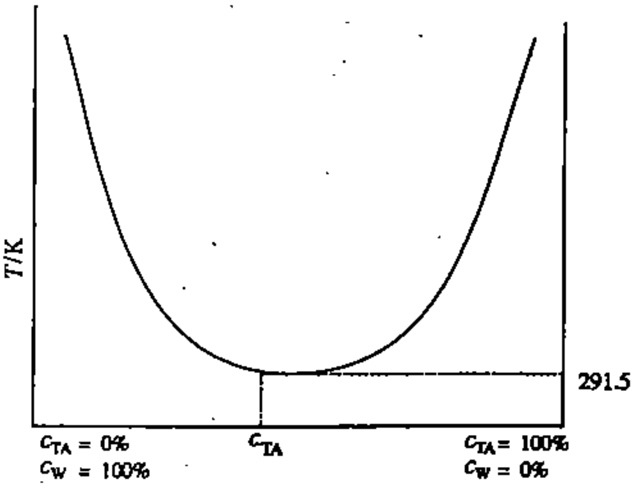


Fig. 12.2: Triethylamine-water system; c_{TA} stands for the composition of triethylamine.

outside the enclosed area, they are completely miscible. The composition corresponding to both the upper and the lower consolute temperatures is the same, i.e., 34% nicotine. Table 12.1 lists the consolute temperatures of some liquid pairs. The two components are denoted as A and B.

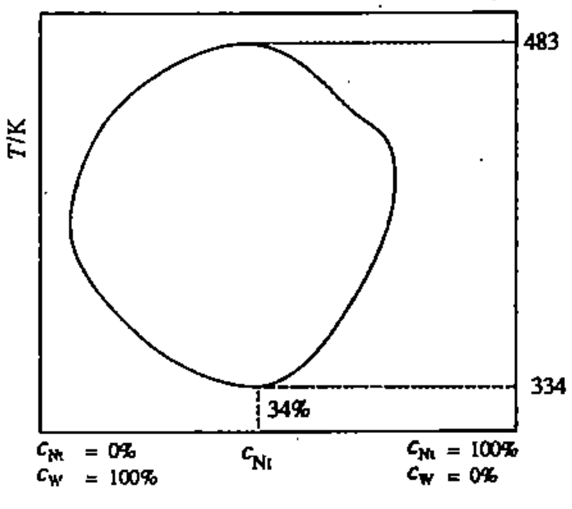


Fig. 12.3: Nicotine-water system; c_{Nt} stands for the composition of nicotine.

Effect of Impurities on CST Values

The presence of an impurity, dissolved in one or both of the phases, changes the CST values as well as the liquid phase composition at CST. Substances soluble in only one of the liquids raise the upper CST and lower the lower CST. For example, one percent solution of sodium chloride raises the upper CST of phenol-water system by 12°. About 0.12 molar solution of naphthalene (insoluble in water) in phenol raises the upper CST of phenol-water system by about 30°. Substances which are soluble in both the liquids tend to lower the upper CST and raise the lower CST. For example, sodium oleate is soluble in both water and phenol. Addition of 1% solution of sodium oleate to phenol-water system lowers the CST value by 45°.

Table 12.1: Consolute Temperatures of Some Liquid Pairs

Components		Consolute temperature/K	
A	B	Upper	Lower
Water Aniline Methanol	Phenol Hexane Carbon disulphide	338.8 333.6 323.5	- - -
Water Water	Diethylamine Triethylamine	- -	316 291.5
Water Glycerine	Nicotine m-Toludine	483 393	334 280

As seen above, the presence of small amounts of impurities produces a very large change in the CST values. The change in CST values is usually a linear function of concentration of impurities. Traces of water present in alcohol are estimated by measuring the CST values for alcohol-cyclohexane system.

As mentioned above, a very small amount of sodium oleate lowers the CST value of phenol-water system considerably. Thus, by making phenol completely miscible with water (by adding appropriate amounts of sodium oleate), lysol-like disinfectants are made.

SAQ 1

Fill in the blanks with appropriate word:

(i) The two liquid layers in equilibrium are known as ____________ solutions.

(ii) The temperature at which the two partially miscible ____________ liquids first become miscible in all proportions is called temperature.

(iii) The critical solution temperature is also called ____________ temperature.

(iv) A system having lower critical solution temperature is ____________ .

(v) A system having both the upper and the lower critical solution temperatures is ______ .

12.3 EXPERIMENT 12A : CST OF PHENOL-WATER SYSTEM

You know that phenol and water constitute a partially miscible liquid pair which has an upper CST. Objective of this experiment is to determine the CST of this system.

12.3.1 Principle

In this experiment miscibility temperatures of different mixtures of phenol and water are determined. A graph is plotted by taking percentage composition of mixture along x-axis and miscibility temperature along the y-axis. Temperature corresponding to the highest point on the dome shaped curve gives the CST of the system.

12.3.2 Requirements

Apparatus

1.	Beaker 250 cm^3	1 No.
2.	Boiling tube	1 No.
3.	Burettes	2 Nos.
4.	Burner	1 No.

Stock solution can be prepared by adding 20 g of distilled water to every 80 g of phenol.

5.	Corks	1 No.
6.	Graduated pipette 10 cm^3	1 No.
7.	Test tubes	5 Nos.
8.	Thermometer 100°	1 No.
9.	Wire gauze	1 No.
10.	Wire stirrer	1 No.

Stock Solution Provided

1. Phenol 80% (mass/mass)

12.3.3 Procedure

Phenol is a highly poisonous and strongly caustic substance. It produces painful burns on coming in contact with skin. Phenol should be handled with abundant care. In case of accidental contact with phenol or its solution, wash the affected part with plenty of water and then apply vaseline.

Set up two burettes, one for phenol solution and the other for distilled water. Take five test tubes and number them 1 to 5. Then prepare the following mixtures of phenol and water in test tubes:

Test tube no.	1	2	3	4	5
80% Phenol Soln. (cm^3)	10.0	9.0	8.0	7.0	6.0
Water (cm^3)	0.0	1.0	2.0	3.0	4.0
% Phenol (mass/mass)	80	72	64	56	48

Take solution no. 1 in the boiling tube. Fix the wire stirrer and thermometer in the boiling tube through the cork and place the boiling tube in the water bath. The bulb of the thermometer should dip in the phenol-water mixture. The level of water in the bath should be 1 cm above the level of mixture in the boiling tube (Fig. 12.4).

The phenol-water mixture in the tube may give rise to two layers. Stir the mixture with the wire stirrer. It will produce a cloudiness or turbidity in the tube. Raise the temperature of the bath slowly while stirring the mixture constantly. **Note down the temperature** (in Table 12.2) of the bath at which the last trace of **cloudiness disappears**. Remove the burner and allow the clear solution to cool slowly while keeping it stirred. **Note down the temperature** at which **cloudiness just reappears**. The average of the two temperatures, which should be nearly equal, is the **miscibility temperature** for the mixture. Transfer the mixture into test tube no. 1.

If the phenol-water mixture does not produce two layers, it means that the miscibility temperature of this mixture is below room temperature. Cool the mixture with ice-cold water. Keep on stirring the mixture. Note down the temperature at which cloudiness just appears in the mixture. Cool the mixture to 4-5° below this temperature and then remove the cold bath. Allow the mixture to warm naturally and note down the temperature at which cloudiness just disappears. Take average of the two temperatures, which would give the miscibility temperature of this mixture.

Find out the miscibility temperature for each mixture in the same manner and record the values in Table 12.2. Now dilute the mixtures 1-5 with an equal volume of water (i.e., 10 cm^3). This will give five more mixtures (no. 6-10) having 40, 36, 32, 28 and 24% phenol, respectively. Find miscibility temperatures for these also and record the values in Table 12.2. After the experiment, transfer all the mixtures to a used **phenol** bottle kept in the laboratory for recovery of phenol by fractional distillation.

Plot a graph by taking percentage composition of mixture along the x-axis and the miscibility temperature along the y-axis. Draw a smooth curve through the points. Mark the maximum point on the curve. Read the temperature and the composition of the mixture at the maximum point from the graph. The temperature for the maximum point on the graph is the critical solution temperature for the phenol-water system.

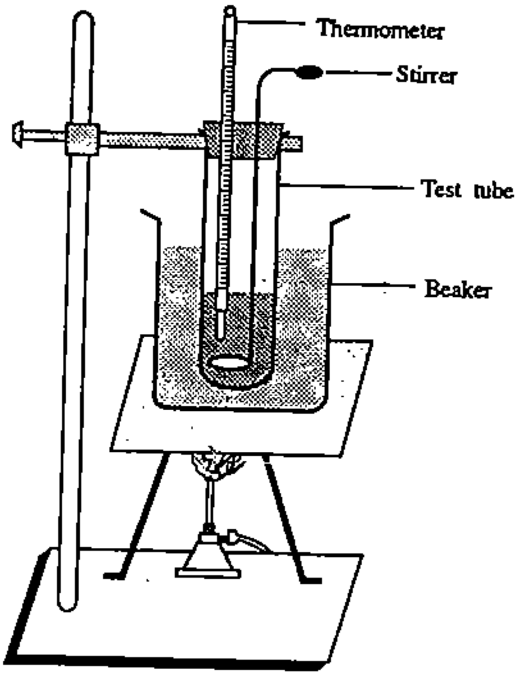


Fig. 12.4 : Determination of miscibility temperature.

12.3.4 Observations

Room temperature = ... °C

Table 12.2 : % Composition - Miscibility Temperature Data

Sl.No.	%Phenol	Miscibility temperature/°C		
		Turbidity disappears	Turbidity re-appears	Average
1	80			
2	72			
3	64			
4	56			
5	48			
6	40			
7	36			
8	32			
9	28			
10	24			

12.3.5 Result

The critical solution temperature (CST) of phenol-water system = ... °C.

12.4 EXPERIMENT 12B : EFFECT OF NaCl ON CST OF PHENOL-WATER SYSTEM

In this experiment, you will study the effect of an impurity (sodium chloride) on the CST of the phenol-water system. You will also determine the concentration of NaCl in an unknown solution by critical solution temperature method.

12.4.1 Principle

In Section 12.2, you studied that the impurities have a marked effect on the CST of a partially miscible liquid pair. Sodium chloride is soluble only in water and not in phenol. Therefore, it will raise the CST of phenol-water system.

In this experiment, the miscibility temperatures for various mixtures of phenol and aqueous solutions of sodium chloride are determined. A calibration curve (usually a straight line) is plotted between the concentration of NaCl and the miscibility temperature.

The miscibility temperature for a mixture of phenol and the unknown NaCl solution is also determined. From the calibration curve, the concentration of unknown NaCl solution is then obtained.

12.4.2 Requirements

Apparatus

1.	Beaker 250 cm^3	1 No.
2.	Boiling tube	1 No.
3.	Burettes	2 Nos.
4.	Burner	1 No.
5.	Cork	1 No.
6.	Graduated pipette	1 No.
7.	Test tubes	7 Nos.
8.	Thermometer 100°	1 No.
9.	Wire stirrer	1 No.
10.	Wire gauze	1 No.

Phenol solution can be prepared as described in Experiment 12A. Sodium chloride solution can be prepared by dissolving 1 g of NaCl in every 100 cm^3 of solution.

Stock Solutions Provided

1.	Phenol	80% (mass/mass)
2.	Sodium chloride	1% (mass/volume)

12.4.3 Procedure

Take seven test tubes and number them from one to seven. Add 5 cm^3 of 80% (m/m) phenol solution to each test tube with the help of a burette. From another burette add 1, 2, 3, 4 and 5 cm^3 of 1% NaCl solution to test tubes numbered 2 to 6, respectively. Add 5 cm^3 of unknown NaCl solution to the test tube numbered 7. Now add 5, 4, 3, 2 and 1 cm^3 of distilled water to test tube numbered 1 to 5, respectively. This makes the volume of mixture 10 cm^3 in each test tube.

Take each mixture in the boiling tube and find out its miscibility temperature as described in Experiment 12A. Record the data in Table 12.3.

Draw a graph between the percentage of sodium chloride (taken as x-axis) and the miscibility temperature (taken as y-axis). Find out the percentage of unknown sodium chloride solution (from the graph) corresponding to its miscibility temperature, using interpolation method discussed in Section 2.6 of Unit 2 of this course.

12.4.4 Observations

Table 12.3 : Composition - Miscibility Temperature Data

Test Tube No.	(Volume of phenol soln. taken)/cm^3	(Volume of 1% NaCl taken)/cm^3	(Volume of distilled water taken)/cm^3	% NaCl in aqueous solution	Miscibility temperature/°C		
					Turbity dis-appears	Turbidity re-appears	Mean
1	5	0.0	5.0	0.0			
2	5	1.0	4.0	0.20			
3	5	2.0	3.0	0.40			
4	5	3.0	2.0	0.60			
5	5	4.0	1.0	0.80			
6	5	5.0	0.0	1.0			
7	5	5.0 (Unknown)	0.0	Unknown			

12.4.6 Result

Concentration of NaCl in unknown solution = ... %

12.5 DISTRIBUTION LAW

Distribution law was given by Nernst, that is why it is also known as the Nernst distribution law. According to this law, at a fixed temperature, a substance X distributes itself between the two immiscible solvents A and B in equilibrium with each other in such a way that the ratio of the concentrations of X in the two solvents is constant, provided that the solute X is in the same molecular state in both the solvents. Mathematically,

$$\frac{\text{Concentration of } X \text{ in solvent A}}{\text{Concentration of } X \text{ in solvent B}} = \frac{c_1}{c_2} = K \qquad \text{..... (12.1)}$$

The constant K is called the distribution or partition coefficient of the solute between the two liquids. It is independent of the total amount of the solute added or the amounts of solvents used or the units in which the concentration is expressed. Generally, it is the convention that the higher concentration is kept in the numerator, so that K is greater than 1.

The value of distribution coefficient depends upon

- nature of the solute
- nature of the solvent, and
- temperature

The distribution law can be derived by taking into account thermodynamic considerations. If you are interested, you can refer to Unit 11 of the CHE-04 course.

Nernst pointed out that the above statement of the distribution law is valid only when the solute undergoes no change such as dissociation or association in either of the solvents. If a solute dissociates into simple molecules or ions, or if it associates to form complex molecules, then the distribution law does not apply to the total concentration of the solute in each of the two phases. It is applicable only to the concentration of a particular species common to both the layers. Let us look at the distribution law in brief in these cases, which we have discussed in detail in Section 11.4 of Unit 11 of the CHE-04 course.

When the Solute Undergoes Association

Suppose the solute X undergoes association in one of the liquids to form associated molecules, X_n, i.e.,

$$nX \rightleftharpoons X_n$$

If the concentration of the solute in this liquid is c_1 before association and that in the other liquid is c_2, then the distribution law would be

$$\frac{(c_1)^{1/n}}{c_2} = K = \text{constant}$$

In benzene and toluene solutions, benzoic acid exists as dimeric molecules (i.e., $n = 2$). In distribution of benzoic acid between benzene or toluene and water, the distribution law would be

$$\frac{(c_1)^{1/2}}{c_2} = \frac{\sqrt{c_1}}{c_2} = K = \text{constant} \qquad \text{.... (12.2)}$$

When the Solute Undergoes Dissociation

Let us suppose that the solute X undergoes dissociation into A and B in one of the liquids. If c_1 is the total concentration of the solute in this liquid before dissociation, and α is the degree of dissociation, then we can write

$$\begin{array}{ccccc} X & \rightleftharpoons & A & + & B \\ c_1(1-\alpha) & & c_1\alpha & & c_1\alpha \end{array}$$

If the concentration of the solute in the other liquid, in which it remains undissociated, is c_2, then the distribution coefficient is given by

$$\frac{c_1(1-\alpha)}{c_2} = K = \text{constant} \qquad \text{..... (12.3)}$$

SAQ 2

Fill in the blanks using appropriate words:

i) The __________ law deals with the distribution of a solid between two immiscible liquids.

ii) The ratio of the concentrations of the solute between two liquids is called ________ coefficient.

iii) The distribution law is valid when the dissolved substance has the ________ molecular form in the two solvents.

12.6 EXPERIMENT 13 : DISTRIBUTION COEFFICIENT OF IODINE IN CARBON TETRACHLORIDE-WATER SYSTEM

Objective of this experiment is to determine the distribution coefficient of iodine in carbon tetrachloride-water system.

12.6.1 Principle

Carbon tetrachloride and water are practically immiscible with each other but iodine dissolves in both of them. When iodine is added to a mixture of CCl_4 and H_2O at a certain temperature, iodine distributes itself between the two immiscible layers. At a particular temperature, let the concentration of iodine in CCl_4 and H_2O be c_1 and c_2, respectively. In both CCl_4 and H_2O iodine exists in molecular form. Therefore, according to the distribution law, we have

$$\frac{c_1}{c_2} = K = \text{constant} \qquad \text{..... (12.3)}$$

Different amounts of iodine are added to a mixture of CCl_4 and H_2O. The concentration of iodine in two layers is estimated by titration against sodium thiosulphate solution. for dilute solutions, the ratio c_1/c_2 is found to be constant within experimental limits and gives the value of distribution coefficient, K.

12.6.2 Requirements

Apparatus			Chemicals
1.	Burette	1 No.	1. Carbon tetrachloride
2.	Graduated pipette 10 cm^3	1 No.	
3.	Pipette 20 cm^3	1 No.	
4.	Pipette 5 cm^3	1 No.	
5.	Conical flask 100 cm^3	1 No.	
6.	Stoppered bottles 250 cm^3	3 Nos.	
7.	Thermometer 100	1 No.	
8.	Glass trough	1 No.	

Stock Solutions Provided

1. Iodine
2. Freshly prepared starch
3. 1.000×10^{-1} M and 1.000×10^{-2} M sodium thiosulphate

Details of preparation of stock solutions are given in Appendix-1.

12.6.3 Procedure

Take three 250 cm^3 glass stoppered bottles and label them with numbers 1, 2 and 3. Using two separate burettes, take 20, 25 and 30 cm^3 of saturated solution of iodine in CCl_4 and add 10, 5 and 0 cm^3 of carbon tetrachloride, respectively to these bottles to make the total volume 30 cm^3 in each bottle.

Now add to each bottle 100 cm^3 of distilled water. Stopper the bottles, shake them vigorously and place them in a thermostat (or glass trough filled with water maintained at room temperature) for about half an hour. Shake the bottles 2-3 times. After the final shaking, wait till there is a complete separation of the two liquid layers. Since carbon tetrachloride is heavier than water, it will form the lower layer, while the upper layer will be the aqueous layer. Note down the temperature of water in the trough. Pipette out 20 cm^3 of aqueous layer into a conical flask from bottle no. 1. Add 4-5 drops of freshly prepared starch solution. The solubility of iodine in water is very low. Titrate this solution with 1.000×10^{-2} M sodium thiosulphate (hypo) solution. The equivalence point is indicated by the disappearance of the blue colour. Repeat the titration to get two concordant readings and record them in Table 12.4. In the same manner take the samples of upper layer from bottle nos. 2 and 3. Perform titrations and record the titre values in the Table 12.4.

While pipetting one of the two layers, you should ensure that the other layer does not enter the pipette. You are advised to take the help of the Counsellor during this operation.

After finishing the titrations of the upper aqueous layer, separate the remaining upper layer by decantation or with the help of a separating funnel. Pipette out 5 cm^3 of CCl_4 layer (of bottle 1 into a 100 cm^3 conical flask. Add about 20 cm^3 of distilled water into it. The addition of water helps in titration by gradually extracting iodine into water layer where the reaction with sodium thiosulphate occurs. By covering the CCl_4 layer with a water layer, loss of iodine as vapour from the exposed solution is also prevented. Add 4-5 drops of freshly prepared starch solution. Titrate the solution with 1.000×10^{-1} M sodium thiosulphate solution. Disappearance of blue colour will indicate the equivalence point. Repeat the titration to get two concordant readings and record them in Table 12.5. In the same manner, take the samples of CCl_4 layer from bottle nos. 2 and 3, perform titrations and record the titre values in Table 12.5.

12.6.4 Observations

Temperature of water in trough = ... °C =

Table 12.4 : Titration of Aqueous layer

Sl. No.	Bottle No.	(Volume of aqueous layer)/cm^3	Burette reading		(Volume of 1.000×10^{-2} M hypo consumed)/cm^3
			Initial	Final	
1	1	20.0			
2	1	20.0			
3	1	20.0			
4	2	20.0			
5	2	20.0			
6	2	20.0			
7	3	20.0			
8	3	20.0			
9	3	20.0			

Table 12.5 : Titration of CCl_4 layer

Sl. No.	Bottle No.	(Volume of CCl_4 layer)/cm^3	Burette reading		(Volume of 1.000×10^{-1} M hypo consumed)/cm^3
			Initial	Final	
1	1	5.0			
2	1	5.0			
3	1	5.0			
4	2	5.0			
5	2	5.0			
6	2	5.0			
7	3	5.0			
8	3	5.0			
9	3	5.0			

12.6.5 Calculations

Sodium thiosulphate reacts with iodine as follows:

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$

If V_a cm^3 of $Na_2S_2O_3$ of molarity M_a react with V_b cm^3 of I_2 of molarity M_b, then using Eq. 1.13 of Unit 1 of this course, we can write,

$$\frac{M_a V_a}{M_b V_b} = \frac{2}{1}$$

or $$M_a V_a = 2 M_b V_b$$

Using this equation, calculate the concentration of I_2 in terms of molarity in aqueous and in CCl_4 layers in each bottle. After that, find out the ratio of concentration of I_2 in CCl_4 layer (c_1) to that in the aqueous layer (c_2), which will give the value of distribution coefficient, K. Remember that the molarities of $Na_2S_2O_3$ used for the titration of aqueous and CCl_4 layers are 1.000×10^{-2} M and 1.000×10^{-1} M., respectively. Record the values in Table 12.6 and report the average value of K.

Table 12.6 : Values of Distribution Coefficient

Bottle	c_1/M	c_2/M	$K = \frac{c_1}{c_2}$	Average value of K
1				
2				
3				

12.6.6 Result

The distribution coefficient of iodine between carbon tetrachloride and water was found to be .

12.7 EXPERIMENT 14 : DISTRIBUTION COEFFICIENT OF BENZOIC ACID IN TOLUENE-WATER SYSTEM

Objective of this experiment is to determine the distribution coefficient of benzoic acid between toluene and water.

12.7.1 Principle

As you know toluene and water are practically immiscible with each other but benzoic acid dissolves in both of them. When benzoic acid is added to a mixture of toluene and water, it distributes itself between the two immiscible layers. In water, benzoic acid exists almost in monomeric form. No doubt benzoic acid is a weak acid. We assume that its dissociation in water is negligibly small to facilitate the calculations in this experiment. In toluene, it undergoes association to form dimers. By performing this experiment, we can verify the validity of these two assumptions.

At a particular temperature, let the concentration of benzoic acid in toluene and in water be c_1 and c_2, respectively. Therefore, according to Eq. 12.2,

$$\frac{\sqrt{c_1}}{c_2} = K = \text{constant} \qquad \text{..... (12.2)}$$

Different amounts of benzoic acid are added to a mixture of toluene and water. The mixture is shaken vigorously and the layers are allowed to separate. The concentrations (c_1 and c_2) of benzoic acid in the two layers are estimated by titrating against standard NaOH solution and the value of K is calculated. The ratio $\sqrt{c_1}/c_2$ is calculated and is found to be constant within experimental limits thereby justifying the assumptions made above. Also, this gives the value of the distribution coefficient.

12.7.2 Requirements

Apparatus

1.	Burette	1 No.
2.	Graduated pipette 10 cm^3	1 No.
3.	Pipette 10 cm^3	1 No.
4.	Pipette 5 cm^3	1 No.
5.	Conical flask	1 No.
6.	Stoppered bottles 250 cm^3	3 Nos.
7.	Thermometer 100°	1 No.
8.	Glass trough	1 No.

Chemical

1. Toluene

Details of preparation of stock solutions are given in Appendix-II.

Stock Solutions Provided

1. Benzoic acid
2. 5.000×10^{-2} and 1.000×10^{-1} M NaOH
3. Phenolphthalein

12.7.3 Procedure

Take three 250 cm^3 capacity stoppered glass bottles and label them 1, 2 and 3. Place 20, 25 and 30 cm^3 of benzoic acid solution and, 10, 5 and 0 cm^3 of toluene to bottles 1, 2 and 3, respectively making the total volume of organic layer 30 cm^3 in each bottle.

Add 100 cm^3 of distilled water to each bottle. Stopper the bottles, shake them vigorously and place them in the trough of water for about half an hour. Allow the layers to separate. Toluene being lighter than water will form the upper layer. Note down the temperature of water in the trough.

While pipetting one of the two layers, you should ensure that the other layer does not enter the pipette. You are advised to take the help of the Counsellor during this operation.

Pipette out 5 cm^3 of toluene layer from bottle 1 in a 100 cm^3 conical flask. Add 25 cm^3 of distilled water and 2 drops of phenolphthalein solution. Titrate the mixture with standard 1.000×10^{-1} M NaOH solution. The equivalence point is indicated by the appearance of a pink colour. Repeat the titration till you get two concordant readings. Similarly perform titration with toluene layer in bottles 2 and 3 separately and record the readings in Table 12.7.

After performing titrations of the upper toluene layer, separate the upper layer by decantation or with the help of a separating funnel. Pipette out 10 cm^3 of lower aqueous layer from bottle 1 into a 100 cm^3 conical flask and add 2 drops of phenolphthalein indicator. Titrate the solution with standard 5.000×10^{-2} M NaOH solution. The equivalence point is marked by the appearance of pink colour. Repeat the titration till you get two concordant readings. Similarly perform titration with aqueous layer in bottles 2 and 3. Record the readings in Table 12.8.

12.7.4 Observations

Temperature of water in trough = ... °C

Table 12.7 : Titration of Toluene layer

Sl No.	Bottle No.	(Volume of toulene layer)/cm^3	Burette reading		(Volume of 1.000× 10^{-1} M NaOH consumed)/cm^3
			Initial	Final	
1	1	5.0			
2	1	5.0			
3	1	5.0			
4	2	5.0			
5	2	5.0			
6	2	5.0			
7	3	5.0			
8	3	5.0			
9	3	5.0			

Table 12.8 : Titration of Aqueous layer

Sl. No	Bottle No.	(Volume of aqueous layer)/cm^3	Burette reading		(Volume of 5.000 ×10^{-2} M NaOH consumed)/cm^3
			Initial	Final	
1	1	10.0			
2	1	10.0			
3	1	10.0			
4	2	10.0			
5	2	10.0			
6	2	10.0			
7	3	10.0			
8	3	10.0			
9	3	10.0			

12.7.5 Calculations

Benzoic acid reacts with sodium hydroxide as follows:

$C_6H_5COOH + NaOH \quad C_6H_5COONa + H_2O$

If V_a cm^3 of benzoic acid of molarity M_a react with V_b cm^3 of sodium hydroxide of molarity M_b, then using Eq. 1.13 of Unit 1 of this course.

$$\frac{M_a V_a}{M_a V_a} = \frac{1}{1}$$

or $\quad M_aV_a = M_bV_b$

Using the above equation, calculate the concentration of benzoic acid solution in terms of molarity in toluene layer (c_1) and in aqueous layer (c_2) in each bottle. After that calculate the ratio $\sqrt{c_1}/c_2$, which will give the value of distribution coefficient, *K*. Record the values of c_1; c_2 and *K* in Table 12.9 and report the average value of *K*.

Table 12.9 : Values of Partition coefficient

Bottle No.	c_1/M	c_2/M	$K = \frac{\sqrt{c_1}}{c_2}$	Average value of *K*
1				
2				
3				

12.7.6 Result

The distribution coefficient of benzoic acid between toluene and water was found to be ....

The constant value for *K* brings out the validity of the assumption made regarding the monomeric nature of benzoic acid in water and the dimeric nature of benzoic acid in toluene.

12.8 SUMMARY

In this unit, you were introduced to the concepts of critical solution temperature and distribution coefficient. Two experiments based on critical solution temperature were discussed. Two experiments for determination of distribution coefficient of iodine between carbon tetrachloride and water, and of benzoic acid between toluene and water were also described.

12.9 TERMINAL QUESTIONS

1. What is CST?
2. What is the effect of impurity on CST?
3. Give the definition of the distribution coefficient.
4. State the form of distribution law when the solute associates in one of the two liquids.
5. State the form of distribution law when the solute dissociates in one of the two liquids.

12.10 ANSWERS

Answers to Self-Assessment Questions

1. i) conjugate
   ii) critical solution or consolute
   iii) consolute

iv) triethylamine-water

v) nicotine-water

2. i) distribution

ii) distribution or partition

iii) same

Answers to Terminal Questions

1. The temperature at which the two partially miscible liquids become miscible in all proportions is called critical solution temperature, CST.
2. Impurities have a marked effect on CST. If an impurity is soluble only in one of the two liquids, it will raise the upper CST, while the lower CST will be lowered. If on the otherhand, it is soluble in both the liquids, the upper CST will be lowered, while the lower CST will be raised.
3. If to a system of two immiscible liquids a substance, which is soluble in both the liquids, is added, the solute will distribute itself in such a way that the ratio of the molar concentrations of the solute in the two liquids is constant at a given temperature.
4. $\frac{(c_1)^{1/n}}{c_2} = K$, where n is the degree of association of the solute in one of the liquids.
5. $\frac{c_1 (1 - \alpha)}{c_2} = K$, where α is the degree of dissociation of the solute in one of the liquids.

FURTHER READING

1. Senior Practical Physical Chemistry, B.D. Khosla, A. Gulati and V.C. Garg, R. Chand & Co., New Delhi, 4th ed., 1985.
2. Practical Chemistry, S. Giri, D.N. Bajpai and O.P. Pandey, S. Chand & Company Ltd., New Delhi, 7th ed., 1993.

APPENDIX - I

Iodine solution : Each student will need about 80 cm^3 of solution. Prepare a saturated solution of iodine by dissolving 25 g of iodine crystals in 500 cm^3 of CCl_4. Filter the solution and store in a brown bottle.

Starch solution : Take 1 g of starch and make a fine paste of it in about 20 cm^3 of distilled water. Add 80 cm^3 of hot water and boil the mixture. Keep the mixture stirred during boiling. Since starch solutions degrade in short time, it is advised to test its suitability. For this, take a small portion of the solution in a test tube and to this, add a little of iodine solution. It should give an intense blue colour.

Sodium thiosulphate : 1.000×10^{-1} M and 1.000×10^{-2} M : Prepare a stock solution of sodium thiosulphate of about 0.25 M concentration by dissolving 62.5 g crystals in distilled water and making up the volume to 1 dm^3. Standardise this solution by titrating against a standard solution of potassium dichromate, as described in Appendix-I to Unit 15 of this course. Let the molarity of stock solution be x mol dm^{-3}.

Prepare sodium thiosulphate solutions of 1.000×10^{-1} M and 1.000×10^{-2} M concentrations by diluting appropriate volumes of the stock solution with distilled water. Volume of stock solution required to prepare 1 dm^3 of 1.000×10^{-1} M and 1.000×10^{-2} M sodium thiosulphate solution can be calculated by using the formula,

$$M_1V_1 = M_2V_2$$

or $$V_1 = \frac{M_2V_2}{M_1}$$

Thus, volume of stock solution (V_1) required to prepare 1 dm^3 of

$$1.000 \times 10^{-1}\text{ M solution} = \frac{1.000 \times 10^{-1}\text{ M} \times 1000\text{ cm}^3}{x\text{ M}}$$

$$= \frac{100}{x}\text{ cm}^3$$

Volume of stock solution (V_1) required to prepare 1 dm^3 of

$$1.000 \times 10^{-2}\text{ M solution} = \frac{1.000 \times 10^{-2}\text{ M} \times 1000\text{ cm}^3}{x\text{ M}}$$

$$= \frac{10}{x}\text{ cm}^3$$

where x is the molarity of the stock solution.

APPENDIX - II

Benzoic acid solution : Prepare a saturated solution of benzoic acid by dissolving about 40 g of acid in 500 cm^3 of toluene. Filter the solution.

Phenolphthalein solution : Dissolve 0.1 g of phenolphthalein in 125 cm^3 of ethanol and add 125 cm^3 of distilled water with constant stirring. Filter the solution if there is any precipitate.

Sodium hydroxide : 1.000×10^{-1} M and 5.000×10^{-2} M : Prepare a solution of NaOH of about 0.1 M concentration by dissolving 4.4 g of NaOH in distilled water and making up the volume to 1 dm^3. Standardise this solution by titrating against a standard solution of HCl using phenolphthalein as indicator. Preparation of standard solution of HCl has been described in Appendix-I to Unit 9 of this Block. Let the concentration of this solution be x M (which will be around 0.1 M).

Take 250 cm^3 of the above solution and dilute to 500 cm^3 in a volumetric flask using distilled water. Concentration of this solution will be $x/2$ M (which will be around 0.05 M).

APPENDIX TO BLOCK 2

UNIT 4 EXPERIMENT NO. 1

i) You can make aqueous solutions of 3-4 common household detergents such as Surf, Wheel, Nirma, Key etc. for the determination of surface tension. You can make 0.5 to 1% aqueous solution of the above detergents by mass. For this, dissolve 1g detergent powder in 100 cm^3 of distilled water by stirring gently. You can warm a little so that you get a clear solution. You should take care that no froth forms in the above process. If you have warmed the contents, then keep this solution for sometime to acquire room temperature.

Determine the surface tension of these solutions as given in Experiment 1 and compare the values so obtained.

ii) For this experiment 1% (w/w) stock solution of a detergent can be made as given above. Dilute this stock solution to 80%, 60%, 40%, 20% and 10% and study the variation of γ with concentration.

UNIT 5 EXPERIMENT NO.2

30% Sucrose Solution: You can make 30% (w/w) aqueous solution of sucrose by dissolving 30g of sucrose in 70 cm^3 of water. The values of viscosity co-efficient for this solution at various temperature are as given below:

Temp/°C	$10^3\,\eta$/Pa s
15	3.757
20	3.187
25	2.735

UNIT 6 EXPERIMENT NO.4

The following solutes could also be used for the determination of integral enthalpy of solution:

i) Potassium nitrate (1:200)

ii) $BaCl_2 \cdot 2H_2O$ (1:400)

iii) $K_2Cr_2O_7$ (1:400)

UNIT 7 EXPERIMENT NO.5

0.50 Mol dm^{-3} HCl

Refer to Appendix of Unit 16 Point No.2

Make the stock solution of hydrochloric acid (A) as in NO.2.

To prepare 0.50 M HCl from hydrochloric acid (A), take $\frac{1000 \times 0.50}{20p} = \frac{25}{p}$ cm^3 of hydrochloric acid (A) in a 1 dm^3 standard flask and make the solution upto the mark with distilled water. You get the resultant solution as 0.50 M HCl.

0.50 M NaOH

First prepare approximately 1 M NaOH solution by dissolving 40 g NaOH in 1 dm^{-3} of distilled water. Take 10 cm^3 of this app. 1 M solution and dilute it to 100 cm^3. Titrate this solution of NaOH with 0.1 M HCl (prepared above) using phenolphthalein as the indicator. Calculate the exact strength of this solution. If the molarity of this solution is y, then the molarity of the initial (1 M NaOH) solution is 10y.

To get 0.50 M NaOH from the NaOH solution of molarity 10y, take 50/y cm^3 of the above solution in 1 dm^3 standard flask and dilute it with distilled water by making up the solution upto the mark. This will give 0.50 M NaOH.

Phenolphthalein solution - kindly see Appendix II of Unit 12.

EXPERIMENT NO.6

0.50 M CH_3COOH

Using a burette, transfer 60 cm^3 of glacial acetic acid into a 1 dm^3 volumetric flask containing 500 cm^3 of distilled water and make the solution upto the mark. This solution (A) is approximately 1 M CH_3COOH. To find out the exact molarity of this solution take 20 cm^3 of A and dilute it to 200 cm^3. Let it be named as B. Titrate CH_3COOH (B) with the standard solution of 0.1 M NaOH (as prepared above) using phenolphthalein as the indicator. Find out the exact molarity of CH_3COOH (B). If the molarity of this solution is x, then the molarity of CH_3COOH (A) is 10x.

To get 0.50 M acetic acid from CH_3COOH (A), take $\frac{50}{x}$ cm^3 of CH_3COOH (A) in a 1 dm^3 volumetric flask and add distilled water to make the solution upto the mark. This will give you 0.50 M CH_3COOH.

Utter Pradesh
Rajarshi Tandon Open University

UGCHE-L4
Chemistry Lab –IV

Block

4

CHEMICAL KINETICS

UNIT 13

Basic Concepts 5

UNIT 14

Initial Rate Method 19

UNIT 15

Integrated Rate Equation Method 37

BLOCK 4 CHEMICAL KINETICS

In the previous block, you studied some experiments based on thermodynamics. Based on the study of thermodynamics, one can ask two kinds of questions. Firstly, whether the reaction would take place or not (i.e. regarding the feasibility of the reaction), and secondly, if it does, how far would it go? Which way would the equilibrium be–towards the products or reactants, i.e., what is the equilibrium constant for the reaction? We can get answers to these questions from thermodynamics. But how about the time aspect? or when would the reaction be over? Would it be instantaneous or would it take a long time?

The aspect of time is quite important for a chemist. Assume that we wish to set up an industry to manufacture a certain chemical 'X'. Also a simple method 'Y' is available for the synthesis of 'X' and the reaction is feasible thermodynamically. Yet we cannot decide to go ahead with the chemical process unless we know about the time required for the reaction to take place. From an industrialist point of view, a reaction is meaningful only if it gives sufficient amount of product (yield) in a reasonable amount of time. The experiments you have been doing in your laboratory courses have been designed in such a manner that you can draw some meaningful conclusion from them in a stipulated time. Can you, for example, in your laboratory course, do an experiment that takes say 3–4 weeks to complete?

Another important question to which one would like to have an answer is–how does a reaction take place? This question relates to the probable sequence of steps that lead to the formation of the product(s) from the reactant(s). The sequence of steps thus proposed constitute the mechanism of a reaction. A reaction mechanism is proposed based on some experimental evidences. The time taken for a reaction and the reaction mechanism are studied under chemical kinetics or reaction kinetics.

A detailed study of reaction mechanism of some (organic) reactions has been made in the course, Organic Reaction Mechanism (CHE-06). We are not going to study the mechanistic details in this course. Instead, we shall take up the study of time aspect of some chemical reactions through some experiments in this block. This block consists of three units. Unit 13 will deal with the basic features of reaction kinetics. In Unit 14, experiments based on initial rate method will be discussed. A few kinetics experiments based on integrated rate equation method will be explained in Unit 15.

Objectives

After studying this block, you should be able to:

- explain the effect of concentration on the rates of chemical reactions,
- perform kinetic experiments based on initial rate method and integrated rate equation method, and
- use methods like titrimetry, conductometry, and colorimetry for following the progress of a reaction.

UNIT 13 BASIC CONCEPTS

Structure

13.1 Introduction
  Objectives
13.2 Rate of a Chemical Reaction
  Defining Rate
  Measurement of Rate
  Factors Affecting the Rate of a Reaction
13.3 Rate Laws
  Differential Rate Laws : Concentration
  Dependence of Rate
  Integrated Rate Laws : Time Dependence of Concentration
13.4 Determination of Order of a Reaction
13.5 Summary
13.6 Terminal Questions
13.7 Answers

13.1 INTRODUCTION

As pointed out in block introduction, kinetics deals primarily with the 'time aspect of chemical reactions. The information obtained from a kinetics experiment may be used in proposing a mechanism for the reaction. In this unit, we shall discuss the basic concepts of chemical kinetics relevant for this laboratory course. In this process, we shall first define rate of a reaction and see various ways of expressing it. We shall explain how the data from a kinetics experiment can be expressed in terms of rate equation and how we can manipulate this data to obtain the order of reaction and rate constant. In the next unit, we shall study two kinetics experiments based on initial rate method.

Objectives

After studying this unit you should be able to :

- state different ways of expressing the rate of a chemical reaction,
- describe different methods of following the progress of a chemical reaction,
- list various factors affecting the rates of chemical reactions,
- explain the terms, differential and integrated rate equations,
- define and differentiate between the terms, order and stoichiometry of reaction,
- describe various methods for the determination of order of a reaction, and
- present the data obtained from a kinetics experiment through suitable equations and graphs and, calculate the rate constant and order of reaction.

13.2 RATE OF A CHEMICAL REACTION

We are used to the concept rate (velocity or speed) in our day to day life. It implies some change in a parameter in a given amount of time. For example, the rate at which water flows from a tap can be expressed in gallons or litres per minute. Speed of a vehicle is expressed in kilometers per hour. Similarly, chemical reactions also occur at a certain rate. Different chemical reactions proceed at different rates. Certain reactions get to equilibrium in a few minutes or seconds, while certain others may take days or even years. The concept of rate of a reaction is very crucial for a proper understanding of chemical kinetics. Let us see how we define the rate of a reaction.

13.2.1 Defining Rate

Let us take up a simple reaction,

$$2A + 3B \longrightarrow C + 4D \qquad ...(13.1)$$

whose progress can be mentioned in terms of change in concentrations of various reactants or products. Let us say that in a time interval Δt (delta 't'), the change in the concentration of the product C is Δ [C]. Then the reaction rate is defined as follows:

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

$$\text{Reaction rate} = \frac{\Delta [C]}{\Delta t} \qquad ...(13.2)$$

The rate of above reaction can equally well be expressed in terms of the 'amount of product 'D'. We see from the stoichiometry of the reaction that four moles of 'D' are produced in the time required for producing one mole of C, i.e., D is produced four times as fast as C. So if we have to define rate in terms of [D], then we have to divide it by four which is its stoichiometric coefficient in the balanced chemical equation. In other words, the rate would be,

$$\text{reaction rate} = \frac{1}{4}\frac{\Delta [D]}{\Delta t} \qquad ...(13.3)$$

As C and D are both products, their concentration increases as the reaction progresses i.e. Δ[C] or Δ[D] is positive. But, if we wish to express the rate in terms of any of the reactants, then the change in concentration would be a negative number. Since customarily, the rate is defined as a positive quantity, we multiply the rate expression in terms of a reactant by –1. In other words, we write the rate as,

The minus sign in the rate equation also signifies the disappearence of the species with respect to which the rate is expressed.

$$\text{rate} = -\frac{1}{2}\frac{\Delta [A]}{\Delta t} \text{ or } = -\frac{1}{3}\frac{\Delta [B]}{\Delta t} \qquad ...(13.4)$$

Note that 2 and 3 are the stoichiometric coefficients of A and B, respectively.

So we see that in the above example, we have four equivalent ways of expressing the rate i.e.,

$$\text{rate} = \frac{\Delta [C]}{\Delta t} = \frac{1}{4}\frac{\Delta [D]}{\Delta t} = -\frac{1}{2}\frac{\Delta [A]}{\Delta t} = -\frac{1}{3}\frac{\Delta [B]}{\Delta t} \qquad ...(13.5)$$

In general the rate is defined as,

$$\text{rate} = \frac{1}{\nu_i}\frac{\Delta c_i}{\Delta t} \qquad ...(13.6)$$

Δc_i has units of mol dm^{-3} while unit of Δt is second. The units of rate, as defined in Eq. 13.6, are mol dm^{-3} s^{-1}.

where Δc_i is the change in the concentration of the i th species and ν_i is the stoichiometric coefficient of the ith species in the balanced chemical equation. ν_i is positive for products and negative for the reactants; also Δt is the change in time.

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

The rate as defined above signifies the average rate of the reaction over a specified period of time. The average rate approaches the so called instantaneous state, as Δt approaches zero (i.e., $\Delta t \rightarrow 0$). Using the standard notation for instantaneous rate, we write the rate as:

$$\text{Instantaneous rate} = \frac{1}{\nu_i}\left(\frac{\Delta c_i}{\Delta t}\right)_{t \to 0}$$

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

Calculation of Reaction Rate

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

$$2NO_2(g) \longrightarrow 2NO(g) + O_2(g) \qquad \text{... (13.8)}$$

In Fig. 13.1 a, b and c, you can see concentration (c) against time (t) plots for NO_2, NO and O_2 as per the values given in Table 13.1. In these figures, the graphical method of calculation of the reaction rates for the consumption of NO_2 and for the formation of NO and O_2 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.

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

$$\text{Rate of reaction} = -\frac{\text{Slope of } c \text{ against } t \text{ curve for the reactant}}{\text{Stoichiometric coefficient of the reactant}} = \frac{\text{Slope of } c \text{ against } t \text{ curve for the product}}{\text{Stoichiometric coefficient of the product}}$$

The concentrations of components are given in molarity (M) unit.

$1\ M = 1\ \text{mol dm}^{-3}$

Table 13.1: Concentrations of NO_2, NO and O_2 at Different Time Intervals at 673 K.

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

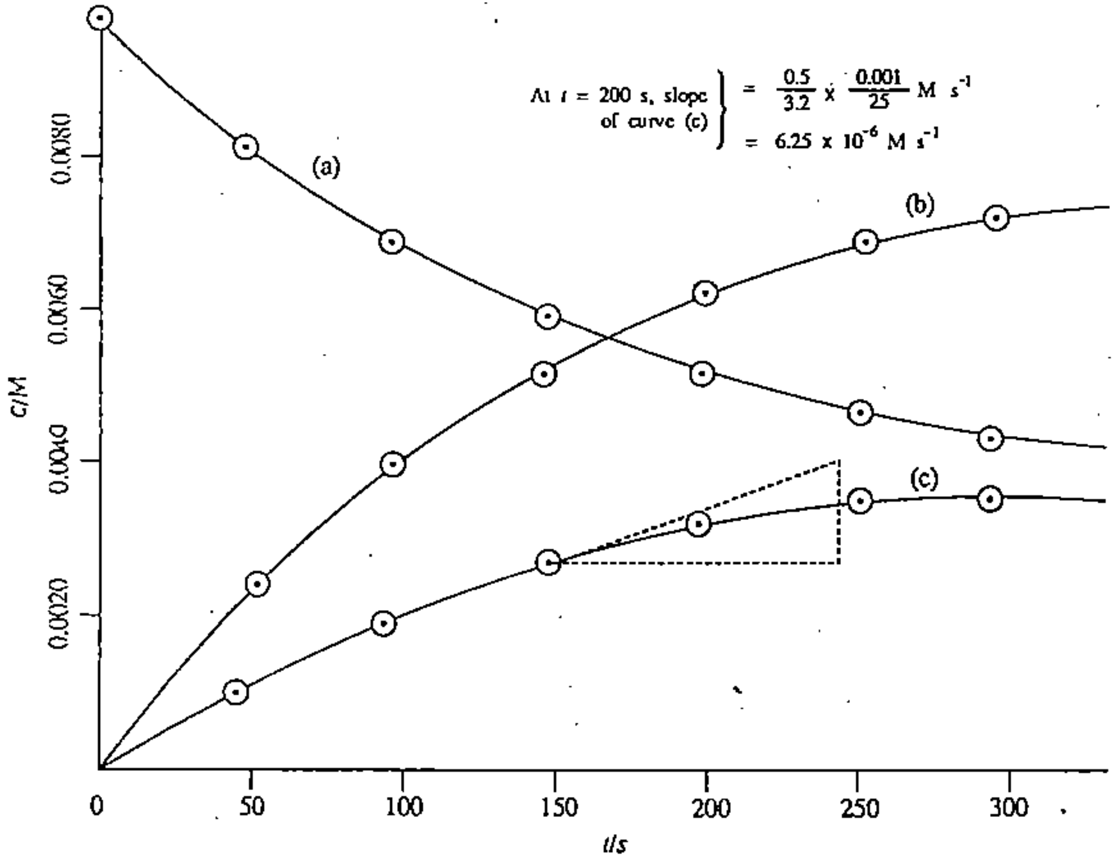


Fig. 13.1:(a)Concentration against time plot for NO_2; note the falling nature of the curve which is characteristic of concentration against time plot for a reactant.

Rate of consumption of NO_2 at $t = 200$ s $\Big\}$ **= (Slope of the tangent line at $t = 200$ s) $= -(-1.31 \times 10^{-5}) M\ s^{-1}$**

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

Reaction rate = (Rate of consumption of NO_2)/2

$= (1.31 \times 10^{-5}\ M\ s^{-1})/2 = 6.55 \times 10^{-6}\ M\ s^{-1}$

(b) Concentration against time plot for NO; note the rising nature of the curve which is characteristic of concentration against time plot for a product.

Rate of formation of NO at $t = 200$ s $\Big\}$ **= (Slope of the tangent line at $t = 200$ s)**

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

Reaction rate = (Rate of formation of NO)/2

$= (1.30 \times 10^{-5}\ M\ s^{-1})/2 = 6.50 \times 10^{-6}\ M\ s^{-1}$

(c) Concentration against time plot for O_2; note again the rising curve. Compared to the curve for NO, the curve for O_2 rises slowly.

Rate of formation of O_2 at $t = 200$ s $\Big\}$ **= (Slope of the tangent line at $t = 200$ s)**

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

For the curves (a) and (b), the tangents are not indicated. Reaction rate = Rate of formation of $O_2 = 6.25 \times 10^{-6}\ M\ s^{-1}$. From the slope values at $t = 200$ s, you can see that the following relationship is nearly correct.

Reaction rate = (Rate of consumption of NO_2)/2 = (Rate of formation of NO)/2

= 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 upto a point where the product amounts are not high.

We have so far learnt about two kinds of rates, the average rate and instantaneous rate defined by Eqs. 13.6 and 13.7 respectively. There is another term called **initial rate**. It is the rate in the initial stages of the reaction i.e. at time 't' close to zero. We would elaborate this at a later stage.

Before going ahead why don't you try the following SAQ?

SAQ 1

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

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

in terms of concentration of N_2 and NH_3.

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

13.2.2 Measurement of Rate

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

i) **Measurement of pressure or volume of a gas:** In some reactions, one of the reactants or products is a gaseous species. In such cases, the measurement of pressure or the volume of the gas produced or consumed provides an elegant method of assessing its concentration. This can be used in obtaining the rate of reaction.

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

For example, the decomposition of H_2O_2

$$H_2O_2(aq) \longrightarrow H_2O(l) + O_2\,(g) \qquad ...(13.9)$$

can be conveniently followed by measuring the volume of $O_2(g)$ evolved as a function of time.

ii) **Titrimetry** : It is one of the most commonly used methods to follow the progress of the reaction. If any of the reactants or products can be suitably titrated without any interference from other species, then this method is useful. For example, the progress of the reaction given above (Eq. 13.9) can equally well be followed by titrating equal volumes of the reaction mixture at different time intervals against $KMnO_4$ solution.

$$5H_2O_2(aq) + 2MnO_4^-\,(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g) \quad ...(13.10)$$

Some of the experiments explained in Units 14 and 15 would be followed by titrimetry.

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

iii) **Conductometry and potentiometry** : In some cases, the progress of the reaction is characterised by a continuous change in the conductance, emf or pH of the reaction mixture. In such cases, a suitable instrumental method can be devised to follow the reaction. For example, the saponification of ethyl ethanoate (ethyl acetate) can be followed conductometrically (details given in Unit 15).

iv) **Spectrophotometry or colorimetry** : In some reactions, one of the components has a distinct absorption band in the visible or ultra-violet region of the spectrum. The progress of such a reaction can be followed in terms of absorbance at a characteristic wave length. For example, iodination of 2- propanone (acetone) can be followed colorimetrically as I_2 has a characteristic absorption band around 565 nm (details given in Unit 15).

v) **Polarimetry** : If in a reaction, an optically active substance is either consumed or produced, then the progress can be followed with the help of a polarimeter. Inversion of sucrose is one of the experiments based on polarimetry.

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

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

NMR : Nuclear magnetic resonance
ESR : Electron spin resonance

SAQ 3

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

i) $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$

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

ii) $CH_3COOC_2H_5\,(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + C_2H_5OH\,(aq)$

iii) $CH_3CHO(g) \longrightarrow CH_4\,(g) + CO(g)$ (at constant volume conditions)

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

13.2.3 Factors Affecting the Rate of a Reaction

There are a number of factors that affect the rate of a chemical reaction. Let us briefly take up the effect of these one by one.

Concentration of reactants : An increase in the concentration of a reactant generally increases the rate of a reaction. Rates of certain reactions increase much more than the others on increasing the concentration. Some reactions even become slow on increasing the concentration of certain species. The dependence of rate on concentration shall be taken up in detail in the next section.

To study the effect of temperature on the rate of a reaction, you may see Unit 18 of CHE-04 course.

Temperature : An increase in temperature normally causes an increase in the rate of reaction. As a thumb rule, the rate becomes double with an increase of about 10°C in the temperature. This kind of study can provide useful information regarding the thermodynamic parametres of a reaction. Since we are not going to perform experiments based on temperature effect on reaction rate, we are not going to discuss it in detail.

Catalysts : Certain substances take part in a chemical reaction but are regenerated unchanged. These are called catalysts. The presence of a catalyst generally increases the rate of a reaction. In one of the experiments (given in the next unit), we would study the effect of metal ions acting as catalyst. In the next unit, we shall discuss the role of a catalyst in a reaction.

Surface area : Certain reactions take place on a surface. It is observed that for such reactions, the rate increases with an increase in surface area. We are not going to do any experiment based on this effect.

Of the four factors listed above, we are going to discuss in detail the effect of concentration of reactants on the reaction rate. Before doing that, we shall define certain important terms.

13.3 RATE LAWS

As pointed out earlier, kinetics experiments are primarily concerned with the determination of concentration of one or more species as a function of time. This leads to the evaluation of rate. There are two types of relationships – one between rate and concentration and the other, between rate and time. These are termed rate laws. The relationship between the former two is called differential rate law, and that between the latter two is referred to as integrated rate law. Let us see these in detail.

13.3.1 Differential Rate Laws : Concentration Dependence of Rate

The rate of reaction may depend on the concentration of one or more reacting species. The proportionality between rate and concentration may be direct or inverse. The actual dependence of rate on the concentration of various species measured by any of the methods described above is put together into an equation called differential rate law or rate equation. For example, for the reaction,

$$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2 \qquad ...(13.11)$$

the experimentally determined rate law has the form

$$\text{rate} = k\,[S_2O_8^{2-}]\,[I^-] \qquad ...(13.12)$$

where k is the proportionality constant, and $[S_2O_8^{2-}]$ and $[I^-]$ indicate the molar concentration (i.e., molarities) of $S_2O_8^{2-}$ and I^-, respectively. Note that the powers of $[S_2O_8^{2-}]$ and $[I^-]$ in Eq. 13.12 are each equal to one, whereas the stoichiometric coefficients of $S_2O_8^{2-}$ and I^- in Eq. 13.11 are 1 and 2, respectively. The rate law such as Eq. 13.12 is to be arrived at from the experimental measurement of dependence of concentration of reactants on the rate of a reaction and **not from the stoichiometric equation.**

Stoichiometric equation: It is a balanced chemical equation such as Eq. 13.1 or 13.13. It shows the relationship between the relative amounts (number of moles) of the reactants and products.

Rate equation or rate law: A rate equation shows the dependence of reaction rate on the concentration of reactants. A rate equation is to be written from experimental studies and not from stoichiometric equation.

For a general reaction,

$$aA + bB + \cdots\cdots \longrightarrow \text{products} \qquad ...(13.13)$$

where a,b, ... etc are the stoichiometric coefficients in the balanced equation, we can write the rate law as

$$\text{rate} = k\,[A]^m\,[B]^n\,... \qquad ...(13.14)$$

Eq. 13.14 is applicable only if the reaction in Eq. 13.13 goes to almost completion. If the reaction is reversible, the equation has a rather complex form.

In this expression, [A], [B]... etc represent the molarities of the concerned species. The exponents m,n, .., are generally small positive integers. However, in certain cases, these may be fractional or even negative also. The exponent of a reactant in the rate law represents the **order of the reaction** with respect to that reactant. The sum of the exponents of the concentration terms in the rate law is called the **overall order.** For the rate law given in Eq. 13.14, we say that the reaction is of mth order with respect to A and of nth order with respect to B and so on. The overall order of the reaction is $m + n + ...$ reaction. In the example given in Eq. 13.11, the reaction is first order each in $S_2O_8^{2-}$ and in I^-. The overall order is 1 + 1 = 2.

There is no relationship between the exponents m,n,... in the experimentally determined rate equation and the corresponding stoichiometric coefficients (a,b,...); but if it happens to be so, it is just a matter of chance.

The proportionality constant 'k' in the rate equation is called the rate constant. It is characteristic of a given reaction and its value depends on temperature and the presence of catalyst etc. The rate constant can be visualised as the rate of reaction when all the species in rate equation are at unit concentration. For this reason, the rate constant is also known as the specific rate. The units of rate constant depend on the overall order of the reaction. It has the units of concentration$^{(1-\text{order})}$. time^{-1}. For a first order reaction, k has the unit, s^{-1} while a second order k has units of dm^3 mol^{-1} s^{-1}.

To obtain the units of rate constant, consider the following generalised rate equation for which the overall order is $m + n$.

$$\text{Rate} = k\,[X]^m\,[Y]^n$$

$$\text{or } k = \frac{\text{Rate}}{[X]^m\,[Y]^n}$$

$$\text{Units of } k = \frac{\text{Units of rate}}{\text{units of }([X]^m - [Y]^n)}$$

$$= \frac{\text{mol dm}^{-3}\,\text{s}^{-1}}{(\text{mol dm}^{-3})^m\,(\text{mol dm}^{-3})^n}$$

$$= (\text{mol dm}^{-3})^{\{1-(m+n)\}}\,\text{s}^{-1}$$

since $m+n$ is the overall order of the reaction.

$$\text{unit of } k = (\text{mol dm}^{-3})^{(1-\text{overall order})}\,\text{s}^{-1}$$

For a reaction which follows first order kinetics.

$$\text{unit } k = (\text{mol dm}^{-3})^{1-1}\,\text{s}^{-1} = \text{s}^{-1}$$

For a reaction which follows second order kinetics.

$$\text{units of } k = (\text{mol dm}^{-3})^{1-2}\,\text{s}^{-1} = \text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1} \text{ or } = M^{-1}\,\text{s}^{-1}$$

(since 1 M = 1 mol dm^{-3})

In a kinetic experiment, we normally measure concentration as a function of time; so we would like to have a relationship between concentration and time. Such a relationship is provided by the integrated rate laws. Let us see how we obtain these rate laws. Before you go ahead, try the following SAQ.

SAQ 3

The experimentally determined rate law for the reaction,

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

is, $\quad \text{rate} = k[NO]^2\,[Cl_2]$

what is the i) order of reaction with respect to $[Cl_2]$
ii) overall order and iii) units for k?

The equations listed in Table 13.1 hold for reactions with only one reactant or for the ones which have more than one reactant but all of them have same concentration. However, if different reactants have different concentrations, then the expressions are slightly complicated. You may refer to the bibliography to find ways of deducing integrated rate equation for such a case.

13.3.2 Integrated Rate Laws : Time Dependence of Concentration

Expressions relating time and concentration can be obtained by integrating the differential rate laws. For first order, second order reaction etc., the integrated rate equation have been derived in Unit 18 of CHE-04 course. You go through that material for understanding the derivations. The differential and integrated rate laws are summarised in Table 13.2. $[A]_0$ and $[A]_t$ represent the concentration of the reactant A at the start and, after the time, t. We shall next explain the term, half life period ($t_{1/2}$).

Table 13.2 : Rate laws and other important data for differential order reaction of the type A ⟶ products.

Order of reaction	Differential rate law	Integrated rate equation	Expression for $t_{1/2}$	Type of plot	Unit for k
Zeroth order	rate = k	$[A]_t = -kt + [A]_0$	$[A]_0/2k$	$[A]_t$ against t	$M\,s^{-1}$
First order	rate = $k[A]$	$\log [A]_t = \frac{-kt}{2.303} + \log [A]_0$	0.693/k	$\log [A]_t$ against t	s^{-1}
Second order	rate = $k[A]^2$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$1/k[A]_0$	$1/[A]_t$ against t	$M^{-1}\,s^{-1}$
Third order	rate = $k[A]^3$	$\frac{1}{2[A]_t^2} = kt + \frac{1}{2[A]_0^2}$	$3/2k[A]_0^2$	$1/[A]_t^2$ against t	$M^{-2}\,s^{-1}$

Half-life Period

The time taken for the concentration of a reactant to decrease to half its initial value is known as half-life period. It is represented by the symbol, $t_{1/2}$. Let us derive an expression for the half-life period of a first order reaction. From Table 13.1, we can write the integrated rate equation for a first order reaction as follows:

$$\log [A]_t = -\frac{kt}{2.303} + \log [A]_0 \qquad \text{... (13.15)}$$

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

or $$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t} \qquad \text{... (13.16)}$$

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

Hence, Eq. 13.16 becomes,

$$k = \frac{2 \cdot 303}{t_{1/2}} \log 2$$

$$= \frac{2.303 \times 0.3010}{t_{1/2}}$$

$$\text{or} \quad t_{1/2} = \frac{0.693}{k} \qquad \text{...(13.17)}$$

We see that for first order reaction, $t_{1/2}$ is independent of initial concentration. Let us see how the rate constant for a 1 order reaction can be obtained through a graphical method.

Graphical Representation of a First Order Reaction

Let us go back to Eq. 13.15. In this equation, only t and log $[A]_t$ are the variables.

$$\log[A]_t = \frac{-kt}{2.303} + \log[A]_0 \qquad \text{...(13.15)}$$

This equation is of the form, "$y = mx + c$" which is an equation for a straight line. This means that a plot between log $[A]_t$ and t would be a straight line (Fig. 13.2).

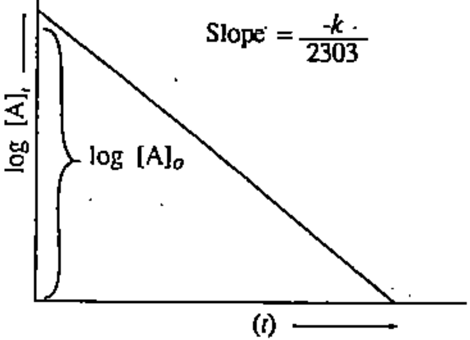


Fig. 13.2 : Linear plot for a first order reaction

From Eq. 13.15, we can see that slope ("m" in straight line equation) is equal to $-k/2.303$. In other words,

$$k = -2.303 \times \text{slope} \qquad \text{... (13.18)}$$

Hence log $[A]_t$ against t plot can help us in determining the rate constant of a first order reaction.

Similarly, for a zeroth order reaction and a second order reaction also, we can get the rate constant from the linear plots as shown in Fig. 13.3 and 13.4. These plots are drawn as per the integrated rate equations given in Table 13.2

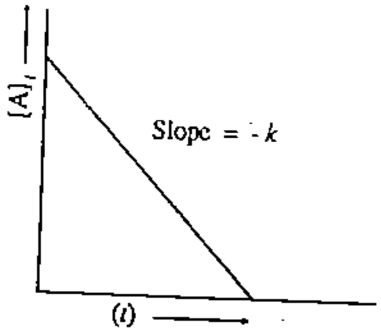


Fig. 13.3 : Linear plot for a zeroth order reaction

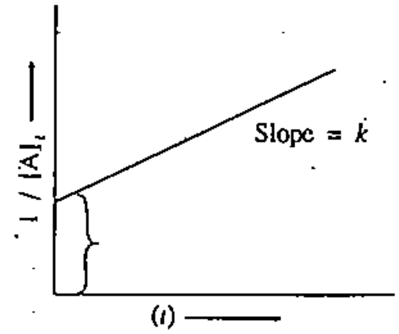


Fig. 13.4 : Linear plot for a second order reaction

SAQ 4

The reaction, A + B $\longrightarrow$ products has the following differential rate equation,

$$\text{rate} = k\,[A]^1\,[B]^1$$

$[A]_0$ and $[B]_0$ are the initial concentrations of A and B, respectively; $[A]_t$ and $[B]_t$ are the concentrations of A and B at a time t. Also $[A]_0$ is not equal to $[B]_0$. The integrated rate law is

$$\log \frac{[B]_0\,[A]_t}{[A]_0\,[B]_t} = \frac{([A]_0 - [B]_0)}{2.303}\,kt$$

Suggest a suitable linear plot which will be useful in calculating the rate constant. Also state the relationship between the rate constant and the slope.

....

....

....

....

....

13.4 DETERMINATION OF ORDER OF A REACTION

To set up the appropriate rate equation for a given reaction, one needs to know the order of reaction with respect to all the species affecting the rate. A number of methods are available for the purpose. The choice of a method depends on its suitability under given reaction conditions. Let us take up some of these methods.

Initial rate method: As defined earlier the initial rate is the rate of reaction as soon as the reactants are mixed. It is the instantaneous rate at a time very close to zero. One way to obtain the initial rate is to plot concentration versus time graph and draw a tangent at $t = 0$. The slope of this tangent gives the initial rate. But usually it is obtained by dividing the change in reactant concentration (Δ [reactant]) by a brief time interval (Δ t) immediately after the mixing of reactants. That is, we measure an average rate over a short time. This method takes advantage of the fact that for a very short time interval in the beginning of the reaction, the concentration versus time curve and the tangent at $t = 0$, almost coincide with each other (Fig. 13.5).

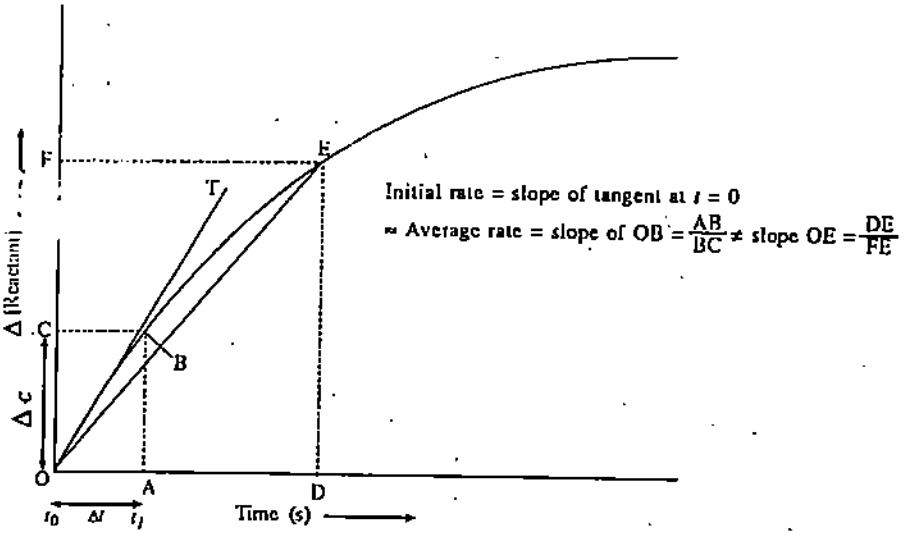


Fig 13.5: Initial rate : In the time Δ t, the average rate (slope of chord OB) is almost equal to the instantaneous rate at t = 0 (slope of tangent OT).

The figure shows that the average rate between time, t_0 and t_1, represents the initial rate to a reasonable degree of accuracy.

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

$$A + B \longrightarrow \text{products} \qquad ...(13.19)$$

for which the rate law is,

$$\text{rate} = k\,[A]^m\,[B]^n \qquad ...(13.20)$$

For a given set of concentrations of A and B, the initial rate is determined. The experiment is repeated with a different concentration of one of the components, while that of the other remains the same. Comparison of these two rates gives the order of the reaction with respect to the species for which the concentration has been changed. It can be shown as follows. Let us assume that the R_1 is the rate when the initial concentrations of A and B are a_1 and a_2, respectively. Also let us assume that R_2 is the rate when we vary the initial concentration of A, from a_1 to a_2, while the concentration of B remains as b_1.

$$(\text{Rate})_1 = R_1 = k\,(a_1)^m\,(b_1)^n \qquad ...(13.21)$$

$$(\text{Rate})_2 = R_2 = k\,(a_2)^m\,(b_1)^n \qquad ...(13.22)$$

Dividing R_2 by R_1 we get,

$$R_2/R_1 = (a_2/a_1)^m \qquad ...(13.23)$$

Taking logarithms, we get,

$$\log R_2/R_1 = \log\,(a_2/a_1)^m = m\,\log\,(a_2/a_1) \qquad ...(13.24)$$

Rearranging we get,

$$n = \frac{\log\,(R_2/R_1)}{\log\,(a_2/a_1)} \qquad ...(13.25)$$

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

$$(\text{Rate})_3 = R_3 = k\,(a_1)^m\,(b_3)^n \qquad ...(13.26)$$

Dividing R_3 by R_1, we get, $R_3/R_1 = (b_3/b_1)^n$

Taking logarithms, we get,

$$\log (R_3/R_1) = n \log (b_3/b_1)$$

Rearranging, we get,

$$n = \frac{\log (R_3/R_1)}{\log (b_3/b_1)} \qquad ...(13.27)$$

Once the values of m and n are known, the overall order can be worked out. We shall next discuss clock reactions which are quite elegant for monitoring initial rates.

Clock Reaction:

Clock reactions are designed in such a way that the appearance of one of the products (in terms of which the reaction is being monitored) is slightly delayed. For this purpose, a small amount of a substance called a monitor-substance (z) is added. This by itself does not take part in the reaction but quickly consumes one of the products (in question) formed. Once whole of this monitor-substance has reacted, the product shows up. Normally, this product is coloured or gives a distinct colour with an 'indicator' added in the reaction mixture.

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

You would recall that we defined initial rate as $\Delta c/\Delta t$ for small values of Δt from $t = 0$. The amount of added monitor substance fixes the value of Δc, and the rate of the reaction is manifested in terms of Δt only. That is why such reactions are called clock reactions. If the rate is fast and the product shows up soon, then Δt is small (i.e., rate $\propto \frac{1}{\Delta t}$)

The reaction between peroxydisulphate and iodide ions is a common example of clock reactions. In this reaction, the product monitored is free iodine (in fact I_3^-), the monitor substance is $S_2O_3^{2-}$ (thiosulphate) and the indicator is starch. The details of the experiment are given in next unit.

Addition of monitor substance is like winding a clock. The more you wind (i.e. add more of 'z'), longer it would take for the product to show up. In certain reactions, once the product has shown up, another lot of substance 'z' is added (the clock is rewound) and once again the time for the appearance of the product is noted. This helps in finding rate of reaction at various stages of reaction. The Harcourt-Esson reaction (Eq.13.28) can be monitored in this way:

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \longrightarrow I_2(aq) + 2H_2O(l) \qquad ...(13.28)$$

Graphical Method: This method of determination of order is based on integrated rate equation developed in the previous section. In this method, different graphs (such as [A] Vs t or ln [A] Vs t or $\frac{1}{[A]}$ Vs t, etc.) are plotted from the concentration-time data obtained in the experiment. The order is ascertained from the plot that gives a straight line. There are also other methods such as.

- half-life method
- vant Hoff isolation method

We shall not discuss them in detail. You are advised to go through Unit 18 of Physical Chemistry (CHE-04) course for further details on these methods.

13.5 SUMMARY

In this unit, we defined the terms such as rate law, instantaneous rate, initial rate, order of the reaction etc. We explained the factors affecting the rate of a reaction. The differential and integrated rate laws were defined and illustrated. The principle of clock reaction was discussed.

13.6 TERMINAL QUESTIONS

1. What do you understand by

   i) average rate

   ii) instantaneous rate and

   iii) initial rate of reaction?

2. The hydrolysis of benzene diazonium chloride can be represented by the following equation

   $$C_6H_5N_2Cl(aq) + H_2O \longrightarrow C_6H_5OH(aq) + N_2(g)\uparrow$$

   Suggest a suitable method to follow the progress of the reaction.

3. For the following reaction, write various equivalent ways of expressing rate:

   $$2CHCl_3(l) + 7OH^-(aq) \longrightarrow CO(aq) + HCOO^-(aq) + 6Cl^-(aq) + 4H_2O(l)$$

4. What is half-life period of a reaction ?

5. What are clock reactions? Give an example.

6. State true (T) or false (F):

   i) order of a reaction can be ascertained from its stoichiometry.

   ii) differential rate law relates concentration to time.

   iii) order is an experimental property.

   iv) graphical method for determination of order is a hit and trial method.

13.7 ANSWERS

Self Assessment Questions

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

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

2. i) spectrophotometry

   ii) pH measurement, conductometry or titration

   iii) pressure measurement.

3. Order with respect to Cl_2 is $= 1$

   Overall order of the reaction $= 2 + 1 = 3$

   Units for $k = M^{-2}s^{-1}$

4. Splitting the log. terms we get,

   $$\log\frac{[A]_t}{[B]_t} - \log\frac{[A]_0}{[B]_0} = \frac{[A_0] - [B_0]}{2.303}kt$$

   which can be rearranged as

   $$\log\frac{[A]_t}{[B]_t} = \frac{[A_0] - [B_0]}{2.303}kt + \log\frac{[A]_0}{[B]_0}$$

A plot of $\log([A]_t/[B]_t)$ versus t would be a straight line with slope equal to

$$\frac{([A]_0 - [B_0])_k}{2.303}$$

Hence, $k = \frac{2.303 \times \text{slope}}{([A]_0 - [B]_0)}$

Terminal Questions

1. i) Average rate is the change in the concentration of a given species divided by the time in which it takes place.

   ii) Instantaneous rate is the rate of change of concentration of a given species with time at a given time. It equals the slope of tangent to the concentration versus time plot at the given time.

   iii) The rate of reaction immediately after the reactants are mixed is called initial rate. It is the average rate at time close to zero.

2. The reaction can suitably be followed by measuring the volume of N_2 produced.

3. $$-\frac{1}{2}\frac{d[CHCl_3]}{dt} = -\frac{1}{7}\frac{d[OH^-]}{dt} = \frac{d[CO]}{dt} = \frac{d[HCOO^-]}{dt} = \frac{1}{6}\frac{d[Cl^-]}{dt} = \frac{1}{4}\frac{d[H_2O]}{dt}$$

4. Half-life period of a reaction is the time taken by the reactants to get the concentration reduced to half the initial value.

5. Clock reactions are the ones in which the appearence of one of the products is delayed by adding a small amount of a substance which consumes it. Such experiments are designed to study the rate of a reaction. The time taken for the product to show up is a measure of rate. An example is the reaction between $S_2O_8^{2-}$ and I^-; the appearence of free I_2 is delayed by adding sodium thiosulphate.

6. i) F ii) F iii) T iv) T.

UNIT 14 INITIAL RATE METHOD

Structure

14.1 Introduction
Objectives
14.2 Experiment No.15 : Kinetics of Reaction Between Sodium Thiosulphate and Hydrochloric Acid by Initial Rate Method
Principle
Requirements
Procedure for Experiment 15 (a) : The Order of Reaction in $S_2O_3^{2-}$ Ions
Observation for Experiment 15 (a)
Calculation for Experiment 15 (a)
Procedure for Experiment 15 (b) : The Order of Reaction in H^+ Ions at Low Concentration Range
Observation for Experiment 15(b)
calculation for Experiment 15(b)
Experiment 15(c) : The Order of Reaction in H^+ Ions at Moderate Concentration Range
Observation for Experiment 15 (c)
Calculation for Experiment 15 (c)
Rate Equations
Result
14.3 Experiment No.16 : Kinetics of Reaction Between Peroxydisulphate and Iodide Ions by Iodine Clock Method
Principle
Requirements
Procedure for Experiment 16 (a) : The Order of Reaction in $S_2O_8^{2-}$ Ions
Observation for Experiment 16 (a)
calculation for Experiment 16(a)
Procedure for Experiment 16 (b) : The Order of Reaction in I^- Ions
Observation for Experiment 16(b)
Calculation for Experiment 16(b)
Rate Constant for the Reaction Between $S_2O_8^{2-}$ and I^-
Procedure for Experiment 16(c): The Effect of Catalyst on the Reaction Between $S_2O_8^{2-}$ and I^-
Observation for Experiment 16(c)
Calculation for Experiment 16(c)
Results
14.4 Summary
14.5 Answers

14.1 INTRODUCTION

In the previous unit, you have learnt about the basic concepts of rate, rate laws, order of a reaction etc. You have also learnt about various methods of determination of order of a reaction. In this unit, we shall discuss in detail two experiments based on initial rate method. In these experiments, you will monitor the time taken for a certain part of reaction to occur. In first experiment, we shall determine the order of reaction with respect to the reactants, and set up the rate equation. In second experiment you will also determine the rate constant and study the effect of catalyst on the rate of the reaction. In the next unit, we shall talk about experiments based on integrated rate equation method.

Objectives

After studying this unit and performing the experiments, you should be able to

- compute the order of a simple reaction with respect to reactants,
- set up the rate equation for the reaction,
- calculate rate constant of a reaction, and
- describe the effect of catalyst on the rate of the reaction.

14.2 EXPERIMENT NO.15: KINETICS OF REACTION BETWEEN SODIUM THIOSULPHATE AND HYDROCHLORIC ACID BY INITIAL RATE METHOD

14.2.1 Principle

Sodium thiosulphate reacts with hydrochloric acid as per the following equation,

$$Na_2S_2O_3(aq) + 2HCl(aq) \longrightarrow H_2O(1) + SO_2(aq) + S(C) + 2NaCl(aq) \quad \ldots (14.1)$$

S(C): Sulphur in colloidal form.

In this reaction, colloidal sulphur precipitates out. Let us see how we can follow the progress of the reaction. In this reaction, there are two reactants and four products, i.e., a total of six species. In principle, the reaction can be followed in terms of any of these six species. However trom practical point of view, we can use the formation of colloidal sulphur to follow the reaction. Sulphur precipitated in colloidal form imparts turbidity to the reaction mixture. It is this property which is exploited to follow the progress of reaction in this experiment. What is done is that a known (fixed) volume of the reactants is taken in a beaker placed on a glazed tile marked with a cross, 'X'. The reaction mixture is clear to begin with and, we can see the cross mark through it.

With the progress of reaction, there is an increase in turbidity and the mark becomes obscure. This would happen only after a certain amount of sulphur has got precipitated. As very small amount of sulphur (corresponding to very little progress of the reaction) is sufficient to obscure the cross mark, the time taken for the mark to disappear (Δt) is a measure of the initial rate and, it is inversely proportional to the initial rate.

i.e., $$\text{initial rate} \propto \frac{1}{\Delta t} \quad \ldots (14.2)$$

or $$\text{initial rate} = \frac{\text{constant}}{\Delta t} \quad \ldots (14.3)$$

Eq. 14.3 can be further explained by considering Fig.15.1. In this figure, it can be seen that the initial rate is expressed to reasonable degree of accuracy by the average rate between time 0 and time t_1.

Average rate between time 0 and time $t_1 = \frac{dc}{dt} =$ slope of chord OP.

where dc is the change in concentration of sulphur and dt is the time needed to obscure the cross.

Therefore,

Slope of tangent, OT, at time zero = slope of chord

$$OP = \frac{c_1}{t_1}$$

Since the slopes of OP and OT are quite close,

initial rate (slope of tangent OT) $\approx \frac{c_1}{t_1}$.

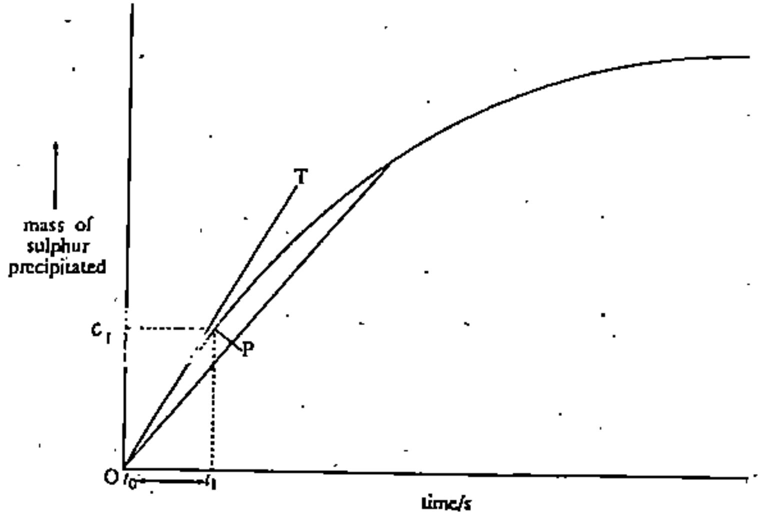


Fig. 14.1 : Variation of amount of sulphur precipitated with time

Although we will be doing this experiment through many parts, we are going to keep volume of the solution same throughout. Therefore, the depth of solution in the beaker is constant each time. Thus, the amount of sulphur needed to obscure the cross is the same in each part of the experiment.

As there are two reactants in the reaction, it is necessary to find how the initial rate for the precipitation of sulphur depends on concentration of each of these. For this, we keep the concentration of one of the reactants constant, while varying that of the other and measure the initial rate. By using the data so obtained, we can find order of reaction with respect to each reactant.

The general form of rate law for this reaction is given below:

$$\text{Rate} = k\,[S_2O_3^{2-}]^m\,[H^+]^n \qquad \ldots (14.4)$$

Where m and n are the orders of reaction in $S_2O_3^{2-}$ and H^+, respectively. Combining Eqs.14.3 and 14.4 for **initial conditions,**

$$\text{Initial rate} \;= \frac{\text{Constant}}{\Delta t} = k[S_2O_3^{2-}]^m\,[H^+]^n$$

$$\text{or} \qquad \frac{1}{\Delta t} = k_1[S_2O_3]^m\,[H^+]^n \qquad \ldots (14.5)$$

$$\text{where} \qquad k_1 = \frac{k}{\text{constant}}$$

Taking logarithms,

$$\log (1/\Delta t) = \log k_1 + m\log [S_2O_3^{2-}] + n\log [H^+] \qquad \ldots (146)$$

Order of Reaction in $S_2O_3^{2-}$

To determine the order of reaction in $S_2O_3^{2-}$, we shall keep the concentration of H^+ ions constant. Since the sum of two constant terms (viz., $\log k_1 + n \log [H^+]$ in Eq. 14.6) is also a constant, we can simplify the equation by writing,

$$\log(1/\Delta t) = m \log [S_2O_3^{2-}] + \text{constant}$$

$$\text{or} \quad -\log(1/\Delta t) = -m \log [S_2O_3^{2-}] - \text{constant} \qquad \ldots (14.7)$$

This resembles an equation for a straight line, $y = mx + c$ (where m is the slope of the line and c is the intercept as discussed in Sec. 2.6 of Unit 2 of this course). When $-\log (1/\Delta t)$ is plotted against $-\log [S_2O_3^{2-}]$, a straight line curve (Graph I) is to be obtained. The slope of this straight line gives the order of reaction with respect to $S_2O_3^{2-}$.

Since $[H^+]$, $[S_2O_3^{2-}]$ and $1/\Delta t$ are fractions, $\log [H^+]$, $\log [S_2O_3^{2-}]$ and $\log (1/\Delta t)$ are negative quantities. But it is convenient to make plots using positive coordinates. Hence plots of $-\log (1/\Delta t)$ against $-\log [S_2O_3^{2-}]$ and $-\log (1/\Delta t)$ against $-\log [H^+]$ are made.)

i.e., order of the reaction in $S_2O_3^{2-} = m$ = slope of graph I ... (14.8)

Order of Reaction in H^+

Similarly we can perform a few experiments, where the concentration of $S_2O_3^{2-}$ ions is kept constant and that of H^+ ions is varied. The modified form of Eq. 14.6 becomes

$$\log(1/\Delta t) = n \log [H^+] + \text{constant}$$

$$\text{or} \quad -\log(1/\Delta t) = -n \log [H^+] - \text{constant} \qquad \ldots (14.9)$$

You will draw graphs I, II and III as per data entered in Observation Tables I, II and III in Sec. 14.2.4, 14.2.7 and 14.2.11.

where constant refers to the sum of the constant terms, viz., $\log k_1 + m \log [S_2O_3^{2-}]$, in Eq. 14.6.

A plot of $-\log(1/\Delta t)$ versus $-\log [H^+]$ is expected to be a straight line (Graphs II and III) with slope equal to the order with respect to $[H^+]$.

i.e., Order of the reaction in H^+ ions = n
(at low concentration) = slope of graph II ... (14.10a)
Order of reaction with respect to H^+ ions = n'
(at moderate concentration) = slope of graph III ... (14.10b)

Rate Laws

Finally we shall write the rate laws for the reaction between $S_2O_3^{2-}$ ions and H^+ ions both at low and moderate concentration of H^+ ions. To write the rate laws under these conditions, we use Eq. 14.4 as follows:

$$\text{Rate} = k_2 [S_2O_3]^m [H^+]^n \qquad \ldots (14.11)$$

(at low H^+ ion concentration)

$$\text{Rate} = k_3 [S_2O_3]^m [H^+]^n \qquad \ldots (14.12)$$

(moderate H^+ ion concentration)

Note that k_2 and k_3 are the rate constants at low and moderate H^+ ion concentrations, respectively.

After performing Experiments 15(a) - (c), we shall calculate m, n and n'. Also we shall substitute these values in Eqs. 14.11 and 14.12 to obtain the rate laws at low and moderate H^+ ion concentration. In this experiment we are not going to calculate the value of k_2 and k_3.

14.2.2 Requirements

Apparatus		Chemicals
Burettes (50 cm^3)	4	Sodium thiosulphate
Beakers (100 cm^3)	10*	Hydrochloric and
Glazed tile	1	Distilled water
Stop watch	1	

If sufficient number of beakers is not available, the experiment can be done with just two Beakers.

Solutions Provided

Sodium thiosulphate (stock) (0.25 *M*)
HCl(I) (3 *M*)
HCl (II) (0.75 *M*)

Details for the preparation of the solutions are given in Appendix-I.

14.2.3 Procedure for Experiment 15 (a) : The order of reaction in $S_2O_3^{2-}$ ions

1. Take tour clean and dry burettes and label them as $S_2O_3^{2-}$, HCl(I), HCl (II) and water respectively. Rinse the burettes with corresponding solutions and fill with them.
2. Take ten clean 100 cm^3 beakers. Arrange these beakers in two rows with 5 in each. Label the beakers of one row as 1 to 5 and that of the other as 6 to 10. The first row is for thiosulphate solution and the second is for hydrochloric acid solution.

Use burettes for adding stock $S_2O_3^{2-}$, solution, water and HCl solutions.

3. Take the beakers corresponding to row I one by one and fill the stock thiosulphate solution into them as given under column II of Observation Table–I. To these, add water as detailed in column number III of Observation Table – I. To the beakers of row II, transfer HCl (I) as given under column IV.
4. Take clean glazed white tile and put a cross mark on it with the help of a ball point pen.
5. Take two beakers marked 1 and 6 and pour HCl from 6 into the contents of 1. Start the stop watch when half of the HCl has been transferred. Place the beaker on the tile on the cross mark and swirl it gently. Turbidity begins to appear and the cross mark starts getting dim. Put off the stop watch when the cross mark just disappears.
6. Record your observations in column VIII of Observation Table – I. Repeat the same mixing the contents of 2 and 7; 3 and 8; 4 and 9; and 5 and 10. Record your data in each case.

Alternatively you can put the cross mark on the bottom (outside) of the beaker and place it over a blank tile or a clean white paper or a filter paper.

14.2.4 Observation for Experiment 15(a)

Molarity of stock sodium thiosulphate solution =
Molarity of HCl (I) =

Observation Table – I

I Sl. No.	II (Volume of stock $S_2O_3^{2-}$ solution) cm^3	III (Volume of water) cm^3	IV (Volume of HCl(I) cm^3	V $[H^+]$ *M*	VI $[S_2O_3^{2-}]$ *M*	VII $-\log[S_2O_3^{2-}]$ *M*	VIII Δt (s)	IX $(1/\Delta t)$s	X $-\log \frac{1}{\Delta t}$ s
1	3	22	15						
2	6	19	15						
3	9	16	15						
4	12	13	15						
5	15	10	15						

NB : $[H^+]$ as per column (V) stands for the molarity of HCl (I) in the reaction mixture and in each case, it is equal to $\frac{15 \times \text{Molarity of HCl (I)}}{40} M$

since HCl(I) is diluted to 40 cm^3 in each case.

$[S_2O_3^{2-}]$ as per column (VI) stands for the molarity of thiosulphate solution in the reaction mixture and it is equal to

$$\frac{(\text{Volume of stock } S_2O_3^{2-}) \times (\text{Molarity of stock } S_2O_3^{2-})}{40} M$$

since stock $S_2O_3^{2-}$ solution is diluted to 40 cm^3 in each case.

15.2.5 Calculation for Experiment 15(a)

Use data from columns X and VII of observation table I and plot graph I with $-\log(1/\Delta t)$ against $-\log[S_2O_3^{2-}]$.

The slope of the straight line plot in graph I =

per Eq. 14.8, the order of the reaction in $S_2O_8^{2-}$ ions = m

= slope of graph I

= .... (to the nearest whole number)

14.2.6 Procedure for Experiment 15(b) : The Order of Reaction in H^+ ions at Low Concentration Range

Prepare solutions as detailed in Observation Table – II. Proceed exactly as in the above case. Note that in this case, water is to be added to HCl (II) solution and not to $S_2O_3^{2-}$. Also you may add $S_2O_3^{2-}$ solution into the beaker containing hydrochloric acid. Record the time taken for the cross mark to be observed and enter in Observation Table – II under column VIII.

14.2.7 Observation for Experiment 15(b)

Molarity of Sodium thiosulphate HCl (II) =

Molarity of HCl (II) =

Observation Table II

I Sl. No.	II (Volume of stock $S_2O_3^{2-}$ cm^3	III (Volume of water) cm^3	IV (Volume of HCl(II)) cm^3	V $[H^+]$ M	VI $[S_2O_3^{2-}]$ M	VII $-\log[H^+]$ M	VIII t (s)	IX $\frac{1}{\Delta t}$ s	X $-\log\frac{1}{t}$ s
1	15	24	1						
2	15	23	2						
3	15	22	3						
4	15	21	4						
5	15	20	5						

NB : $[H^+]$ as per column (V) $= \dfrac{(\text{Volume of HCl (II)}) \times (\text{Molarity of HCl (II)}}{40} M$

$[S_2O_3^{2-}$ as per column (VI) $= \dfrac{15 \times \text{Molarity of stock } [S_2O_3^{2-}]}{40} M$

Note that HCl(II) and stock $S_2O_3^{2-}$ are diluted to 40 cm^3 in each case.

142.8 Calculation for Experiment 15(b)

Plot graph II with $-\log(1/\Delta t)$ against $-\log[H^+]$ using columns X and VII of Observation Table II.

The slope of the straight line plot in graph II =

As per Eq. 14.10a, the order of the reaction in H^+ at low concentration range = n

= slope of graph II

=. . . (to the nearest whole number)

14.2.9 Experiment 15(c) : The Order of Reaction in H^+ Ions at Moderate Concentration Range

Prepare solutions as detailed in Observation Table – III. Proceed exactly as in case of Experiment 15(b). Record your time data in column VIII of Observation Table – III. Note that HCl(I) is used as stock solution in this case to prepare solutions of desired H^+ concentration.

14.2.10 Observation for Experiment 15(c)

Molarity of sodium thiosulphate =

Molarity of HCl (I) =

Observation Table III

I Sl. No.	II (Volume of stock $S_2O_3^{2-}$ solution) cm^3	III (Volume of water) cm^3	IV (Volume of HCl(I)) cm^3	V $[H^+]$ M	VI $[S_2O_3^{2-}]$ M	VII $-\log[H^+]$ M	VIII Δt (s)	IX $\frac{1}{\Delta t}$ s	X $-\log\frac{1}{\Delta t}$ s
1	15	13	12						
2	15	10	15						
3	15	7	18						
4	15	4	21						
5	15	1	24						

NB : $[H^+]$ as per column (V) $\dfrac{\text{Volume of HCl (I)} \times \text{Molarity of HCl (I)}}{40} M$

$[S_2O_3^{2-}]$ as per column (VI) $= \dfrac{15 \times \text{Molarity of stock } S_2O_3^{2-}}{40} M$

14.2.11 Calculation for Experiment 15(c)

Plot graph III with $-\log(1/\Delta t)$ against $-\log[H^+]$ using columns X and VII of Observation Table III.

The slope of the straight line plot in graph III =
As per Eq. 14.10b, the order of the reaction in H^+ at moderate concentration range = n'
= slope of graph III
= .... (to the nearest whole number)

15.2.12 Rate Equations

Depending on the value of n and n', the rate equations are written as follows:

(i) Rate equation in low concentration range of H^+ :
Using Eq. 14.11, rate $= k_2[S_2O_3]^m [H^+]^n$
$= k_2$ ....

(ii) Rate equation in moderate concentration range of H^+:
Using Eq. 14.12, rate $= k_3[S_2O_3]^m[H^+]^{n'}$
$= k_3$ ....

A possible explanation for the change in order with respect to hydrogen ion is that in concentated hydrochloric acid the concentration of hydrogen ion is smaller as the ions begin to associate into the ion pair, H^+Cl^-.

14.2.13 Result

Overall order of reaction at low H^+ concentration $= m + n$ (at low H^+ concentration)
Overall order of reaction at moderate H^+ concentration $= m + n'$ (at moderate H^+ concentration)
Rate equation at low H^+ ion concentration $= k_2$ ....
Rate equation at moderate H^+ ion concentration $= k_3$ ....

SAQ 1

Can we follow the progress of the reaction in terms of the concentration of H^+ ions? Give reasons.

....

....

....

....

....

EXPERIMENT NO.16 : KINETICS OF THE REACTION BETWEEN PEROXYDISULPHATE AND IODIDE IONS BY IODINE CLOCK METHOD

14.3.1 Principle

In the previous unit, you have learnt about the clock reactions. In this experiment we are going to make use of such a technique to determine the order of the reaction with respect to each of the two reactants, peroxydisulphate ions and iodide ions ($S_2O_8^{2-}$ and I^-). These two reactants react as follows:

$$S_2O_8^{2-}\,(aq) + 2I^-(aq) = 2SO_4^{2-}\,(aq) + I_2(aq) \quad \ldots (14.13)$$

In this reaction $S_2O_8^{2-}$ oxidizes iodide ion to iodine and, gets reduced to SO_4^{2-} ion. Iodine by itself is coloured, but in very dilute solutions the colour is too faint to be observed distinctly. So an indicator, starch, is added for the purpose.

In fact I_2 has very poor solubility in water. It reacts with free iodide ions and stays in solution in the form of complex ion, I_3^-. The following equilibrium exists in aqueous solutions.

$$I_2 + I^- \rightleftharpoons I_3^-$$

Iodine gets liberated as soon as the reaction begins. In order to design the clock reaction, we add sodium thiosulphate as the monitor-substance. It reacts with I_2 as per the following equation:

$$I_2\,(aq) + 2S_2O_3^{2-}(aq) = 2I^-(aq) + S_4O_6^{2-}(aq) \qquad \ldots (14.14)$$

The iodine liberated due to oxidation does not give blue color with starch in the presence of $S_2O_3^{2-}$ since $S_2O_3^{2-}$ reduces iodine back to I^-. It continues till all the added $S_2O_3^{2-}$ is exhausted. The quantity of iodine produced before the blue colour appears is controlled by the amount of thiosulphate ions present. As we are interested in initial rate of the reaction we add very small amount of $S_2O_3^{2-}$ ions. Although we are going to perform this experiment in three parts, we shall keep the concentration of thiosulphate same. As very small amount of iodine liberated after complete consumption of thiosulphate is enough to give blue colour with starch solution, the time (Δt) taken for the appearance of blue colour is a measure of the initial rate.

The rate equation for the reaction between $S_2O_8^{2-}$ and I^- can be written as follows:

$$\text{Rate} = \frac{-\Delta[S_2O_8^{2-}]}{\Delta t} = k\,[S_2O_8^{2-}]^m\,[I^-]^n \qquad \ldots (14.15)$$

Note that 'rate' here means initial rate.

where m and n are the orders of reaction in $S_2O_8^{2-}$ and I^-, respectively.

For the convenience of calculating the reaction rate, we use the following technique which is partly arithmetic and partly experimental.

We add up Eqs. 14.13 and 14.14 to get the Eq. 14.16.

$$S_2O_8^{2-}(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2SO_4^{2-}(aq) + S_4O_6^{2-}(aq) \qquad \ldots (14.16)$$

From this, you can see that the rate of consumption of $S_2O_8^{2-}$ is related to the rate of consumption of $S_2O_3^{2-}$ as per the following equation:

$$\text{Rate} = \frac{-\Delta[S_2O_8^{2-}]}{\Delta t} = \frac{1}{2}\frac{-\Delta[S_2O_3^{2-}]}{\Delta t} \qquad \ldots (15.17)$$
$$= \frac{1}{2}\frac{\Delta[S_2O_3^{2-}]\ \text{consumed}}{\Delta t}$$

Note that $\frac{1}{2}\frac{\Delta[S_2O_3^{2-}]}{\Delta t}$ is a positive quantity, since $-\Delta[S_2O_3^{2-}]$ is equal to the concentration $\Delta[S_2O_3^{2-}]$ consumed.

While doing this kinetics experiment, we take a known concentration of thiosulphate and note the time taken for its consumption (by way of appearance of blue colour due to iodine). Hence, we can easily calculate the rate of reaction in terms of thiosulphate consumed.

You have to note carefully that the rate for the reaction between $S_2O_3^{2-}$ and I^- ions is measured in terms of consumption of $S_2O_3^{2-}$ ions. This is made possible through Eqs. 14.16 and 14.17.

Now we shall see under two different headings as to how to calculate the rates of reaction in $S_2O_8^{2-}$ and I^- ions.

From Eqs. 14.15 and 14.17, we can write,

$$\text{rate} = \frac{1}{2}\frac{\Delta[S_2O_3^{2-}]\ \text{consumed}}{\Delta t} = k\,[S_2O_8^{2-}]^m\,[I^-]^n \qquad \ldots (14.18)$$

Taking logarithms,

$$\log(\text{rate}) = \log\frac{\Delta[S_2O_3^{2-}]\ \text{consumed}}{2\,\Delta t}$$
$$= \log k + m\log[S_2O_8^{2-}] + n\log[I^-] \qquad \ldots (14.19)$$

Using Eqs. 14.18 and 14.19, we intend calculating

- the order of reaction in $S_2O_8^{2-}$ ions *(m)*
- the order of reaction in I^- ions *(n)*,
- the rate constant *(k)*, and
- the effect of catalyst on the reaction rate.

The Order of Reaction in $S_2O_8^{2-}$ Ions

In a series of experiments under Experiment 16(a), we shall keep $[I^-]$ as constant while varying $[S_2O_8^{2-}]$. Then, among these experiments, $\log k + n \log [I^-]$ is a constant.

Thus Eq. 14.19 becomes,

Note that in all the parts of experiment 16, the concentration of $S_2O_8^{2-}$ is kept constant.

$$\log (\text{rate}) = \log \frac{\Delta[S_2O_3^{2-}] \text{ consumed}}{2\,\Delta t}$$
$$= m \log [S_2O_8^{2-}] + \text{ constant} \qquad \ldots (14.20)$$

Since rate is known from $\Delta[S_2O_3^{2-}]$ consumed and Δt values, it is possible to calculate log (rate).

The data are entered in Observation Table-IV. By plotting log (rate) against $\log [S_2O_8^{2-}]$, a straight curve (Graph IV) is expected. The slope of Graph IV gives the order of reaction in $[S_2O_8^{2-}]$ ions *(m)*.

The Order of Reaction in I^- Ions

In a series of experiments under Experiment 16(b), we shall keep $[S_2O_8^{2-}]$ as constant which varying $[I^-]$. Then, among these experiments $\log k + m \log [S_2O_8^{2-}]$, is a constant. Thus Eq. 14.19 becomes,

$$\log (\text{rate}) = \log \frac{\Delta\,[S_2O_3^{2-}] \text{ consumed}}{2\,\Delta t}$$
$$= m \log [I^-] + \text{constant} \qquad \ldots (14.21)$$

Since rate is known from $\Delta[S_2O_8^{2-}]$ consumed and Δt values, it is possible to calculate log (rate). The data are entered in Observation Table – V. By plotting log (rate) against $\log [I^-]$, a straight curve (Graph V) is expected. The slope of Graph V gives the order of reaction in I^- ions *(n)*.

Rate Constant for the Reaction Between $S_2O_8^{2-}$ and I^-

Using $[S_2O_8^{2-}]$, $[I^-]$, *m* and *n*, we shall calculate the rate constant of the reaction using Eq. 14.22.

$$k = \frac{\text{Rate}}{[S_2O_8^{2-}]^m\,[I^-]^n} \qquad \ldots (14.22)$$

The Effect of Catalyst on the Reaction between $S_2O_8^{2-}$ and I^-

All the catalysts do not increase the rate; some even make the reaction slower. For details on catalysts and their mode of action, refer to Unit 21 of Physical Chemistry (CHE-04) course.

In experiment 16(c), we are going to study the effect of a catalyst on the rate of reaction. You would recall that catalysts are substances which alter the rate of chemical reaction without actually being consumed. A catalyst provides an alternate route for a reaction. This route generally has a much lower activation energy, as compared to the reaction without a catalyst. The rate constant generally increases linearly with the concentration of catalyst added. In this regard, we can write a generalised equation as follows:

$$k = k_0 + k_c\,[\text{catalyst}] \qquad \ldots (14.23)$$

where k_0 is the rate constant in the absence of a catalyst and k_c is the rate constant in the presence of a catalyst.

In Experiment 15(c), we shall measure the rate of reaction between $S_2O_8^{2-}$ and I^- in the absence and presence of Cu^{2+} ions (catalyst) and enter the data in Observation Table VI. We shall then calculate k for each case. A plot is made with k against $[Cu^{2+}]$ (Graph VI). The slope of Graph VI gives the value of k_c.

$$k_c = \text{slope of Graph VI} \qquad \ldots . (14.24)$$

The y –intercept of this plot gives k_0 value which should be close to the k value obtained in Subsec. 14.3.9 as per Eq. 14.22.

Now we will do three sets of kinetic experiments for calculating these kinetic parameters.

14.3.2 Requirements

For all these sets of experiments we require the following apparatus, chemicals and solutions.

Apparatus

Burettes (50 cm^3) = 5
Beakers (100 cm^3) = 10
Stop Watch = 1
Graduated pipette (10 cm^3) –1

Chemicals

Potassium peroxydisulphate
Potassium iodide
Sodium thiosulphate
Copper sulphate (0.0025 *M*)
Starch
Distilled water

Stock Solutions Provided w

Potassium iodide (0.2 *M*)
Potassium peroxydisulphate (0.01 *M*)
Sodium thiosulphate (0.002 *M*)
Starch solution

Details for the preparation of the stock solutions are given in Appendix II.

14.3.3 Procedure for Experiment 16(a) : The Order of Reaction in $S_2O_8^{2-}$ ions

(1) Take four clean and dry burettes and label them as $S_2O_3^{2-}$, I^-, $S_2O_3^{2-}$ and water, respectively. Rinse the burettes with corresponding solutions and fill with them.

(2) Starch solution can be transferred using a small (10 cm^3) measuring cylinder or a graduated pipette. However if a burette can be made use of, it would be better.

(3) Similar to the previous experiment take ten 100 cm^3 beakers and distribute into two batches of five each. Label one batch as 1 to 5 and, the other as 6 to 10. One batch is for peroxydisulphate and the other is for iodide solutions.

(4) Take the beakers of first batch and transfer the solution of $S_2O_8^{2-}$ into them from the burette as per column II of Observation Table IV. To this, add water as detailed in column III of Observation Table IV.

(5) Similarly, in the second batch of beaker, transfer I^-, $S_2O_3^{2-}$ and starch solutions as detailed in column numbers IV, V & VI of Observation Table IV.

(6) Once the solutions are ready, take first pair of beakers marked 1 & 6, and pour $S_2O_8^{2-}$ solution from 1 to 6 and start the stop watch, when half of $S_2O_8^{2-}$ solution has been poured. Gently swirl the beaker, and look for the appearance of blue colour. Put off the stop watch as soon as the blue colour appears and record the time in Observation Table IV (column VII).

(8) Repeat the same with rest of the four pairs of beakers and, record your data in Observation Table IV.

14.3.4 Observation for Experiment 16(a)

Molarity of stock $S_2O_8^{2-}$ solution =

Molarity of stock I_2 solution =

Molarity of stock $S_2O_3^{2-}$ solution =

Observation Table IV

I Sl. No.	II (Volume of $S_2O_8^{2-}$ solution) cm^3	III (Volume of water) cm^3	IV (Volume of I^- solution) cm^3	V Volume of $S_2O_3^{2-}$ ion solution) cm^3	VI (Volume of starch solution) cm^3	VII Δt/s
1	10.0	10.0	20	9	1	
2	12.5	7.5	20	9	1	
3	15.0	5.0	20	9	1	
4	17.5	2.5	20	9	1	
5	20.0	0.0	20	9	1	

14.3.5 Calculation for Experiment 16(a)

Note that total volume in each case is 50 cm^3.

Since $[S_2O_3^{2-}]$ taken for each experiment is consumed completely. $[S_2O_3^{2-}]$ present initially in a reaction mixture $= [S_2O_3^{2-}]$ consumed.

$[S_2O_8^{2-}]$ in each case =

$$\frac{(\text{Volume of } S_2O_8^{2-} \text{ solution}) \times (\text{concentration of stock } S_2O_8^{2-} \text{ solution})}{50} M$$

$$[I^-] \text{ in each case} = \frac{20 \times (\text{concentration of stock } I^- \text{ solution})}{50} M$$

since 20 cm^3 of I^- solution is taken each time.

$[S_2O_3^{2-}]$-consumed in each case

$$= \frac{9 \times \text{concentration of stock } S_2O_3^{2-} \text{ solution}}{50} M$$

since 9 cm^3 of $S_2O_3^{2-}$ is taken each time and is completely consumed.

The values of $[S_2O_8^{2-}]$, $[I^-]$ and $[S_2O_3^{2-}]$ are entered in Table A given below. Note that in each case, rate is equal to $[S_2O_3^{2-}]$ consumed/2 Δt.

Table A

I Sl. No	II $[S_2O_8^{2-}]$ M	III $[I^-]$ M	IV $[S_2O_8^{2-}]$ consumed M	V (Rate) $M\,s^{-1}$	VI log (rate) $M\,s^{-1}$	VII log $[S_2O_8^{2-}]$ M
1						
2						
3						
4						
5						

graph is plotted with log (rate) against log $[S_2O_8^{2-}]$ (graph IV).

From Graph IV, slope of the line = ...

The order of reaction with respect to $S_2O_8^{2-} = m =$ ....(to the nearest whole number)

14.3.6 Procedure for Experiment 16(b) : The Order of Reaction in I^- ions

Proceed in a way similar to the Experiment 16(a) and make solutions as detailed in Observation Table V. Note in this case, water is added to iodide ion solution and not to $S_2O_8^{2-}$. Record your time data in this table.

14.3.7 Observation for Experiment 16(b)

Observation Table V

I Sl. No.	II (Volume of $S_2O_8^{2-}$ solution) cm^3	III (Volume of water) cm^3	IV (Volume of I^- solution) cm^3	V (Volume of $S_2O_3^{2-}$ solution) cm^3	VI (Volume of starch solution cm^3	VII Δt s
1	20	10.0	10.0	9	1	
2	20	7.5	12.5	9	1	
3	20	5.0	15.0	9	1	
4	20	2.5	17.5	9	1	
5	20	0.0	20.0	9	1	

14.3.8 Calculation for Experiment 16(b)

As done under Experiment 16(a), the values of $[S_2O_8^{2-}]$, $[I^-]$, $[S_2O_3^{2-}]$ consumed, rate, log rate and I^- are calculated and entered in Table B.

Table B.

I Sl. No	II $[S_2O_8^{2-}]$ M	III $[I^-]$ M	IV $[S_2O_8^{2-}]$ consumed M	V Rate $M\,s^{-1}$	VI log (rate) $M\,s^{-1}$	VII log $[I^-]$ M
1						
2						
3						
4						
5						

A graph is plotted log (rate) against $[I^-]$ (Graph V).

From Graph V, slope of the line = ...

The order of reaction with respect to I^- = n

= .... (to the nearest whole number)

14.3.9 Rate Constant for the Reaction Between $S_2O_8^{2-}$ and I^-

We shall calculate the rate constant of this reaction using Eq. 14.22. For that, we enter the values of $[S_2O_8^{2-}]$, $[I^-]$, m and n as obtained from Experiments 16(a) and (b) in Table C.

Calculation

While entering the value in Table C, use three values each from observation table IV and V. Note that k is calculated using Eq. 14.22.

Note that the units of k are equal to $M^{1-(m+n)}\,s^{-1}$ where M stands mol dm^{-3}. You include units of k in your results.

Table - C

I Sl. No.	II $[S_2O_8]$ M	III $[I^-]$ M	IV Rate $M\,s^{-1}$	V k $M^{1-(m+n)}\,s^{-1}$
1				
2				
3				
4				
5				
6				

Average value of k =

14.3.10 Procedure for Experiment 16(c): The Effect of Catalyst on the Reaction Between $S_2O_8^{2-}$ and I–

1. Take a clean and dry burette and label it as Cu^{2+} Rince the burette with $CuSO_4$ solution and fill with it.
2. Prepare solutions as detailed in Observation Table VI. Note that one batch of beakers will have solutions of $S_2O_8^{2-}$ and Cu^{2+} ions along with water, while

the second batch would contain solutions of I^-, $S_2O_3^{2-}$ and starch. Record your time data in Observation Table VI. Proceed as per Experiments 16(a) and (b) and record the time (Δt) for the appearance of blue colour.

14.3.11 Observation for Experiment 16(c)

Observation Table–VI

I Sl. No	II (Volume of $S_2O_8^{2-}$ (Solution) cm^3	III (Volume of Cu^{2}+ solution) cm^3	IV (Volume of water) cm^3	V (Volume of I^-solution) cm^3	VI (Volume of $S_2O_8^{2-}$ (Solution) cm^3	VII (Volume of starch solution cm^3	VII Δt s
1	15.0	0.0	10.0	15.0	9	1	
2	15.0	2.0	7.0	15.0	9	1	
3	15.0	5.0	5.0	15.0	9	1	
4	15.0	7.5	2.5	15.0	9	1	
5	15.0	10.0	0.0	15.0	9	1	

14.3.12 Calculation for Experiment 16 (c)

Based on the Observation Table VI, complete the following table (Table D). Plot a graph (Graph - VI) using data from column V and VII of Table D.

Table – D

I Sl. No.	II $[S_2O_8^{2-}]$ M	III $[I^-]$ M	IV Rate $M\,s^{-1}$	V k $M^{1-(m+n)}\,s^{-1}$
1				
2				
3				
4				
5				
6				

k is calculated using Eq. 14.22 as in Table C.

From graph VI, slope = k_c =

intercept from graph VI = k_0 =

14.3.13 Result

Order of the reaction with = m =
respect to $S_2O_8^{2-}$

Order of the reaction with = n =
respect to I^-

Average value of k =
(from subsec. 15.3.9)

k_o =

k_c =

SAQ 2

Difference between k_o and k_c.

....

....

....

....

....

14.4 SUMMARY

In this unit, we have discussed the details of Experiments 15 and 16 which deal with the kinetics of reaction between sodium thiosulphate and hydrochloric acid and initial rate method and kinetics of reaction between peroxydisulphate and iodide ions by iodine clock method.

14.4 ANSWERS

Self Assessment Question

1. HCl is consumed in the reaction. But, SO_2 obtained as a product, also gives an acid (H_2SO_3) on dissolution in water. As this acid is weak, its dissociation would depend on its concentration (which is changing continuously) and, we would not know its contribution towards the acidity of the solution. Hence, we could not use H^+ concentration to monitor the progress of the reaction.

2. k_o stands for the rate constant for the reaction between $S_2O_8^{2-}$ and I^- in the absence of Cu^{2+} ions while k_c stands for that in the presence of Cu^{2+} ions.

APPENDIX - I

Sodium thiosulphate 0.25 *M* : Prepared by dissolving about 62.5 g of sodium thiosulphate crystals ($Na_2S_2O_3.5H_2O$) in distilled water and making up the volume to 1 dm^3.

Sodium thiosulphate ($Na_2S_2O_3.5H_2O$) is not a primary standard. It has to be standardised. It can be standardised by titrating against standard potassium dichromate solution iodometrically using starch as indicator. The procedure is given below:

Sodium thiosulphate solution is somewhat unstable. It can easily be attacked by air borne bacteria with the liberation of sulphur. So the solution should normally be prepared fresh before use. In case a turbidity is observed, the solution should be discarded.

Standardisation of $[S_2O_3^{2-}]$

The dichromate solution can be prepared by weighing accurately about 3 g $K_2Cr_2O_7$, dissolving in water and making up to 250 cm^3 in a standard flask. Then moleuity will be about 0.04 M.

Into a 250 cm^3 conical flask, pipette 20 cm^3 of standard potassium dichromate solution (0.04 *M*). Add 10 cm^3 of 1 *M* sulphuric acid and 1 g of sodium hydrogen carbonate into the conical flask with gentle swirling. Then add 0.5 g potassium iodide or 10 cm^3 of 5% KI solution, swirl, cover the flask with watch glass and allow the solution to stand for 5 minutes in a dark place. Titrate against sodium thiosulphate solution taken in the burette, until a light pale yellow colour is obtained. Add 2 cm^3 of starch solution and continue the titration till the blue colour of starch iodine complex disappears. If M_1 and V_1 are the molarity and the volume of $K_2Cr_2O_7$ used whereas M_2 and V_2 are the molarity and volume of thiosulphate required for titration, then the molarity of $Na_2S_2O_3$ solution could be obtained as follows:

As per Eq. 1.13 and the stoichiometric equation given in the margin,

$$\frac{M_1 V_1}{M_2 V_2} = \frac{1}{6}$$

or $$M_2 = \frac{6M_1 V_1}{V_2}$$

or Molarity of thiosulphate solution $= M_2$

$$= \frac{120M_1}{V_2}$$

(since $V_1 = 20\ cm^3$)

We take 0.0417 *M* thiosulphate solution to titrate against 0.25 *M* dichromate solution in order to keep the molarity of thiosulphate 1/6 that of dichromate. This will help you in keeping the titre value to around 20 cm^3 when titrating against 20 cm^3 of dichromate solution. You can understand this using Eq. 1.13 of Unit 1 of this course, and the stoichiometric equation given below:

$$Cr_2O_7^{2-} + 14H^+ + 6S_2O_3^{2-} \longrightarrow 2Cr^{3+} + 3S_4O_6^{2-} + 7H_2O$$

HCl (I)

This is prepared by taking 250 cm^3 of concentrated hydrochloric acid and diluting it to 1 dm^3 using distilled water.

HCl (II)

This is prepared by taking 250 cm^3 of HCl (I) and diluting to 1 dm^3. HCl (II) can be standardised by titrating against a standard solution of Na_2CO_3 using methyl orange as indicator.

Standardisation of Hydrochloric acid (HCl-II)

Pipette out 20 cm^3 of standard Na_2CO_3 (0.4 *M*) solution into a 100 cm^3 conical flask. Add 2-3 drops of methyl orange indicator; the solution would turn yellow on addition of this indicator. Titrate with HCl (II) taken in the burette. Swirl the conical flask after each addition. Continue the titration till a permanent red colour is obtained as the end point. If M_1 and V_1 are the molarity and volume of Na_2CO_3 solution, whereas M_2 and V_2 are the molarity and volume of HCl, then the molarity of HCl would be given by the following formula (as per Eq. 1.13 and the stoichiometric equation given in the margin):

Molarity of HCl (II) $= M_2 = \frac{2\,M_1 V_1}{V_2} = \frac{40\,M_1}{V_2}$

(since $V_1 = 20\ cm^3$)

The molarity of HCl (I) can be calculated using the strength of HCl (II) as follows:

Molarity of HCl (I) = 4 × Molarity of HCl (II)

0.4 *M* Na_2CO_3 can be prepared by dissolving 4.24 gm Na_2CO_3 in 100 cm^3 distilled water

$$CO_3^{2-} + 2H^+ \longrightarrow H_2O + CO_2$$

APPENDIX - II

Potassium iodide : (0.2 *M*) : Prepared by dissolving 33.2 g of KI in distilled water and making up the volume to 1 dm^3. Should be made fresh.

Potassium peroxydisulphate (0.01 *M*) : Prepared by dissolving 2.7 g of $K_2S_2O_8$ in distilled water and making up the volume to 1dm^3.

Sodium thiosulphate : (0.002 *M*) : Prepared by dissolving 0.496 g of $Na_2S_2O_3.5H_2O$ in distilled water and making up the volume to 1 dm^3. This solution need not be standardised unless we are interested in knowing actual value of reaction rate. The concentration should not be too different from 0.002 M, as it would alter the time of appearance of the product. The solution should be prepared fresh as it does not have good bench-life.

Copper sulphate : (0.0025 *M*) : Prepared by dissolving 0.625 g of $CuSO_4.5H_2O$ in distilled water and making up the volume to 1 dm^3.

Starch Solution : 1 g of starch is dispersed in about 20 cm^3 of distilled water to get a fine paste. To this, 80 cm^3 of distilled water is added and the mixture is boiled with stirring. Since starch preparations degrade in short time, it is advised to test the suitability of the indicator prepared. For this, take a small portion of the solution in a test tube and to this, add a little of iodine solution. It should give intense blue colour.

UNIT 15 INTEGRATED RATE EQUATION METHOD

Structure

15.1 Introduction
    Objectives
15.2 Experiment 17 : Kinetics of Iodination of Acetone - Titrimetry
    Principle
    Requirements
    Procedure for Experiment 17(a) : Determination of the Order of Reaction in Iodine
    Observation for Experiment 17(a)
    Calculation for Experiment 17(a)
    Procedure for Experiment 17(b) : Determination of the Order of Reaction in Acetone
    Observation for Experiment 17(b)
    Calculation fo Experiment 17(b)
    Procedure for Experiment 17(c) : Determination of the Order of Reaction in H^+ ions
    Observation for Experiment 17(c)
    Calculation fo Experiment 17(c)
    Result
    Precautions
15.3 Experiment 18 : The order of Iodination of Acetone in Iodine – Colorimetry
    Principle
    Requirements
    Procedure
    Observation
    Calculation
    Result
    Precautions
15.4 Experiment 19 : Kinetics of Acid Catalysed Hydrolysis of Ester – Titrimetry
    Principle
    Requirements
    Procedure
    Observation
    Calculation
    Result
15.5 Experiment 20 : Kinetics of Saponification of Ester – Titrimetry
    Principle
    Requirements
    Procedure
    Observation
    Calculation
    Result
    Precaution
15.6 Experiment 21 : Kinetics of Saponification of Ester – Conductometry
    Principle
    Requirements
    Procedure
    Observation
    Calculation
    Result
    Precautions
15.7 Summary
15.8 Appendix

15.1 INTRODUCTION

In Unit 14 we determined some simple kinetic parameters like order, rate constant, etc. of two reactions by the initial rate method. Although the initial rate method is easy to carry out, this method may not reveal the full rate law in a complex reaction. Sometimes the products themselves may get involved in intermediate steps. For example, in the synthesis of HBr, the true rate law involves the concentration of HBr. But HBr being a product is not present initially. A study of this reaction by the initial rate method will give the rate only in terms of amount of hydrogen and bromine, thus not giving the correct rate equation. To avoid this, the rate law should be fitted to the data throughout the course of the reaction. In order to do so, we can use the integrated rate equations and, try to fit the data collected during the entire reaction or a good part of the reaction. In this unit, we will study the procedures for the following five experiments for obtaining the order and/or rate constant of different reactions using the integrated rate equation method.

(i) Two experiments on the kinetics of iodination of acetone, one by titrimetry and another by colorimetry

(ii) One experiment on the kinetics of acid catalysed hydrolysis of ester by titrimetry

(iii) Two experiments on the kinetics of saponification of ester, one by titrimetry and another by conductometry.

Finally the preparation of solutions used in Experiments 17–21 is discussed in the appendix.

Objectives

After performing the experiments mentioned in this unit, you should be able to:

- study experimentally the kinetics of simple reactions using titrimetry, colorimetry and conductometry,
- explain Ostwald's isolation method,
- describe the use of graphical method in determining the order of reaction, and
- fit the experiment data into an integrated rate equation to obtain the rate constant of a reaction.

15.2 EXPERIMENT 17 : KINETICS OF IODINATION OF ACETONE — TITRIMETRY

15.2.1 Principle

In aqueous solution, acetone and iodine react according to the equation:

$$CH_3COCH_3(aq) + I_2(aq) \longrightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq) \quad \ldots (15.1)$$

Both acids and bases catalyse this reaction. The iodination of acetone occurs rapidly at both high pH and low pH but occurs only slowly around pH 7. The kinetics of this reaction in acid solution can be conveniently studied by measuring the concentration of iodine as a function of time during the reaction. The reaction mixture is prepared by adding iodine into a mixture of acetone and hydrochloric acid starting the stop watch simultaneously. Then samples of the reaction mixture are withdrawn at known times, discharged into sodium hydrogen carbonate solution for quenching the reaction. The iodine remaining is titrated with sodium thiosulphate solution. From the titre values, the concentration of iodine remaining is calculated. Using graphical method, the order of reaction with respect to iodine, acetone and the mineral acid is found out. The rate constant is also finally calculated.

Quenching : Quenching is the process of stopping or slowing down a chemical reaction suddenly by lowering temperature or by adding a reagent which consumes one of the reactants or the catalyst. In the iodination of acetone, the addition of reaction mixture to $NaHCO_3$ solution more or less stops the reaction due to consumption of H^+ ions and the liberation of carbon dioxide gas.

$$HCO_3(aq) + H^+(aq) \longrightarrow H_2O(l) + CO_2(g)$$

We shall first discuss the calculation of concentration of iodine using the titrimetric method.

Calculation of concentration of iodine in the reaction mixture.

The unreacted iodine in the reaction mixture is estimated by titrating it with standardised sodium thiosulphate solution as per the reaction:

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI \quad \ldots (15.2)$$

Sodium hydrogen carbonate should be pure and, should not contain sodium carbonate, since aqueous sodium carbonate solution could also react with iodine. Instead of sodium hydrogen carbonate solution, sodium acetate solution can also be used.

To determine the end point in the titration, starch solution is added, when the titrated mixture is pale yellow in colour. That is, the starch is added towards the end point. If starch solution is added much earlier to the end point, then the starch gets coagulated and, the end point cannot be determined accurately. The end point is the disappearance of violet colour formed by the interaction between starch and iodine.

Iodine is dissolved in excess of potassium iodide which yields potassium triiodide.

$$I^- + I_2 \rightleftharpoons I_3^-$$

Both I_2 and I_3 are effective iodinating agents for acetone. The treatment of results is unaffected when I_2 is substituted for I_3.

Let us represent the molarity and volume of sodium thiosulphate by M_1 and V_1, and, those of iodine (in the reaction mixture) by M_2 and V_2, respectively.

Using Eq. 1.13 of Unit 1 of this course, we can write

$$\frac{M_1 V_1}{M_2 V_2} = \frac{2}{1} \quad \ldots (15.3)$$

since the stoichiometric coefficients of $Na_2S_2O_3$ and I_2 are 2 and 1, respectively as per Eq. 15.2.

Hence, molarity of iodine in the reaction mixture,

$$M_2 = \frac{M_1 V_1}{2V_2} \quad \ldots (15.4)$$

Eq. 15.4 is used for calculating the concentration of iodine $[I_2]$ in the reaction mixture at various time intervals. From $[I_2]$ values, those of $\log [I_2]$ and $1/[I_2]$ can also be calculated at various time intervals using logarithmic tables. Next, let us discuss the generalised form of rate equation for the iodination of acetone.

Rate Equation

The generalised form of rate equation for the iodination of acetone is given below:

$$\frac{-d[I_2]}{dt} = k[I_2]^x\,[CH_3COCH_3]^y\,[H^+]^z \quad \ldots (15.5)$$

where x, y and z are orders of reaction in iodine, acetone and H^+ ions, respectively and, k is the rate constant of iodination of acetone.

Note that we are measuring the amount of iodine remaining as a function of time; the rate hence determined is $-d[I_2]/dt$. As we are interested in getting the orders x, y and z individually, we are going to use the Ostwald's isolation method.

Ostwald's isolation method : This is a convenient method for the determination of order of reaction when more than one reactant is present. To determine the order of reaction in one reactant, all the other reactants are taken in excess and the kinetics is studied. The experiment is repeated to find the order of reaction with respect to each reactant. If you want to know more about isolation method, go through Sec. 18.7 of Unit 18 of CHE–04 course.

We will next study the principles behind the determination of order of reaction with respect to each species.

Order of reaction in iodine (*x*)

In keeping with isolation method, we will take acetone in excess concentration, that is, choose the condition such that [acetone] >> $[I_2]$. Under these conditions, the change in the concentration of acetone during the reaction will be negligible; that is, [acetone] remains almost constant during the course of the reaction. The rate equation (Eq. 15.5) gets modified to:

$$\frac{-d[I_2]}{dt} = k_a [I_2]^x \text{ where } k_a = k\,[CH_3COCH_3]_a^y\,[H^+]_a^z \qquad \ldots (15.6)$$

We have included $[H^+]$ along with the constants because H^+ being a catalyst remains unconsumed. Also, $[CH_3COCH_3]_a$ and $[H^+]_a$ stand for the respective concentrations in Experiment 17(a).

We shall perform the kinetic run as per the details given in the procedure under Experiment 17(a) to determine the order in iodine (*x*). We shall calculate the concentration of iodine ($[I_2]_t$) in the reaction mixture at various time intervals, *t*. We shall enter the values in the observation table I under Sec. 15.2.4

We shall use graphical method for the determination of order in iodine. In Subsec. 13.3.2 of Unit 13, the graphical method of arriving at the order of reaction has been discussed. Accordingly, the types of plots expected for zeroth order, first order and second order kinetics with respect to iodine are given below:

Graph (i)	: $[I_2]_t$ against t	for zeroth order
Graph (ii)	: $\log [I_2]_t$ against t	for first order
Graph (iii)	: $1/[I_2]_t$ against t	for second order

We have to try all these three plots. The order of reaction in iodine corresponds to that plot which gives a straight line. Note that all the above plots are made using the data in observation Table I under Sec. 15.2.4.

You shall see that the zeroth order plot (i.e., $[I_2]_t$ against t plot), gives a straight line. That is, the reaction is zeroth order in iodine or $x = 0$. Hence, Eq. 15.6 can be written as,

$$\frac{-d[I_2]}{dt} = k_a \text{ where } k_a = k\,[CH_3COCH_3]_a^y\,[H^+]_a^z \qquad \ldots (15.7)$$

$$\text{since } [I_2]^x = [I_2]^0 = 1$$

For determining *y* and *z* (orders of reaction in acetone and H^+), we shall use modified form of Eq. 15.7.

Further, we can determine k_a from the slope of $[I_2]_t$ against t plot, (graph (i)), since the reaction is zeroth order with respect to iodine. This can be understood by comparing the integrated equation for a zeroth order reaction with the equation for a straight line.

Integrated equation for
zeroth order reaction as per Eq. 15.7
(and Table 13.1 of Unit 13) : $[I_2]_t = [I_2]_o - k_a t$ . . . (15.8)

$[I_2]_o$ and $[I_2]_t$ stand for the concentration of iodine in the reaction mixture at the start and, after a time interval, *t*.

Equation for a straight line : ($y = c + mx$) . . . (15.9)

Hence from Eqs. 15.8 and 15.9,

$$\text{slope} = m = -k_a$$

$$\text{or} \quad k_a = -\text{slope of graph (i)} \qquad \ldots (15.10)$$

Hence the slope of graph (i) of Experiment 17(a) gives k_a as per Eq. 15.10. Hence from Experiment 17(a), we shall find

(i) that the order of the reaction in iodine is zero,

i.e. $x = 0$

(ii) the value of k_a from Eq. 15.10 as, $k_a = -$slope of graph(i). Next let us determine the order of reaction in acetone.

In Table 13.1 of Unit 13 of this course, generalised form of integrated rate equation (Eq. 15.8) is given.

For understanding the straight line plots, see Sec. 2.6 of Unit 2 of this course

Determination of Order of Reaction in Acetone *(y)*

Experiment 17(b) is performed to determine the order of reaction in acetone. The concentrations of iodine and H^+ in Experiment 17(b) are maintained same as in Experiment 17(a). But the concentration of acetone is reduced to half the concentration of acetone taken in Experiment 17(a).

$$\left.\begin{array}{l}[H^+]_b = [H^+]_a \\ [I_2]_b = [I_2]_a\end{array}\right\} \qquad \ldots (15.11)$$

and $[CH_3\,COCH_3]_b = \frac{1}{2}[CH_3COCH_3]_a$

Similar to Eq. 15.7, we can write

$$\frac{-d[I_2]}{dt} = k_b \text{ where } k_b = k\,[CH_3COCH_3]_b^y\,[H^+]_b^z \qquad \ldots (15.12)$$

where k_b is the constant to be obtained from Experiment 17(b).

In Experiment 17(b), the concentrations of iodine in the reaction mixture are determined at various time intervals and the values are entered in observation table II under Sec. 15.2.7. Using $[I_2]t$ and t values at various time intervals, graph (iv) is plotted ($[I_2]_t$ against t plot). The slope of graph (iv) gives k_b as per Eq. 15.13.

$$k_b = -\text{slope of graph (iv)} \qquad \ldots (15.13)$$

From k_a and k_b, we can obtain y as follows. Using Eq. 15.11 in Eq. 15.12, we can write,

$$k_b = k\,([CH_3COCH_3]_a/2)^y\,[H^+]_a^z$$

i.e. $k_b = (1/2)^y\,k\,[CH_3COCH_3]_a^y\,[H^+]_a^z$

using Eq. 15.7, $k_b = k_a\,(1/2)^y \qquad \ldots (15.14)$

Taking logarithms, $\log k_b = \log k_a + y \log 1/2$

or $\log k_b - \log k_a = -y\,(0.3010)$

$\log k_b/k_a = -0.3010\,y$

i.e., $y = -\dfrac{\log k_b/k_a}{0.3010}$

$$y = -\frac{1}{0.3010}\log\frac{\text{slope of graph (iv)}}{\text{slope of graph (i)}} \qquad \ldots (15.15)$$

[since $\dfrac{k_b}{k_a} = \dfrac{-\text{slope of graph (iv)}}{-\text{slope of graph (i)}}$ as per Eqs. 15.10 and 15.13]

Hence, the order in acetone *(y)* can be calculated from the slopes of plots in Graphs (i) and (iv).

Order of reaction in H^+ (z)

To determine the order in H^+, Experiment 17(c) is performed. In Experiment 17(c), $[H^+]$ is reduced to half the value in Experiment 17(a). Otherwise, the concentrations of iodine and acetone in Experiment 17(c) are maintained the same as in Experiment 17(a).

i.e.,

$$\left.\begin{aligned}[H^+]_c &= 1/2\,[H^+]_a\\ [I_2]_c &= [I_2]_a\\ [CH_3COCH_3]_c &= [CH_3COCH_3]_a\end{aligned}\right\} \qquad \ldots (15.15)$$

Similar to Eq. 15.12, we can write,

$$\frac{-d[I_2]}{dt} = k_c \text{ where } k_c = k\ [CH_3\,COCH_3]^y_c\,[H^+]^z_c \qquad \ldots (15.17)$$

In Experiment 17(c), the concentrations of iodine in the reaction mixture are determined at various time intervals and the values are entered in Observation Table III under Sec. 15.2.10. Then : $[I_2]_t$ against t plot (Graph (v)) is made. The slope of Graph (v) gives k_c as per Eq. 15.18.

$$k_c = -\text{ slope of graph (v)} \qquad \ldots (15.18)$$

From k_a and k_c, we can obtain z as follows:

Using Eqs. 15.16 and 15.17, we can write

$$k_c = k[CH_3COCH_3]^y_a\,([H^+]_a/2)^z \qquad \ldots (15.19)$$

Using steps similar to those used in obtaining Eq. 15.15 from Eq. 15.14, we can obtain Eq. 15.20 from Eq. 15.19.

i.e.,

$$z = \frac{-\log k_c/k_a}{0.3010}$$

$$= -\frac{1}{0.3010}\log\frac{\text{slope of graph (v)}}{\text{slope of graph (i)}} \qquad \ldots (15.20)$$

Thus we could find out x, y and z. Finally we shall calculate the rate constant k for the iodination of acetone using Eq. 15.6 and the data under Experiment 17(a).

$$k = k_a/[CH_3COCH_3]^y_a\,[H^+]^z_a \qquad \ldots (15.21)$$

Hence by substituting for k_a and initial concentrations of acetone and H^+ from Experiment 17(a), we can calculate k.

15.2.2 Requirements

Apparatus

Burettes ($50\ cm^3$) – 3
Pipettes graduated ($20\ cm^3$) – 3
Conical flasks ($250\ cm^3$) – 2
Conical flasks ($100\ cm^3$) – 7
Boiling tube – 1
Test tube – 1
Beaker ($250\ cm^3$) – 1
Beaker ($400\ cm^3$) – 1

Chemicals

Acetone
Iodine
Potassium iodide
Hydrochloric acid
Sodium hydrogen carbonate
Sodium thiosulphate
Starch
Deionised water

Wash bottle (with deionised water) – 1

Burette stands (with clamps) – 3

Thermometer – 1

Stopwatch – 1

Water trough/Thermostat – 1

Solutions that are provided for all the three experiments, (17(a), 17(b) and 17(c):

1. $0.05\ M\ I_2$ in $0.4\ M$ KI
2. $1.0\ M$ HCl
3. $0.10\ M\ NaHCO_3$
4. $0.01\ M\ Na_2S_2O_3$
5. Starch solution 1%

Details for the preparation of the solution are given in Appendix.

15.2.3 Procedure for Experiment 17(a)

Determination of the Order of Reaction in Iodine

1. Bring to your work – table all the required apparatus and solutions as given under 15.2.2.
2. Rinse and fill burette 1 with sodium thiosulphate solution.
3. Rinse and fill burette 2 with 1 *M* HCl.
4. Rinse and fill burette 3 with deionised water.
5. Pipette out 10 cm^3 of 0.1 *M* $NaHCO_3$ solution into each of five 100 cm^3 conical flasks.
6. Withdraw into a 250 cm^3 conical flask from the burettes 10 cm^3 of 1 *M* HCl and 70 cm^3 of deionised water. Pipette into this, 10 cm^3 of acetone and stopper the flask.
7. Pipette 10 cm^3 of iodine solution into a boiling tube and stopper it. Keep both the 250 cm^3 conical flask and the boiling tube in a water trough (or thermostat). Note the temperature.
8. Pour the iodine solution into the flask containing acetone, HCl and water, starting the stop watch at the same time. Mix well by pouring from one into the other.
9. Withdraw 10 cm^3 of the reaction mixture and run this sample into the flask containing 10 cm^3 of $NaHCO_3$ solution, noting the time when the pipette is half empty. Mix well by shaking and then titrate the residual iodine with $Na_2S_2O_3$ solution till the solution becomes pale yellow in colour. Add 2 cm^3 of starch solution. Continue titrating this blue solution with $Na_2S_2O_3$ till the solution turns colourless (end point). Note the burette reading.
10. Repeat the titration of 10 cm^3 samples of the reaction mixture giving an interval of about 2 minutes between sampling.
11. After the titration is over, wash the flasks with large quantities of water because the reaction mixture contains iodoacetone, a powerful lachrymator.
12. Calculate $[I_2]_t$, $\log[I_2]_t$ and $1/[I_2]_t$ and enter these in Observation Table 1.
13. Plot $[I_2]_t$ vs t, $\log[I_2]_t$ vs t and $1/[I_2]_t$ vs t as Graphs (i), (ii) and (iii), respectively.

100 cm^3 reaction mixture is made from

(i) 10 cm^3 of 1 *M* HCl
(ii) 70 cm^3 of water (deionised)
(iii) 10 cm^3 of acetone
} in 250 ml conical flask
and
(iv) 10 cm^3 of the solution – in a boiling tube.

If the reaction mixture is at 35°C, then 2–3 minute intervals are suitable. If the students work in pairs, they will be able to manage doing titrations at 2 minutes interval. For performing titrations at 5–7 minutes interval at 35°C, the concentrations of HCl and (or) of acetone may be decreased. This instruction holds good for Experiments 17(a), (b) and (c). On the other hand if the temperature is 25°C, 5–7 minute intervals could be given.

Even with two 100 cm^3 flasks, the experiment can be performed.

Lachrymator is a substance that stimulates formation of tears.

15.2.4 Observation for Experiment 17(a)

Molarity of thio (M_1) = M

Volume of the reaction mixture withdrawn at each time t(V_2) = 10 cm^3

As per Eq. 15.4, $[I_2]$ in the reaction mixture = $[I_2]_t$

$$= M_2 = \frac{M_1 V_1}{2V_2} = \frac{M_1 V_1}{20}$$

$$(\text{since } V_2 = 10 \text{ cm}^3)$$

Volume of $NaHCO_3$ solution taken for quenching the reaction = 10 cm^3

Solution taken in the burette =0.01 M $Na_2S_2O_3$

Volume of starch solution added just before the end point = 2 cm^3

Temperature of the reaction mixture =...................°C

Observation Table – I

t/s	Burette reading		(Volume of thio (V'_1))/cm^3	$[I_2]_t/M$ $= \frac{M_1V_1}{20}$	$\log[I_2]_t/M$	$\frac{M}{[I_2]_t}$
	Initial	Final				

15.2.5. Calculations for Experiment 17(a)

Draw inference from the graphs (i), (ii) and (iii) about the order of the reaction in iodine. Also obtain the slope of Graph (i).

The order of the reaction in iodine is ....

Using Eq. 15.10, k_a = – slope of graph (i)

= .... $M\ s^{-1}$

15.2.6 Procedure for Experiment 17(b)
Determination of the Order of Reaction in Acetone

Repeat instructions 1 to 5 and 7 to 11 as in Experiment 17(a) under Sec. 15.2.3. In the place of instruction (6), do the following: Withdraw into a 250 cm^3 conical flask from the burettes, 10 cm^3 of 1 M HCl and 75 cm^3 of deionised water. Pipette into this, 5 cm^3 of acetone and stopper the flask. That is, we take in this experiment half the concentration of acetone taken in Experiment 17(a). You can withdraw reaction mixture at 7–10 minutes interval and do the titration against standardised thio.

Calculate $[I_2]_t$ at various intervals and enter the data in observation table II. Also plot $[I_2]_t$ against t (Graph iv).

100 cm^3 reaction mixture contains

(i) 10 cm^3 of 1 M HCl
(ii) 70 cm^3 of water (deionised)
(iii) 5 cm^3 of acetone
} in 250 ml onica flask
and
(iv) 10 cm^3 of iodine solution – in a boiling tube.

15.2.7 Observation for Experiment 17(b)

Observation Table – II

t/s	Burette reading		(Volume of thio (V_1))/cm^3	$[I_2]_t/M^*$	$= \frac{M_1V_1}{20}$
	Initial	Final			

---

[*] Use M_1 value from Experiment 17(a).

15.2.8 Calculation for Experiment 17(b)

From Graph (iv), find out the slope of the line.

From Eq. 15.13, k_h = – slope of Graph (iv)

$= \ldots\ldots M\ s^{-1}$

Order of the reaction in acetone = y

(using Eq. 15.15) $= -\frac{1}{0.3010} \log \frac{\text{slope of graph (iv)}}{\text{slope of graph (i)}}$

100 cm^3 reaction mixture contains

(i) 5 cm^3 of 1 M HCl
(ii) 75 cm^3 of water (deionised)
(iii) 10 cm^3 of acetone
} in 250 ml onical flask
and
(iv) 10 cm^3 of iodine solution – in a boiling tube.

15.2.9 Procedure for Experiment 17(c)

Determination of the Order of Reaction in H$^+$ ions

Repeat instructions 1 to 5 and 7 to 11 as in Sec. 15.2.3 under Experiment 17(a). In place of instruction 6 do as follows:

Withdraw into a 250 cm^3 conical flask from the burettes, 5 cm^3 of 1 M HCl and 75 cm^3 of deionised water. Pipette into this, 10 cm^3 of acetone and stopper the flask. That is, we take half the concentration of hydrochloric acid taken in Experiment 17(a). You can withdraw reaction mixture at 7–10 minutes interval and do titration against standardised thiosulphate solution.

Calculate $[I_2]_t$ at various intervals and enter the data in observation Table III. Also plot $[I_2]_t$ against t (graph v).

15.2.10 Observation for Experiment 17(c)

Observation Table – III

t/s	Burette reading		(Volume of thio (V_1))/cm^3	$[I_2]_t/M^* = \frac{M_1V_1}{20}$
	Initial	Final		

---

[*] Use M_1 value from Experiment 17(a).

15.2.11 Calculation for Experiment 17(c)

From graph (v), find out the slope of the line.

From Eq. 15.18, $k_c = -$ slope of graph (v) = ... $M\,s^{-1}$

From Eq. 15.20, the order of the reaction in H^+

$$= z = -\frac{1}{0.3010}\log\frac{\text{slope of graph (v)}}{\text{slope of graph (i)}}$$

We can also calculate the rate constant of iodination of acetone, k.

From Eq. 15.21, $$k = \frac{k_a}{[CH_3COCH_3]_a\,[H^+]_a}$$

But $k_a = -$ slope of graph (i) (using Eq. 15.10)

Also, $[CH_3COCH_3]_a = 1.36$ M and $[H^+]_a = 0.1$ M

Hence $$k = \frac{k_a}{(1.36)^y\,(0.1)^z}$$

$$= \ldots\ldots M^{1-(y+z)}$$

[M stands for molarity unit].

$[H^+]$ is 0.1 M since in Experiment 17(a), 10 cm^3 of 1 M HCl is made up to 100 cm^3 (as reaction mixture)

$[CH_3COCH_3]_a$ is equal to 1.36 M as per the calculation indicated below:

The reaction mixture contains 10 cm^3 of acetone in a total volume of 100 cm^3 in Experiment 17(a).

$$[CH_3COCH_3]_a = \left\{\begin{matrix}\text{Molarity of}\\ \text{acetone in}\\ \text{Experiment 17(a)}\end{matrix}\right\} = \frac{\text{Mass of acetone}}{(\text{molar mass} \times (\text{volume of solution of acetone}) \text{ in } dm^3)} \quad \ldots(16.22)$$

Mass of acetone = (Volume of acetone × density of acetone)

$= 10\,cm^3 \times 0.79\,g\,cm^{-3}$

$= 7.9\,g$

Volume of solution = $100\,cm^3 = 0.1\,dm^3$ (reaction mixture)

Molar mass of acetone = $58.08\,g\,mol^{-1}$

Substituting these in Eq. 15.22,

$$[CH_3COCH_3]_a = \frac{7.9\,g}{58.08\,g\,mol^{-1} \times 0.1\,dm^{-3}} = 1.36\,mol\,cm^{-3} = 1.36\,M$$

15.2.12 Result

Order of the reaction in iodine = x =

Order of the reaction in acetone = y =

rder of the reaction in H^+ ions = z =

Rate constant for the iodination of acetone = k =

15.2.13 Precautions

1. Laboratory samples of acetone often contain peroxides which liberate iodine from acidified KI. This produces a small amount of iodine in the reaction mixture. But the liberated iodine is getting used up in the main reaction. The peroxides thus get destroyed and the data obtained after the first 1–2 minutes give a linear graph (Inclusion of data obtained in the first 1–2 minutes gives a curvature to the line).
2. Iodoacetone, a product of the reaction is a very powerful lachrymator. All solutions containing this should be disposed of immediately after the experiment, and the apparatus washed with plenty of water.
3. Iodine solution and acetone should be kept in well stoppered bottles.
4. Sodium thiosulphate solution and starch solution should be prepared on the same day the experiment is to be done.

15.3 EXPERIMENT 18 : THE ORDER OF IODINATION OF ACETONE IN IODINE – COLORIMETRY

15.3.1 Principle

The kinetics of acid catalysed iodination of acetone (Eq. 15.1) is to be followed colorimetrically in this experiment. We shall confine ourselves to the determination of order of reaction in iodine only. It is our aim to familiarise you with the colorimetric method of following the kinetics of iodination reaction.

You will be using low–cost colorimeter for performing the experiment. Although, iodine forms triiodide ion (I_3^-) in presence of iodide, both I_2 and I_3^- have same absorption pattern. Both of them iodinate acetone. Hence what we are going to measure is the total concentration of I_2 and I_3^- Again, the total concentration of I_2 and I_3^- is proportional to absorbance as per Beer-Lambert law. When you use a low-cost colorimeter, you measure meter reading (R) values which are proportional to absorbance as well as to concentration of iodine.

Since we are interested in finding only the order of the reaction in iodine but not the actual rate constant, it is not necessary to examine the reaction in terms of $[I_2]_t$. It is enough to study the reaction in terms of meter reading values. Hence, instead of using $[I_2]_t$, $\log [I_2]_t$ and $1/[I_2]_t$, we will be using the corresponding meter reading values, viz., R_t, $\log R_t$ and $1/R_t$

To find the order of the reaction in iodine, we will try zeroth order, first order and second order plots as shown below:

R_t against t plot : for zeroth order reaction
$\log R_t$ against t plot : for first order reaction
$1/R_t$ against t plot : for second order reaction.

You will see that R_t against t plot gives a much better straight line, which brings out the zero order dependence in I_2 concentration.

15.3.2 Requirements

Apparatus

Burettes (50 cm^3) – 4
Beakers (250 cm^3) – 1
Test tubes (20 cm^3) – 10
Colorimeter – 1
Stopwatch – 1
Thermometer – 1
Wash bottle (with deionised water) – 1
Burette stands with clamps – 4
Water trough/Thermostat – 1

Chemicals

Acetone
Iodine
Potassium iodide
Hydrochloric acid
Deionised water

Solutions that are needed for this experiment:

1. 0.05 M I_2 in 0.4 M KI
2. 1.0 M HCl
3. 4 M Acetone

Details for the preparation of the solution are given in Appendix.

15.3.3 Procedure

1. Plug the colorimeter into the mains and switch it on.
2. Keep the colour selector knob at green. (If it is a commercial colorimeter, use the green filter. If it is a spectrophotometer, adjust the wavelength knob to read 565 nm.)
3. Take a clean cuvette, make a mark at the top on one plain side, if it is already not marked. Rinse and fill it with deionised water. Wipe the outside dry with tissue paper.
4. Insert the cuvette into the cuvette holder with the marked side facing the LEDs. (In a commercial instrument, the mark on the cuvette should be made to coincide with the mark outside on the holder). Everytime you insert the cuvette into the holder, maintain this position.
5. Adjust the set zero knob till the meter reads zero.
6. Then mix 3 cm^3 of iodine solution and 7 cm^3 of deionised water in a boiling tube. After mixing the solution thoroughly, rinse and fill the same cuvette

with this iodine solution. Wipe the outside dry with tissue paper. Insert into the holder.

7. Adjust the sensitivity knob till the meter reads somewhere near the end of the scale, say 8. After this adjustment, do not disturb the sensitivity knob for the rest of the entire experiment. You do steps 8 and 9 only if you are working with a low cost colorimeter.

8. Rinse and fill the same cuvette with deionised water. Wipe the outside dry and insert into the holder. If the meter does not read zero, then adjust the set zero knob till it reads zero. After this adjustment, do not disturb the set zero knob for the rest of the entire experiment.

9. Withdraw from the burettes, 4 cm^3 deionised water, 2 cm^3 of hydrochloric acid and 2 cm^3 of acetone solution into a 250 cm^3 beaker.

10. Withdraw 2 cm^3 of iodine solution from the burette into a test tube. Keep the beaker and the test tube in a water trough (or a thermostat) and note the temperature.

11. Pour the iodine solution into the solution in the beaker, starting the stop-watch at the same time. Mix well by pouring one to the other.

12. Rinse the cuvette with the reaction mixture, fill with the same, wipe the outside, insert into the holder noting the mark on the cuvette.

13. Hold the stopwatch close to the meter and read the stop-watch as the needle passes by marked divisions on the meter-scale. (Avoid taking reading when the needle is in between divisions). Note 8– 10 such meter readings and the corresponding time readings. Enter these in the observation Table IV.

14. Remember that iodoacetone is a powerful lachrymator. Hence discard all solutions containing this and, wash your glass apparatus with plenty of water.

15. Calculate log R_t and $1/R_t$ and enter these in the same Table.

10 cm^3 reaction mixture is made as follows:

(i) 4 cm^3 of deionised water
(ii) 2 cm^3 of 1 M HCl
(iii) 2 cm^3 of 4 M acetone
} in a 250 cm^3 beaker
(iv) 2 cm^3 of 0.05 M iodine – in a test tube solution

15.3.4 Observation

Temperature of the reaction mixture =..... °C

Observation Table – IV

t/s	R_t	log R_t	$1/R_t$

15.3.5 Calculation

Plot three graphs: 1) graph (vi): R_t vs t; 2) graph (vii): log R_t vs t; and 3) graph (viii): $1/R_t$ vs t. Infer the order of the reaction in I_2 from the graphs.

The order of the reaction in iodine =

15.3.6 Result

The order of the reaction in iodine =

15.3.7 Precautions

The first three precautions given in the previous experiment also apply here. Further, the adjusted knobs should not be disturbed during the experiment.

15.4 EXPERIMENT 19 : KINETICS OF ACID CATALYSED HYDROLYSIS OF ESTER – TITRIMETRY

15.4.1 Principle

The hydrolysis of an ester is quite slow and reversible. But this reaction is catalysed by acids and alkalies. In this experiment, we shall study the hydrolysis of methyl acetate in presence of hydrochloric acid.

$$CH_3COOCH_3(aq) + H_2O(l) \xrightarrow{H^+} CH_3COOH(aq) + CH_3OH(aq)$$

This reaction is an example of pseudo first order reaction. The concentration of water is high and, it almost remains constant throughout the reaction. The concentration of mineral acid which catalyses the reaction also remains constant. Thus the reaction rate depends only on the concentration of ester.

i.e., $\text{Rate} = k\,[CH_3COOCH_3]$ ... (15.23)

Using the integrated rate equation for a first order reaction as given in Table 14.1 of Unit 14, we can write,

$$k = \frac{2.303}{t} \log \frac{c_0}{(c_0 - x)} \quad \text{... (15.24)}$$

where c_0 is the initial concentration of the ester and $(c_0 - x)$ is the concentration of the ester at a time, t. Let us next discuss the outline of this experiment.

We mix known amounts of the ester and the mineral acid and withdraw equal volumes of the reaction mixture at definite intervals into vessels containing ice-cold water. The ice-cold water is added to decrease the rate of the reaction. The reaction mixture so withdrawn is titrated against standardised alkali using phenolphthalein as the indicator. The end point is the appearance of pink colour which does not disappear within ten seconds. From the titre values at various time intervals, the rate constant is calculated using the procedure indicated below:

The reaction mixture withdrawn each time contains a definite amount of hydrochloric acid and also acetic acid formed due to hydrolysis. Each titre value represents by the volume of sodium hydroxide solution required to neutralise both these acids.

Suppose that V_0, V_t and V_∞ are the titre values initially, at a time t and at the end of the reaction (infinite reading). V_0 is proportional to the amount of hydrochloric acid present in a definite volume of reaction mixture, when no acetic acid is formed.

V_∞ is proportional to the amount of hydrochloric acid, and acetic acid present in a definite volume of reaction mixtue after the completion of the reaction.

V_t is proportional to the amount of hydrochloric acid and acetic acid present in a definite volume of reaction mixture after a time, t.

$(V_\infty - V_0)$ is proportional to the amount of acetic acid formed when hydrolysis is complete or it is proportional to the initial concentration of ester (c_0)

i.e., $(V_\infty - V_0)$ is proportional to c_0 ... (15.25)

Similarly, $(V_t - V_0)$ is proportional to the acetic acid formed at a time t or is proportional to the concentration of ester hydrolysed (x) at a time, t.

Hence the concentration of ester remaining unhydrolysed at a time t (i.e., $(c_0 - x)$) is proportional to

$$[(V_\infty - V_0) - (V_t - V_0)]$$

i.e.; $(c_0 - x)$ is proportional to $(V_\infty - V_t)$ ... (15.26)

Using Eqs. 15.24 to 15.26,

$$k = \frac{2.303}{t} \log_{10} \frac{(V_\infty - V_o)}{V_\infty - V_t} \qquad \text{... (15.27)}$$

or

$$\log_{10}(V_\infty - V_t) = \log (V_\infty - V_o) - \frac{k_t}{2.303} \qquad \text{... (15.28)}$$

k can be calculated either by substituting V_o, V_t and V_∞ into Eq. 15.27 or by graphical method. For calculation by graphical method, $\log_{10}(V_\infty - V_t)$ is plotted against t. As per Eq. 15.28, this should give a straight line plot, the slope being equal to $-k/2.303$.

In other words, $k = -2.303 \times \text{slope}$ ... (15.29)

15.4.2 Requirements

Apparatus

50 cm^3 Burettes	– 2
100 cm^3 conical flasks	– 4
250 cm^3 conical flask	– 1
5 cm^3 pipettes	– 2
Stopwatch	– 1
Copper water bath	– 1
Thermometer	– 1
Water trough/Thermostat	– 1

Chemicals

Methyl acetate
Hydrochloric acid
Phenolphthalein
Sodium hydroxide
Ice water (prepared from carbon dioxide free water)

Details for the preparation of the solution are given in Appendix.

Solutions that are needed for this experiment:
0.5 M hydrochloric acid
0.125 M sodium hydroxide
Phenolphthalein indicator solution

15.4.3 Procedure

1) Using a 50 cm^3 burette, take 50 cm^3 of 0.5 *M* hydrochloric acid in a 250 ml conical flask.

2) Pipette out 5 cm^3 of methyl acetate in a test tube and keep both the conical flask and the test tube in a water trough (or a thermostat) for about five minutes.

3) Transfer the ester to the conical flask containing hydrochloric acid. Start the stop–watch when nearly half the volume of ester has been added.

4) After complete transfer, shake the mixture in the conical flask.

55 cm^3 of the reaction mixture is prepared from

(i) 50 cm^3 of 0.5 *M* hydrochloric acid - taken in a 250 cm^3 conical falsk

(ii) 5 cm^3 of methyl acetate - taken in a test tube

5) Immediately pipette out 5 cm^3 of the mixture into a 100 cm^3 conical flask containing 25 cm^3 of ice-cold water. Add a drop of phenolphthalein and titrate the resultant solution against 0.125 *M* sodium hydroxide solution. The end point is the appearance of light pink colour.

6) The first titre value represents V_0 and enter this in observation Table V. At intervals of 10 minutes upto 1 hour, repeat the process of pipetting 5 cm^3 of reaction mixture into a conical flask containing 1 drop of phenolphthalein and 25 cm^3 of ice-cold water and, titrating against 0.125 *M* sodium hydroxide solution. Enter the titre values in observation table V. Each of the titre values from second onwards constitute V_t.

) After taking six readings, pipette out 10 cm^3 of a mixture into a 100 cm^3 conical flask and close it with a loose cork. Heat the conical flask on a copper water bath at 50°C for about 30 minutes. Then cool the conical flask to room temperature and titrate 5 cm^3 of this mixture against 0.125 *M* sodium hydroxide solution using phenolphthalein as indicator. The last titre value represents the infinite reading (V_∞).

5.4.4 Observation

oom temperature = ... °C

Observation Table – IV

t/s	Burette reading		Titre value	$\log (V_\infty - V_t)$/cm^3
	Initial	Final		

5.4.5 Calculation

sing Eg. 15.27, $k = \frac{2.303}{t} \log \frac{(V_\infty - V_o)}{(V_\infty - V_t)}$

ive values of k are calculated and entered below:

) k = ... s^{-1}
i) k = ... s^{-1}
ii) k = ... s^{-1}
/) k = ... s^{-1}
) k = ... s^{-1}

....

Average k = s^{-1}

....

is calculated from log ($V_\infty - V_t$) against t plot (Graph IX) Using Eq. 15.29,

= −2.303 × slope

= .... s^{-1}

.4.6 Result

k (by calculation) = ... s^{-1}

k (by graphical method) = ... s^{-1}

.5 EXPERIMENT 20 : KINETICS OF SAPONIFICATION OF ESTER – TITRIMETRY

.5.1 Principle

mentioned earlier, the hydrolysis of ester is catalysed by acids and alkalies. The aline hydrolysis of ester is known as saponification. The equation for the onification of ethyl acetate is given below:

${}_3COOC_2H_5(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + C_2H_5OH(aq)$ ...(15.30)

Soaps are prepared by the alkaline hydrolysis of oils (which are esters of fatty acids of higher molecular weight). Hence alkaline hydrolysis of esters came to be known as saponification.

This reaction is irreversible, whereas the acid catalysed reaction is reversible. This reaction can be followed volumetrically by estimating the concentration of OH^- in the reaction mixture at different t values. The reaction mixture is prepared by mixing equal volumes of a solution of sodium hydroxide ($M/40$) and a solution of ethyl acetate ($M/40$) noting the time simultaneously. Then equal volumes of the reaction mixture are pipetted out at definite intervals into a known excess of cold standardised hydrochloric acid ($M/40$) and the left over acid back titrated with a standardised solution of sodium hydroxide ($M/40$). Pouring into excess hydrochloric acid solution neutralises the OH^- in the reaction mixture, thus quenching the reaction. As the reaction progresses, the concentration of OH^- in the reaction mixture decreases and the concentration of the unreacted hydrochloric acid in the quenched reaction mixture increases. The data that we collect is the volume of NaOH, V_t, required to react with the left over hydrochloric acid in the quenched reaction mixture at time t. Let us next see how we calculate k value from such a set of data.

The rate equation for the reaction can be written as:

$$\frac{-d[OH^-]}{dt} = k\,[CH_3COOC_2H_5][OH^-] \qquad \ldots (15.31)$$

The reaction is first order each in ethyl acetate and hydroxide ions. Assuming this, we are going to find the second order rate constant, k. Further, we take the ester and alkali of the same concentration initially (c_o) and assume that the concentration of each becomes (c_o-x) after a time t.

Then Eq. 15.31 can be written as,

The generalised form of Eq. 15.33 is given in Table 13.1 of Unit 13 of this course.

$$\frac{-d[OH^-]}{dt} = (c_o - x)^2 \qquad \ldots (15.32)$$

On integration Eq. 15.31 becomes,

$$\frac{1}{c_o - x} = \frac{1}{c_o} + kt \qquad \ldots (15.33)$$

Next let us see how to relate the titre value V_t of NaOH solution to $(c_o - x)$.

Let us assume that 10 cm^3 of the reaction mixture is added to 25 cm^3 of $M/40$ HCl for quenching.

Volume of reaction mixture = 10 cm^3.
Volume of $M/40$ HCl added to it = 25 cm^3
25 cm^3 of $M/40$ HCl ≡ 25 cm^3 of $M/40$ NaOH

Volume of $M/40$ NaOH required for neutralisation of the excess hydrochloric acid

= V_t (say)

Acid used for the neutralisation of unreacted NaOH in 10 cm^3 of the reaction mixture } = $(25 - V_t)$ cm^3 of $M/40$ NaOH

Concentration of unreacted NaOH in the reaction mixture

$$= (c_o - x) = \frac{(25 - V_t)}{10} \cdot \frac{M}{40} = \frac{(25 - V_t)}{400} M \qquad \ldots (15.34)$$

Since equal volumes of $M/40$ ester and $M/40$ alkali are mixed, initial concentration of NaOH = $c_o = M/80$ … (15.35)

Using Eqs. 15.33 to 15.35,

$$\frac{400}{(25 - V_t)} = 80 + kt \quad \text{(without mentioning units)} \qquad \ldots (15.36)$$

or $$k = \frac{1}{t}\left(\frac{400}{(25-V_t)} = 80\right) \quad \ldots (15.37)$$

Hence by substituting V_t at different time intervals, k can be calculated (using Eq. 15.37). Also by plotting $(400/(25-V_t))$ against t, a straight line will be obtained, the slope being equal to k.

$$\text{Slope} = k \quad \ldots (15.38)$$

15.5.2 Requirements

Apparatus		**Chemicals**
Burette (50 cm^3)	– 1	Ethyl acetate
Pipettes (10 cm^3)	– 2	Sodium hydroxide
Beaker (250 cm^3)	– 1	Hydrochloric acid
Conical flask (250 cm^3)	– 1	Phenolphthalein
Conical flasks (100 cm^3)	– 2	Ice (from deionized water)
Water trough/Thermostat	– 1	
Thermometer	– 1	
Stopwatch	– 1	

Solutions that are provided:

1. $M/40$ ethyl acetate
2. $M/40$ NaOH
3. $M/40$ HCl
6. Phenolphthalein solution (for use as indicator)

Details for the preparation of the solution are given in Appendix.

15.5.3 Procedure

1. Bring to your work table all the required apparatus and solutions as given under Sec. 15.5.2.
2. Keep approximately 250 cm^3 of $M/40$ HCl in ice for cooling.
3. Withdraw 50 cm^3 of $M/40$ ester (from the burette kept commonly for the class) into a 250 cm^3 conical flask.
4. Rinse and fill your burette with $M/40$ NaOH.
5. Withdraw from the burette 50 cm^3 of $M/40$ NaOH into a 250 cm^3 beaker and fill the burette again.
6. Keep the conical flask containing the ester solution and the beaker containing NaOH in a water trough (or thermostat) and note the temperature.
7. Start the reaction only after HCl (that has been kept for cooling) has reached a temperature near 5° C.
8. Start the reaction by pouring NaOH (in the beaker) into the ester solution (in the flask) and note the time simultaneously. Mix well by pouring from one into the other.
9. Pipette 25 cm^3 of ice cold HCl into a 100 cm^3 conical flask. Pipette 10 cm^3 of the reaction mixture into this HCl, noting the time when the pipette is half empty. Add a drop of phenolphthalein and titrate with $M/40$ NaOH.
10. Repeat the sampling and titration at 5 minutes intervals initially and increase the intervals gradually to 20 minutes. Take in all 8 – 9 readings.
11. Enter the burette readings and time in Observation table VI.

100 cm^3 of the reaction mixture contains

(i) 50 cm^3 of $M/40$ NaOH solution (in 250 cm^3 beaker) and

(ii) 50 cm^3 of $M/40$ ester (in 250 cm^3 conical flask)

15.5.4 Observation

Temperature of the reaction mixture=°C

V_t in Observation Table VI refers to the volume of $M/40$ NaOH required for neutralisation of excess acid.

Observation Table VI

t/s	Burette reading Initial Final	$\frac{V_t}{\text{cm}^3}$

15.5.5 Calculation

Five values of rate constants are calculated using Eq. 15.37 and their average is found out:

(i) $k =$ .... $M^{-1}\,s^{-1}$
(ii) $k =$ .... $M^{-1}\,s^{-1}$
(iii) $k =$ .... $M^{-1}\,s^{-1}$
(iv) $k =$ .... $M^{-1}\,s^{-1}$
(v) $k =$ .... $M^{-1}\,s^{-1}$
Average $k =$ .... $M^{-1}\,s^{-1}$

A plot of $\frac{400}{(25-V_t)}$ against t (graph X) is made

As per Eq. 15.38, $k =$ slope
= .... $M^{-1}\,s^{-1}$

15.5.6 Result

The rate constant for the saponification of ester (by titrimetry)

(i) by calculation = ... $M^{-1}\,s^{-1}$
(ii) by graphical method =.. $M^{-1}\,s^{-1}$

15.5.7 Precaution

Ethyl acetate solution should be prepared the day it is to be used because slow hydrolysis reaction occurs even in the absence of OH^- ions.

15.6 EXPERIMENT 21 : KINETICS OF SAPONIFICATION OF ESTER – CONDUCTOMETRY

15.6.1 Principle

In the previous experiment, we followed the saponification of ester volumetrically by titrating the alkali remaining unreacted in the reaction mixture, as the reaction progresses. In this experiment, we will be following the same reaction by measuring the conductance of the reaction mixture. As the reaction progresses, OH^- ions are replaced by acetate ions which have a much lower conductance (i.e.) ($\frac{1}{5}$ th that of OH^-). Consequently the conductance of the reaction mixture falls. The change in the conductance is approximately proportional to the amount of reaction that has taken place.

In this experiment, equal concentrations of the ester and alkali will be taken just as in the case of last experiment. We shall assume that the reaction is first order in each reactant and find out the second order rate constant. Thus Eqs. 15.30 to 15.33 hold good for this experiment also. We shall rewrite Eq. 15.33 for use in this experiment.

$$\frac{1}{(c_0-x)} = \frac{1}{c_0} + kt \qquad \ldots (15.33)$$

Once we relate the conductance values to (c_0-x) and c_0, we can calculate k. Let us first see the outline of the experiment.

The reaction mixture is prepared by mixing $M/40$ solution of ethyl acetate and $M/40$ solution of sodium hydroxide, noting the time simultaneously. Then the conductance values, G_t, of the reaction mixture are measured at definite time (t) intervals. If G_0 and G_∞ are the conductances of the reaction mixture at $t=0$ and at $t = \infty$ (end of the reaction) respectively, then

$$c_0 - x \text{ is proportional to } (G_t - G_\infty) \qquad \ldots (15.39)$$
$$\text{and} \quad c_0 \text{ is proportional to } (G_0 - G_\infty)$$

Introducing Q as the constant of proportionality, we write,

$$(c_0-x) = Q\,(G_t - G_\infty) \qquad \ldots (15.40)$$
$$\text{and} \quad c_0 = Q\,(G_0 - G_\infty)$$

The value of Q can be obtained from Eq. 15.40 since c_0 and (c_0-x) (i.e., the concentration OH^- at the start of the reaction and after a time, t) as also G_t ,G_0 and G_∞ are known.

Substituting for $[OH^-]$ in terms of conductance values from Eq.15.40 into Eq.15.33, we get,

$$\frac{1}{(G_t - G_\infty)} = \frac{1}{(G_0 - G_\infty)} + Qkt \qquad \ldots (15.41)$$

It is possible to calculate k using Eq. 15.41. In order to obtain k by graphical method, $1/(G_t - G_\infty)$ values are plotted against t. The rate constant, k, is obtained from the straight line plot.

$$\text{Slope} = Qk \qquad k = \text{Slope}/Q \qquad \ldots (15.42)$$

15.6.2 Requirements

Apparatus		**Chemicals**
Conductometer	– 1	Ethyl acetate
Conductivity cell	– 1	Sodium hydroxide
Stopwatch	– 1	Acetic acid
Thermometer	– 1	Phenolphthalein
Pipette (50 cm^3)	– 1	Deionized water
Pipette (25 cm^3)	– 1	
Volumetric flasks (100 cm^3)	– 2	
Beakers (250 cm^3)	– 2	
water trough/Thermostat	– 1	
Wash bottle		

Details for the preparation of the solution are given in Appendix.

Solutions that are provided for the experiments(a) and (b):

1. *M*/40 ester solution
2. *M*/40 NaOH
3. 0.1 *M* acetic acid
4. Phenolphthalein indicator solution

15.6.3 Procedure

1. Bring to your work - table all the required apparatus and solutions as given under 15.6.2.
2. Prepare *M*/80 NaOH by pipetting 50 cm^3 of *M*/40 NaOH into a 100 cm^3 volumetric flask and making upto the mark with deionised water. Leave this flask in a water trough (or a thermostat).
3. Prepare *M*/80 sodium acetate by pipetting 50 cm^3 of *M*/40 NaOH into a 100 cm^3 volumetric flask. Add a drop of phenolphthalein and titrate this with 0.1 *M* acetic acid till the solution turns colour less. Then make up this solution to the mark with deionised water. Leave this flask too in the water trough (or thermostat).
4. During the time taken by the solutions of sodium hydroxide and sodium acetate to come to the temperature of the bath, get the solutions of ester and NaOH required for the kinetic run ready. Pipette 25 cm^3 of *M*/40 ester into a 250 cm^3 beaker. Then pipette 25 cm^3 of *M*/40 NaOH into another 250 cm^3 beaker. Allow these beakers to stand in a water trough (or a thermostat).

50 cm^3 of the reaction mixture contains

(i) 25 cm^3 of *M*/40 ester (in a 250 cm^3 beaker) and
(ii) 25 cm^3 of *M*/40 NaOH (in another beaker)

5. Connect the conductometer to the mains and to the conductivity cell. Switch on the conductometer keeping the mode selector at CAL. Set the range selector at 20. Adjust the sensitivity control to set the meter reading to mid scale. After this adjustment, do not disturb the sensitivity control.
6. Rinse and fill the conductivity cell with *M*/80 NaOH. Shift the mode selector to READ, note the conductance of the solution (G_0) and enter under observations.
7. Shift the mode selector to CAL. Rinse and fill the conductivity cell with *M*/80 sodium acetate. Shift the selector to READ, note the conductance (G_∞) and enter under observations. Shift to CAL.
8. Pour 25 cm^3 of *M*/40 NaOH in the beaker into the other beaker containing 25 cm^3 of *M*/40 ester solution, noting the time simultaneously. Mix the solutions well by pouring from one beaker to the other. Rinse and fill the conductivity cell with this reaction mixture.
9. Shift the knob to READ. Note the conductance of the reaction mixture at frequent time intervals. Take 12–15 readings of conductance (G_t) and time (t) and enter these in Table VII.

Note :

It is more convenient and accurate to read the time for certain conductance values than to read the conductance for certain time values. By this we can avoid making approximate estimates of conductance when the meter needle is in between two divisions. Read the time when the meter needle is against a division.

10. Note the temperature of the thermostat and enter under observations.

15.6.4 Observation

Temperature of the reaction mixture = °C
Conductance of M/80 sodium hydroxide solution (G_0) = mS
Conductance of M/80 sodium acetate solution (G_∞) = mS

Observation Table VII

G_t/mS	t/s	$(G_t - G_\infty)$/mS	$(G_t - G_\infty)$/mS

15.6.5 Calculation

Using Eq. 15.40, (i) $Q = \dfrac{(c_0 - x)}{(G_t - G_\infty)}$

$= M \text{ mS}^{-1}$

(ii) $Q = \dfrac{c_0}{(G_0 - G_\infty)}$

Average value of $Q = M \text{ mS}^{-1}$

Using Eq. 15.41, five k values are calculated.

(i) $k =$ .... $M^{-1}\,s^{-1}$
(ii) $k =$ .... $M^{-1}\,s^{-1}$
(iii) $k =$ .... $M^{-1}\,s^{-1}$
(iv) $k =$ .... $M^{-1}\,s^{-1}$
(v) $k =$ .... $M^{-1}\,s^{-1}$
Average $k =$ .... $M^{-1}\,s^{-1}$

$1/(G_t - G_\infty)$ is plotted against t (Graph xi). The slope of the straight line is calculated.

Using Eq. 15.42, $k =$ Slope/Q

$=$ .... $M^{-1}\,s^{-1}$

15.6.6 Result

The rate constant for the saponification of ester (by conductometry);

(i) by calculation = ... $M^{-1}\,s^{-1}$
(ii) by graphical method = ... $M^{-1}\,s^{-1}$

15.6.7 Precaution

Ethyl acetate solution should be prepared the day it is to be used because a slow hydrolysis reaction occurs even in the absence of OH^- ions.

15.7 SUMMARY

In this unit, we have described the procedure for five experiments in kinetics. Of these, three are based on titrimetry, one each on colorimetry and conductometry. These experiments illustrate the use of integrated rate equations in obtaining the order of the reaction and/or rate constant. These experiments also illustrate the method of following reactions obeying zeroth order, first order and second order kinetics. The preparation of solutions used in Experiments 17–21 is discussed in the next section.

15.8 APPENDIX

Preparation of Solutions for Experiments 17(a) – (c) and 18 :

1. $0.05\ M\ I_2$ in $0.4\ M$ KI (approximately) :
   Weigh 12.7 g of iodine and place this in a 250 cm^3 beaker. Add to the beaker, 66.4 g of KI and approximately 40 cm^3 of deionised water. Stir to dissolve all the iodine and, transfer the solution to a 1 dm^3 volumetric flask and make up to the mark with deionised water.

2. 2 *M* HCl (approximately) :
   Transfer in small lots 180 cm^3 of concentrated hydrochloric acid (11 *M*) using a measuring cylinder to a 1 dm^3 volumetric flask which contains approximately 500 cm^3 of deionised water. Shake the flask after the addition of each lot. Make up to the mark with deionised water. Let us call this solution by the name, hydrochloric acid (A). To know the molarity of solution (A) exactly, let us dilute the solution by 20 times (10 cm^3 of A diluted to 200 cm^3). Let this be called solution (B). Let us titrate solution (B) against 0.1 *M* sodium carbonate solution using methyl orange indicator. If the molarity of hydrochloric acid (B) is *p*, then the molarity of hydrochloric acid (A) is 20 *p*.

For the purpose of standardisation of HCl solution (B), 250 cm^3 of sodium carbonate solution is prepared by weighing accurately about 1.325 g sodium carbonate, dissolving in minimum quantity of water and making up to the mark in a 250 cm^3 standard flask.

3. 1 *M* HCl :
   To prepare 1 *M* HCl (accurately) from hydrochloric acid (A), the following procedure is adopted. Transfer ($1000/20\,p = $) $50/p$ cm^3 of hydrochloric acid (A) into a 1 dm^3 standard flask and make up to the mark with deionised water. The resultant solution is 1 M HCl.

4. 0.10 *M* $NaHCO_3$ (approximately) :
   Weigh 33.6 g $NaHCO_3$ and transfer to a 5 dm^3 bottle or jar. Add 4 dm^3 of deionised water in small lots, dissolve $NaHCO_3$ and shake the solution well. As this solution is used only for quenching, the molarity need not be exact. Hence one can make this solution in any big bottle (5 dm^3) or plastic jar. One need not look for a volumetric flask.

5. 0.01 *M* $Na_2S_2O_3$ (approximately) :
   Weigh 4.96 g of $Na_2S_2O_3.5H_2O$ and transfer to a 2 dm^3 volumetric flask. Dissolve and make up to the mark with deionised water. Prepare this solution on the day the experiment is to be done. Standardise this solution with standard $K_2Cr_2O_7$ titrimetrically.

For the purpose of standardisation of sodium thiosulphate, 0.01 *M* $K_2Cr_2O_7$ (about 0.7356 g solid $K_2Cr_2O_7$ weighed accurately, dissolved and made up to 250 cm^3) is prepared. 20 cm^3 of standard $K_2Cr_2O_7$ solution is treated with 10 cm^3 of 10% KI solution and the liberated iodine is titrated using sodium thiosulphate solution prepared above. The titration is carried out till straw yellow coloured solution is obtained, whereby a few drops of 1% starch solution is added. A blue colour develops due to starch – iodine complex and the titration is conducted till the blue colour disappears leaving a green coloured solution. From the titre values, the molarity of sodium thiosulphate can be calculated.

6. 1% Starch solution :
   Heat about 900 cm^3 of deionised water in a beaker. Then make a paste of 10 g of soluble starch and 100 cm^3 of deionised water. Pour this gradually with stirring into the boiling water and, continue boiling for a few minutes. Then cool the solution. Starch solution should always be prepared just before use.

7. Acetone :
   Acetone is to be used as such for Experiments 17(a) - (c). But, for Experiment 18, 4 *M* acetone is to be used. The preparation of 4 M acetone is done as follows:

   Using a burette, transfer 73.5 cm^3 of acetone into a 250 cm^3 flask and, make up the solution to mark with deionised water.

Preparation of Solutions for Experiment 19 :

For this experiment, the concentration of the following solutions need not be known exactly.

1. 0.5 *M* HCl :
   Transfer 45 cm^3 of concentrated hydrochloric acid (11 *M*) using a measuring cylinder to a 1 dm^3 volumetric flask which contains approximately 500 cm^3 of deionised water. Shake the flask after the addition of each lot. Make up to the mark with deionised water.

2. 0.125 *M* NaOH :
   Dissolve 10 g sodium hydroxide pellets in 2 dm^3 of deionised water kept in a 5 dm^3 jar.

3. Phenolphthalein indicator solution :
   Dissolve 5 g of phenolphthalein in 500 cm^3 of ethanol. Add 500 cm^3 of water stirring it constantly. Filter the solution, if there are any solid particles.

Preparation of Solutions for Experiments 20 & 21

1. *M*/40 $CH_3COOC_2H_5$:

Pipette 4.9 cm^3 of ethyl acetate into a 2 dm^3 flask containing some deionised water and then make up to the mark with deionised water. This solution should be prepared on the day it is to be used because a slow reaction takes place even in the absence of OH^- ions.

If 4.9 cm^3 of ester is made up to 2 dm^3 in a standard flask, the molarity of ester can be calculated knowing that density of ester is 0.90 g/cm^3 and its molar mass is 88 g/mol.

$$\text{Molarity of ester} = \frac{\text{Mass of ester}}{\text{Molar mass} \times \text{Volume of the solution in } dm^3} = \frac{4.9 \times 0.9}{88 \times 2} M = 0.025\ M$$

If you want to prepare a more exact solution of ester, then adopt the following procedure. This method also reduces error due to the volatalisation of the ester. Take a clean dry weighing bottle and weigh it with some deionised water. Pipette 4.9 cm^3 of the ester into the weighing bottle and weigh it again. Transfer the ester solution carefully into a 2 dm^3 volumetric flask, repeatedly wash the weighing bottle with deionised water and transfer the washings also into the standard flask. Finally make up the solution to the mark.

$$\text{The molarity of ester} = \frac{\text{Mass of ester}}{\text{Molar mass of ester} \times \text{Volume of solution in } dm^3}$$

2. 0.1 *M* NaOH (approximately) :
   Prepare an approximately 0.1 M NaOH solution by dissolving 8 g (weighed approximately on a rough balance) of sodium hydroxide pellets and dissolving in 2 dm^3 of deionised water. The exact strength of this solution is found by titrating against a standard solution of potassium hydrogen phthalate. Let the molarity of this solution be *p*.

3. *M*/40 NaOH :
   To prepare M/40 NaOH solution, (2000/40*p* cm^3 =) 50/*p* cm^3 of sodium hydroxide solution of molarity p prepared above, is taken in a 2 dm^3 standard flask, made up to the mark with deionised water and shaken well. The resultant solution is *M*/40 NaOH.

For the purpose of standardisation of NaOH solution, 0.1 M potassium hydrogen phthalate is prepared by weighing accurately about 5.105 g potassium hydrogen phthalate (molecular weight : 204.2), dissolving it in water and making up to 250 cm^3. Phenolphthalein is to be used as indicator for the titration between potassium hydrogen phthalate and sodium hydroxide. From the titre values, the molarity of sodium hydroxide solution (say, p) is calculated.

4. *M*/40 HCl :
   Transfer 4.5 cm^3 of concentrated HCl (11 *M*) using a measuring cylinder to a 2 dm^3 volumetric flask which contains approximately 1 dm^3 deionised water and shake the flask. Make up to the mark with deionised water. Standardise this acid using *M*/40 NaOH solution prepared above and phenolphthalein indicator.

5. Phenolphthalein indicator solution :
   This is to be prepared as given in Experiment 19.

6. 0.1 *M* acetic acid :
   Using a burette, transfer 7.5 cm^3 of glacial acetic acid into a 250 cm^3 volumetric flask containing 100 cm^3 of water and make up the solution to the mark. This solution (say, acetic acid (A)) is approximately 0.5 *M*. 20 cm^3 of this solution is diluted to 100 cm^3 in a standard flask to obtain acetic acid

(B). The molarity of acetic acid (B) is found out by titrating against standardised p molar solution of sodium hydroxide prepared above using phenolphthalein indicator. If the molarity of acetic acid (B) is y, then the molarity of acetic acid (A) is $5y$.

To prepare 250 cm^3 of 0.1 M acetic acid, $(250 \times 0.1/5y =)$ $5/y$ cm^3 of acetic acid (A) is diluted to 250 cm^3 in a standard flask.