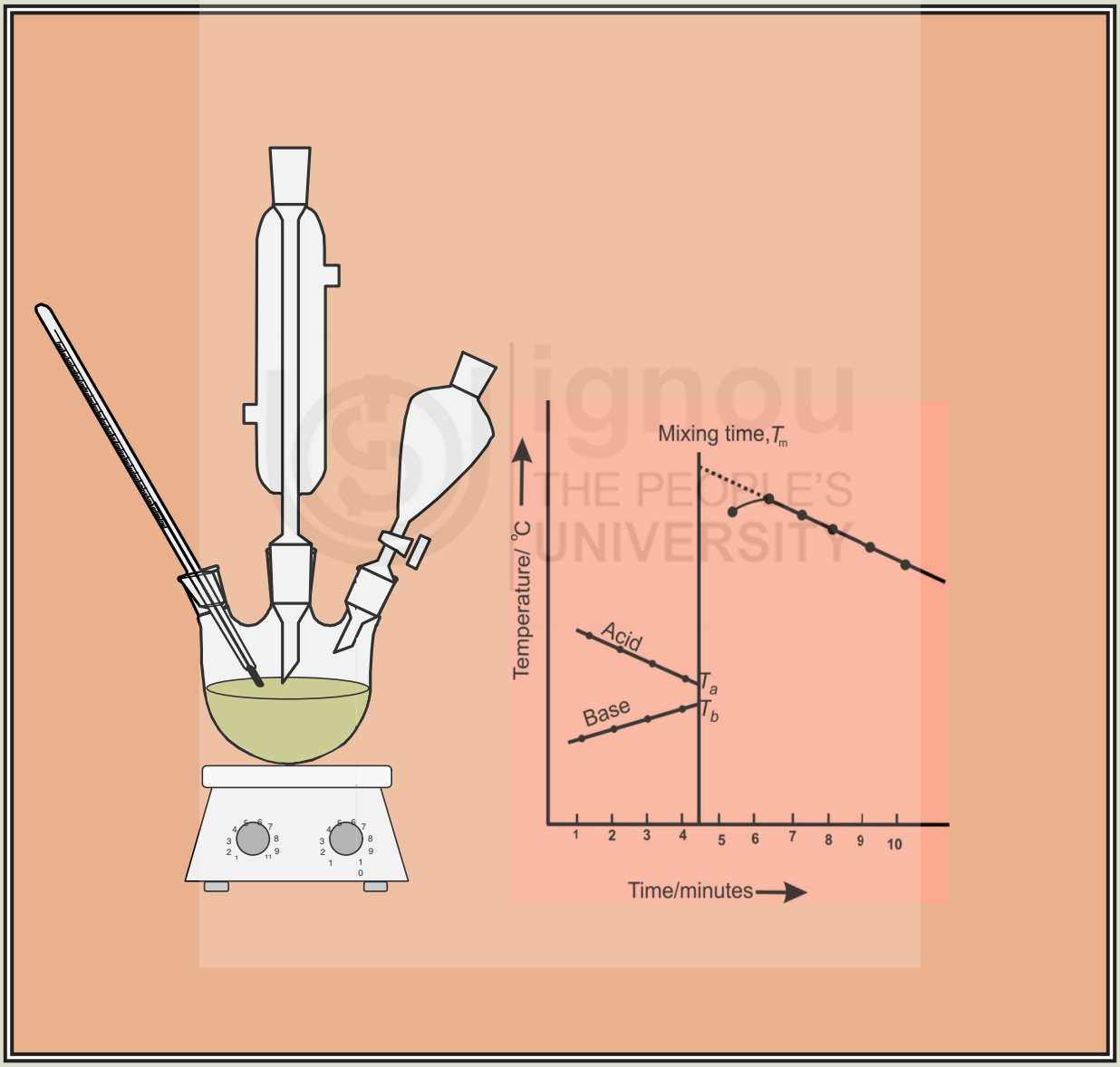
Indira Gandhi National
Open University
School of Sciences

BCHCL-134

CHEMISTRY LAB-II: CHEMICAL ENERGETICS, EQUILIBRIA AND FUNCTIONAL ORGANIC CHEMISTRY-I



''शिक्षा मानव को बन्धनों से मुक्त करती है और आज के युग में तो यह लोकतन्त्र की भावना का आधार भी है। जन्म तथा अन्य कारणों से उत्पन्न जाति एवं वर्गगत विषमताओं को दूर करते हुए मनुष्य को इन सबसे ऊपर उठाती है।''

– इन्दिरा गाँधी

''Education is a liberating force, and in our age it is also a democratising force, cutting across the barriers of caste and class, smoothing out inequalities imposed by birth and other circumstances.''

– Indira Gandhi

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SECTION A

UNIT 1
Thermochemistry and Determination of Enthalpy of Neutralisation 7

EXPERIMENT 1A
Determination of the Heat Capacity of a Calorimeter 13

EXPERIMENT 1B
Determination of the Enthalpy of Neutralisation of Hydrochloric Acid with Sodium Hydroxide 17

EXPERIMENT 2
Determiantion of Enthalpy of Ionisation of a Weak Acid 21

EXPERIMENT 3
Determination of the Integral Enthalpy of Solution of Ammonium Chloride/Potassium Nitrate 26

EXPERIMENT4
Determination of Enthalpy of Hydration of Anhydrous Copper Sulphate 31

EXPERIMENT 5
Determination of Dissolution Enthalpy of Benzoic Acid by Studying Temperature Dependence of its Solubility 44

EXPERIMENT 6
Measurement of pH of Aerated Drinks, Fruit Juices, Soaps and Shampoos using pH Metre 53

EXPERIMENT 7
Preparation & Measurement of pH Values of Buffer Solutions and their Comparison with theoretical Values 60

SECTION B

UNIT 2
Techniques in Organic Laboratory 67

EXPERIMENT 8
Purification of Organic Compounds by Recrystallisation and Distillation 85

EXPERIMENT 9
Criteria of Purity: Determination of Melting and Boiling Points 97

EXPERIMENT 10
Bromination of Aniline 107

EXPERIMENT 11
Benzoylation of Phenols 117

EXPERIMENT 12
Preparation of Oxime and Phenylhydrazone 125

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CHEMISTRY LAB II: CHEMICAL ENERGETICS, EQUILIBRIA AND FUNCTIONAL ORGANIC CHEMISTRY-I

Welcome to the Second Semester laboratory course in chemistry. This manual gives the procedural details of various experiments you are required to perform in the course of this lab work. Appropriate conceptual basis has also been laid for each experiment to make this manual complete in itself.

This Laboratory manual has two sections. Section A deals with experiments in physical chemistry and Section B with experiments in organic chemistry. There are seven experiments in the Section A. First six experiments of this section are based on thermochemistry. These experiments explain how to determine the enthalpies of solution, neutralisation, ionisation, hydration and dissolution. Last two experiments provides procedural detail for the measurement of pH of some commercial products such as aerated drinks, fruit juices, soaps, shampoos and buffer solutions using pH-meter.

In Section B, various preparatory techniques along with some organic preparations have been discussed. You are going to use simple laboratory techniques such as heating, cooling, stirring and filtration as well as separation and purification techniques like crystallisation and distillation. You are also going to perform five experiments based on organic preparations.

All the twelve experiments of this course are to be performed in about six days.

Expected Learning Outcomes

After studying this course and performing the given experiments, you will be able to:

- explain the basic concepts pertaining to thermochemistry;
- define the enthalpies of solution, enthalpy of neutralization, ionisation, hydration and explain the methods of their determination;
- state the principles involved in measurement of pH,
- record observations and calculate the results after performing the experiments of Section A;
- describe basic preparatory techniques such as heating, cooling, stirring and filtration;
- explain the basic principles involved in separation and purification techniques;
- select and use appropriate apparatus and techniques for various types of experiments related to chemistry given in Section B organic;
- perform experiments related to organic preparations; and
- maintain laboratory records for the experiments performed during this course.

Study Guide

The general pattern of discussion of experiments in this course is similar to that of 1st semester Chemistry Lab I (BCHCL-132) course. In this lab course, you would be doing twelve experiments. In this course, the performance of the experiments, recording the data, calculations and expression of result are to be done as in earlier chemistry lab course. The

maintenance of Laboratory note book may be done as per the detail guidelines given for each Section. Some general guidelines for the maintaining Laboratory note book are given on next page. Remember that each experiment is going to be evaluated. Hence, read the Lab manual before going the laboratory for performing the experiments. This will help you in doing experiment in a proper way.

We want you to share the thrill of learning by doing. There is no better way to learn.

So, Best of Luck.

Laboratory Notebook

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 points may be kept in mind.

- A bound note book should be used for laboratory record. You may use a laboratory record 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.
- 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 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.
- The detailed calculations are to be shown.
- Results and conclusions drawn should be summarised 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.

IMPORTANT

- **Attendance** is compulsory in the Laboratory Course work held generally at the Study Centre.
- The Laboratory Course is worth **2 credits** to be completed over **7 days** duration:
  - **6 days** of the **Guided** Laboratory work
  - **1 day** of the **Unguided** Laboratory work
- To successfully complete the laboratory course you will have to pass (at least **35% marks**) in the Guided and Unguided components separately.

UNIT 1

THERMOCHEMISTRY AND DETERMIANTION OF ENTHALPY OF NEUTRALISATION

Structure

1.1 Introduction

Objectives

1.2 Some Fundamental Concepts

1.3 The First Law of Thermodynamics

1.4 The Enthalpy of a Reaction

1.5 The Enthalpy of Neutralisation

1.6 Experiment 1a: Determination of the Heat Capacity of the Colorimeter

Principle

Requirements

Procedure

Observations

Calculations

Result

1.7 Experiment 1b: Determination of the Enthalpy of Neutralisation of Hydrochloric Acid with Sodium Hydroxide

Principle

Requirements

Procedure

Observations

Calculations

Result

1.8 Answers

1.1 INTRODUCTION

This is the first unit of this course. In this unit, you will study about the heat changes associated with chemical reactions and physical processes. You are aware that the 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**. There are many 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 dealing with the determination of enthalpy of neutralisation.

We will be first explaining some fundamental concepts of thermodynamics. We will describe the first law of thermodynamics and discuss about the enthalpy of a reaction. After that we shall discuss the actual determination of enthalpy of neutralisation heat of solution.

Expected Learning Outcomes

After studying this unit and having the experiments performed, you should be able to:

- ❖ explain various terms used in thermochemical studies;
- ❖ state the first law of thermodynamics;
- ❖ define the enthalpy of a reaction;
- ❖ define the enthalpy (heat) of neutralization;
- ❖ explain how to determine the heat capacity of a calorimeter;
- ❖ determine ΔH_{neut} for the neutralisation of a strong acid with a strong base; and
- ❖ give reason for the constant value of ΔH_{neut} for the neutralisation of a strong acid with a strong base.

A reaction in an open beaker is an example of an **open system** as **both m**atter and energy transactions are possible with the surroundings.

A reaction in a closed flask is an example of a c**losed 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. B**oth matter and energy transactions with the surroundings are **not** allowed.

1.2 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 bold 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.

1.3 THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics deals with the **conservation of energy**. It states *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 $(\mathrm{d}q)$ 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** $\mathrm{d}q$ and a decrease the in internal energy of the system.

Similarly, if the work $(\mathrm{d}w)$ is done **on the system**, it is said to be **positive** because it **increases** the internal energy of the system. On the other hand, when work is done **by the system**, $\mathrm{d}w$ is said 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 $(\mathrm{d}U)$, when it absorbs $\mathrm{d}q$ amount of heat and a work $\mathrm{d}w$ is done on it, can be given as.

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w \text{ (for infinitesimal changes)} \qquad \ldots(1.1)$$

For larger changes, we can say that

$$U = q + w \qquad \ldots(1.2)$$

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 neutralisation reactions.

1.4 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:

$$\begin{array}{ccc} R & \longrightarrow & P \\ T_1 & & T_2 \end{array} \qquad \ldots(1.3)$$

To restore the system to its initial temperature (T_1), heat must flow either *to* 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 temperature (T_1). In this case, the reaction is called **exothermic** and by convention, the 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 temperature. 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. 1.2 heat transfer 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,

$$\begin{array}{ccc} R & \longrightarrow & P \\ T_1, V & & T_2, V \end{array} \qquad q_v = \Delta U \qquad \ldots(1.4)$$

$$\begin{array}{ccc} R & \longrightarrow & P \\ T_1, p & & T_2, p \end{array} \qquad q_p = \Delta H \qquad \ldots(1.5)$$

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 $p\,dV$ is the work done by it, then according to Eq. 1.2 the change in internal energy can be written as follows:

$$\Delta U = q_p + (-p\,dV) \qquad \ldots(1.6)$$

where q_p is the heat absorbed at constant pressure and $-\,p\,dV$ 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. The, Eq. 1.6 can be written as,

$$U_2 - U_1 = q_p - p(V_2 - V_1)$$

$$= q_p - pV_2 + pV_1$$

rearranging, we get,

$$q_p = (U_2 + pV_2) - (U_1 + pV_1) \qquad \ldots(1.7)$$

At this stage, we can represent $U + pV$ by H, the enthalpy. Thus, we can rewrite Eq. 1.7 as,

$$q_p = H_2 - H_1 = \Delta H \qquad \ldots(1.8)$$

Work could be of various varieties: mechanical, volume-expansion, compression, surface increase, electrical, gravitational etc.

Since U, p and V are state variables, H is also a state variable. Thus, by Eq. 1.8, 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) and pressure (p) to products at the same initial temperature (T) and pressure (p):

$$\begin{array}{ccc} \mathrm{R} & \longrightarrow & \mathrm{P} \\ T, p & & T, p \end{array} \qquad \Delta H_r \qquad \ldots(1.9)$$

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 1^0C is called the **heat capacity**. The symbol for heat capacity is C and it can be expressed by the following relation:

$$C = \frac{\mathrm{d}q}{\mathrm{d}T} \qquad \ldots(1.10)$$

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. 1.8, you know that heat absorbed at constant pressure is equal to change in enthalpy. Then, substituting dq is Eq. 1.10 by ΔH, we get,

$$C_p = \frac{\Delta H}{\mathrm{d}T} \qquad \text{or} \qquad \Delta H = C_p \mathrm{d}T \qquad \ldots(1.11)$$

Having understood the above concepts, you can now proceed to the next section which explains enthalpy of neutralisation.

1.5 THE ENTHALPY OF NEUTRALISATION

The **enthalpy of neutralization** (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 neutralisaiton 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

$$\mathrm{HCl\,(aq)} \longrightarrow \mathrm{H^+(aq) + Cl^-\,(aq)}$$

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 $HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O$

$$\Delta H_{neut} = -57.3\,kJ\ mol^{-1}$$

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.

To determine the enthalpy changes associated with reactions, we use the following **principle of calorimetry**.

Heat lost by one part of the system = Heat gained by the other part of the system

Using this principle, you will be performing thermochemical experiments by using an isolated system such as a calorimeter kept in a thermos flask.

The experimental determination of the integral enthalpy of neutralisation involves the measurement of rise or fall in temperature during the reaction (or the process) using a container called **calorimeter** as mentioned above. A calorimeter, when kept in a thermos flask is insulated from outside so that no heat is lost to or gained from the surroundings.

The calorimeter could be made of stainless steel or copper plated with gold. For most practical purposes, glass beakers are used as calorimeters. In case of glass calorimeters, due to the poor thermal conductivity of glass, heat capacity actually varies with the area of the glass in contact with the liquid content. It is, therefore, essential to calibrate the calorimeter with the volume of water that is to be used in subsequent experiments.

The following two methods are generally adopted for determining the heat capacity of the calorimeter: (1) Dilution method, (2) Heat exchange method. Here, we will discuss the second method in detail because you will be actually

using this method for experimental determination of heat capacity of the calorimeter. So, let us begin with the details of this experiment.

1.6 EXPERIMENT 1A: DETERMINATION OF THE HEAT CAPACITY OF A CALORIMETER

1.6.1 Principle

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. Thus,

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. 1.11, 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:

$$[C_p(\text{cold water}) + C_p(\text{calorimeter})]\,[T_m - T_c] = C_p(\text{hot water})[T_h - T_m] \quad \ldots(1.12)$$

The left hand side of Eq. 1.12 is obtained from Eq. 1.11 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. 1.12, 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

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:

$$[m \times s\,(\text{cold water}) + C_p\,(\text{calorimeter})]\,[T_m - T_c] = m \times s\,[\text{hot water}][T_h - T_m] \quad \ldots(1.13)$$

We assume that,

s (cold water) = s (hot water) = s (say)

In other words, specific heat of water is taken to be constant irrespective of the temperature.

Hence, Eq. 1.13 becomes,

$$[ms + C_p(\text{calorimeter})][T_m - T_c] = ms(T_h - T_m) \quad \ldots(1.14)$$

$$\therefore \quad ms + C_p(\text{calorimeter}) = ms\,\frac{(T_h - T_m)}{(T_m - T_c)}$$

Specific heat (s) is the heat required to raise the temperature of 1g (0.001 kg) of a substance through 1^0C.

For a calorimeter, the product of the two quantities, viz., the mass and its specific heat (m x s) is also known as its **water equivalent. *W*.**

$$C_p(\text{calorimeter}) = ms\frac{(T_h - T_m)}{(T_m - T_c)} - ms$$

$$= ms\left[\frac{(T_h - T_m)}{(T_m - T_c)} - 1\right] \quad \ldots(1.15)$$

We shall now discuss the values of *m* and *s* individually.

Value of *m*

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 × 10^{-3} kg
× 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

(1cm)^3 = (10^{-1} dm)^3

= 10^{-3} dm^3

We know that mass of a substance = volume × density. The density of water is 1kg dm^{-3}. You will be measuring the volume in cm^3 units. But you should express the volume dm^3 in units for compatibility of units.

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

Volume of cold water = Volume of hot water = V cm^3

$$= \frac{V}{10^3} \text{ dm}^3$$

Hence, mass of cold water (m)

= mass of hot water (m)

= Volume × density

$$= \frac{V}{10^3} \text{ dm}^3 \times d_w \text{ kg dm}^{-3}$$

i.e. $$m = \frac{V}{10^3} d_w \text{ kg} \quad \ldots(1.16)$$

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.,

$$s = 4.185 \times 10^3 \text{ J K}^{-1} \text{ kg}^{-1} \quad \ldots(1.17)$$

Substituting Eqs. 1.16 and 1.17 in Eq. 1.15, we get,

$$C_p(\text{calorimeter}) = \frac{V.d_w}{10^3} \text{ kg} \times 4.185 \times 10^3 \text{ J K}^{-1}\text{Kg}^{-1}\left[\frac{T_h - T_m}{T_m - T_c}\right]$$

$$C_p(\text{calorimeter}) = 4.185 V d_w \left[\frac{T_h - T_m}{T_m - T_c} - 1\right] \text{J K}^{-1} \quad \ldots(1.18)$$

Having measured the volume in cm^3 units, you substitute it as such in Eq. 1.18 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.

1.6.2 Requirements

Apparatus			Chemicals
Thermos flask	—	1	only water is needed
Glass Stirrer	—	1	
Thermometer – 110^0C ($1/10^0C$)	—	1	
Stop watch or stop clock	—	1	
Beaker 250/400 cm^3	—	2	
Measuring cylinder 100 cm^3	—	1	

1.6.3 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.**

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. 1.1. 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. 1.18.

Repeat the experiment to get reproducible results.

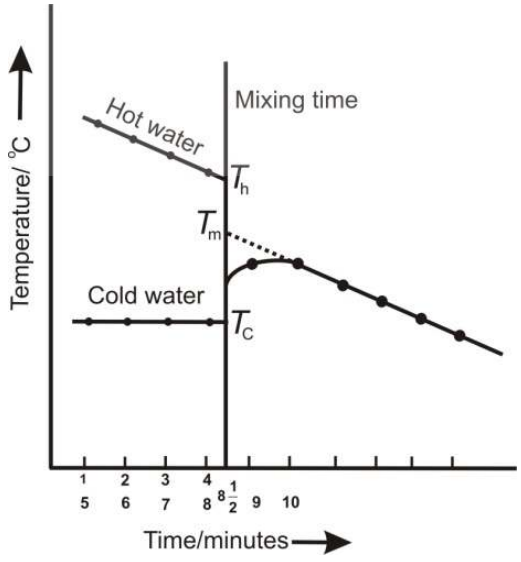


Fig. 1.1 Temperature-time curve.

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. 1.1.

1.6.4 Observations

SET I

Volume of cold water, $V = 100\,\text{cm}^3 = 0.1\,\text{dm}^3$

Volume of hot water, $V = 100\,\text{cm}^3 = 0.1\,\text{dm}^3$

Temperature – time data for cold, hot water and the mixture:

Time/s	Temperature/^{o}C		Time/s	Temperature/^{o}C Mixture
	Cold Water	Hot Water		
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....

Time of mixing = ...S

SET II: Similar observations as reported above.

Time/s	Temperature/^{o}C		Time/s	Temperature/^{o}C (Mixture)
	Cold Water	Hot Water		
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....

Time of mixing = ...S

You can do the calculations as shown below:

1.6.5 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. 1.21 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.

1.6.6 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 enthalpy of neutralisation of solution.

1.7 EXPERIMENT 1B: DETERMINATION OF THE ENTHALPY OF NEUTRALISATION OF HYDROCHLORIC ACID WITH SODIUM HYDROXIDE

1.7.1 Requirements

Apparatus			**Chemicals**
Thermos flask	—	1	Sodium hydroxide
Glass Strirrer	—	1	Hydrochloric acid
Thermometer 110°C (1/10 °C)	—	1	
Stop watch or stop clock	—	1	
Beaker 250/400 cm^3	—	2	
(1 as calorimeter)			
Measuring cylinder 100 cm^3	—	1	

Solutions Provided

0.50 mol dm^{-3} NaOH

0.50 mol dm^{-3} HCl

1.7.2 Procedure

Measure 100 cm^3 of HCl in a beaker for which heat capacity has already been determined in Experiment 1a. 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:

1.7.3 Observations

Neutralisation of HCl with NaOH:

SET I

Volume of HCl in the calorimeter, $V_{acid} = 100\,cm^3$

Volume of NaOH in the beaker, $V_{base} = 100\,cm^3$

Temperature – time data for acid, base and for mixture:

Time/s	Temperature/^oC		Time/s	Temperature/^oC 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, $V_{acid} = 100\,cm^3$

Volume of NaOH in the beaker, $V_{base} = 100\,cm^3$

Temperature-time data for acid, base and for mixture:

Time/s	Temperature/°C		Time/s	Temperature/°C Mixture
	HCl	NaOH		
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....

Time of mixing = ...s

1.7.4 Calculations

(1) Plot temperature – time curve for the neutralisation of HCl with NaOH data. You will get a plot as given in Fig. 1.2. 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.

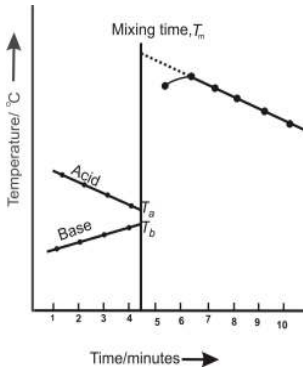


Fig. 1.2: Temperature-time curve for neutralisation.

(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. 1.19 as given below:

ΔH = – [Heat gained by the calorimeter + Heat gained by the solution] …(1.19)

= – [(Heat capacity of the calorimeter × Rise in temperature of the calorimeter) + (Mass of base × Specific heat of base × Rise in temperature of base) + (Mass of acid × Specific heat of acid × Rise in temperature of acid)]

= – [{C_p(c) as obtained in the earlier experiment 1a × ($T_m - T_a$)} + { V_{base} × sp. heat of base × ($T_m - T_b$)} + {V_{acid} × sp. heat of acid × ($T_m - T_a$)}] …(1.20)

Using Eq. 1.21,

$$\Delta H = -[C_p(\text{c})(T_\text{m} - T_\text{a}) + V_\text{base}\, s(T_\text{m} - T_\text{b}) + V_\text{acid}\, s(T_\text{m} - T_\text{a})] \quad \ldots(1.22)$$

Calculate ΔH from Eq. 1.22 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) form Experiment 1a] and specific heat ($s = 4.185\ \text{J K}^{-1}\text{kg}^{-1}$). ΔH so obtained in the above equation is the enthalpy change for the neutralisation of $100\,\text{cm}^3$ of 0.5 M HCl with $100\,\text{cm}^3$ of 0.5 M NaOH. From this ΔH, you can now calculate the ΔH_neut as follows.

You know that the enthalpy of neutralisation is the enthalpy change per mole of the substances neutralised. Thus, we have to first calculate the amount (number of moles) of HCl present in the volume of solution taken for neutralsation in the experiment. As given in the procedure, when $100\,\text{cm}^3$ of 0.5 M HCl is neutralised using $100\,\text{cm}^3$ of 0.5 M NaOH, then, the amount (no. of moles) of HCl present in the $200\,\text{cm}^3$ solution ($100\,\text{cm}^3$ acid + $100\,\text{cm}^3$ base) will be equal to 0.05 mole.

To calculate the heat of neutralisation, we have to divide the ΔH obtained by Eq. 1.22 by amount (the number of moles) of hydrochloric acid, i.e.,

$$\Delta H_\text{neut} = \frac{\Delta H \text{ (obtained from Eq.1.22)}}{\text{amount (No. of moles) of HCl}}$$

$$= \frac{\Delta H \text{ (obtained from Eq.1.22)}}{0.05}$$

$$= \ldots\ldots\text{J mol}^{-1}$$

Now report your result as given below:

1.7.5 Result

The heat of neutralisation of hydrochloric acid with sodium hydroxide is .....J mol^{-1}. You will later study a similar experiment using acetic acid instead of hydrochloric acid.

1.8 ANSWERS

Self Assessment Question

1. Heat capacity is given by the expression *ms*.

   Thus, the units of heat capacity $= \text{kg J K}^{-1}\ \text{kg}^{-1}$

   $= \text{J K}^{-1}$.

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.

The specific heat of water is 4.185 $\text{JK}^{-1}\ \text{kg}^{-1}$. 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* ... (1.21)

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)

$= \frac{0.5}{10}$ mole = 0.05 mole

Because 1 dm = 10 cm
and $(1\ \text{dm})^3 = (10\ \text{cm})^3$
$(1\ \text{dm})^3 = 1000\ \text{cm}^3$

or 100 $\text{cm}^3 = \frac{1}{10}$ dm^3

Thus, to get the amount (number of moles) present in 100 cm^3 of 0.5 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.

EXPERIMENT 2

DETERMIANTION OF ENTHALPY OF IONISATION OF A WEAK ACID

Structure

2.1 Introduction
Expected Learning Outcomes
2.2 Principle
2.3 Requirements
2.4 Procedure
2.5 Observations
2.6 Calculations
2.7 Result
2.8 Answers

2.1 INTRODUCTION

In the Unit 1, you have studied about the determination of the enthalpy of neutralisation. Now, we will be discussing the determination of the enthalpy of ionisation using the enthalpy of neutralisation. We will first determine the enthalpy of neutralisation of acetic acid and then calculate its enthalpy of ionisation from the enthalpy of neutralisation.

Expected Learning Outcomes

After performing this experimet, you should be able to:

- explain how to calculate the enthalpy of ionisation of a weak acid or a weak base from the enthalpy of its neutralisation;
- determine the enthalpy of neutralisation of acetic acid, and
- calculate the enthalpy of ionisation of acetic acid.

2.2 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.

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-{}_{(aq)} + H^+(aq) \quad \ldots(2.1)$$

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 the lower than that of the enthalpy of neutralisation of a strong acid with a strong base (i.e., –57.3 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.,

$$\Delta H_{\text{ionis}} + \Delta H_{\text{neut}} = \Delta H_{\text{observed}} \quad \ldots(2.2)$$

$$\Delta H_{\text{ionis}} = \Delta H_{\text{obs}} - \Delta H_{\text{neut}}$$

$$= \Delta H_{\text{obs}} - (-57.3\,\text{kJ mol}^{-1})$$

$$\Delta H_{\text{ionis}} = \Delta H_{\text{obs}} + 57.3\,\text{kJ mol}^{-1} \quad \ldots(2.3)$$

Since the ΔH_{obs} has a negative sign and is smaller in value than 57.3 kJ mol^{-1}, ΔH_{ionis} is positive. Thus, ionisation is endothermic.

2.3 REQUIREMENTS

Apparatus			Chemicals
Thermos flask	—	1	Acetic acid
Glass Strirrer	—	1	Sodium Hydroxide
Thermometer — 100°C (1/10th°C)	—	1	
Stop watch or stop clock	—	1	
Beaker 250/400 cm^3	—	2	
Measuring cylinder 100 cm^3	—	1	

Solutions Provided

0.50 mol dm^{-3} CH_3COOH

0.50 mol dm^{-3} NaOH

2.4 PROCEDURE

Do exactly in a similar way as done in the previous experiment using acetic acid instead of hydrochloric acid.

Record your observations in the following manner.

2.5 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/^oC		Time/s	Temperature/^oC
	CH_3COOH	NaOH		Mixture
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....

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

2.6 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_n), the base (T_b) and the mixture (T_m). Now, substitute the values of T_a, T_b and T_m in Eq. 1.22 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 100 cm^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.

$$\Delta H_{neut} \text{ of acetic acid} = \frac{\Delta H \text{ (obtained above)}}{0.05 \text{ mol}} \qquad \ldots(2.4)$$

$$= .....\text{kJ mol}^{-1}$$

Now calculate the enthalpy of ionisation of acetic acid as given below:

$$\Delta H_{ionis} = \Delta H_{neut} \text{ (strong acid with strong base)} - \qquad \ldots(2.5)$$

$$\Delta H_{neut} \text{ (acetic acid with NaOH)}$$

$$= (57.3\,\text{kJ mol}^{-1}) + (\text{vaue of } \Delta H_{neut} \text{ as obtained above})$$

$$= .....\text{kJ mol}^{-1}$$

2.7 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.

2.8 ANSWERS

Self Assessment Questions

1. $1000\ cm^3$ acetic acid solution contains 0.150 mol acetic acid

$$75.0\ cm^3 \text{ acetic acid solution contains } \frac{0.150\ mol \times 75.0\ cm^3}{1000\ cm^3}$$

$$= 0.01125\ mol$$

$$= 0.01125\ mol \times 0.0600\ kg\ mol^{-1}$$

$$= 6.75 \times 10^{-4}\ kg$$

The molar mass of acetic acid is 0.0600 kg mol^{-1}.

EXPERIMENT 3

DETERMINATION OF THE INTEGRAL ENTHALPY OF SOLUTION OF AMMONIUM CHLORIDE/POTASSIUM NITRATE

Structure

3.1 Introduction
Expected Learning Outcomes
3.2 Principle
3.3 Requirements
3.4 Procedure
3.5 Observations
3.6 Calculations
3.7 Result

3.1 INTRODUCTION

In this experiment, we will discuss the determination of integral enthalpy of solution of a solute. We will describe the experiment for ammonium chloride as the solute. Similarly, the enthalpy of solutions of potassium nitrate can also be determined.

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:

$$NH_4Cl + 100\ H_2O \longrightarrow NH_4Cl.100\ H_2O \qquad \Delta H_1 \qquad \ldots(3.1)$$

The integral enthalpy of solution is found to be dependent upon the amount of the solvent added: for example, the addition of 200 moles of water to the same 1 mole of ammonium chloride will yield a different enthalpy of solution, ΔH_2.

$$NH_4Cl + 200\ H_2O \longrightarrow NH_4Cl.\ 200\ H_2O \quad \Delta H_2 \qquad \ldots(3.2)$$

It has also been observed that the integral enthalpy of solution approaches a limiting value when more and more solvent is used. The difference of the above equations can be written as follows:

$$NH_4Cl\ .100\ H_2O + 100\ H_2O \longrightarrow NH_4Cl.\ 200\ H_2O \quad \Delta H = \Delta H_2 - \Delta H_1 \qquad \ldots(3.3)$$

The enthalpy change in the above reaction (Eq. 3.3) is termed as the **enthalpy or heat of dilution**. The enthalpy of dilution depends upon original concentration of the solution and on the amount of the solvent added.

In addition to the integral enthalpy of solution, we can define another type of enthalpy change the **differential enthalpy of solution.** This is defined as *the enthalpy change when 1 mol of solute is dissolved in a sufficiently large volume of a solution of concentration, C, so that the final concentration remains almost unchanged.* A special case of enthalpy of solution is *the enthalpy change which occurs when a sufficiently large amount of solvent is used so that further dilution does not yield any heat changes*. This is called the **enthalpy of solution at infinite dilution.** Here, you will study about the determination of the integral enthalpy of solution of salts such as potassium nitrate and ammonium chloride.

Expected Learning Outcomes

After performing this, you should be able to:

- explain the integral and differential enthalpies of solution; and
- determine the integral enthalpy of solution of a given solute.

3.2 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)]

$$q_p = [C_p(\mathrm{P}) + C_p(\mathrm{C})](T_2 - T_1] \qquad \ldots(3.4)$$

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 1(a). 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.,

C_p(P) = Mass of water (m_w) × specific heat of water (s) …(3.5)

$= m_w s = m_w \times 4.185 \text{ J K}^{-1}$ …(3.6)

The enthalpy of solution for one mole of the solute can thus be calculated as:

$$\Delta H_{sol} = q_p / n \quad \ldots(3.7)$$

where n is the amount (number of moles) of the solute added, i.e.

$$n = \frac{\text{mass of solute/g}}{\text{molar mass of solute/g mol}^{-1}} = \frac{m_2}{M} \text{.....mol} \quad \ldots(3.8)$$

Using Eqs. 3.4 to 3.8, we can say,

$$\Delta H_{sol} = \frac{q_p}{n} = [m_1 s + C_p(C)](T_1 - T_1)\frac{M}{m_2} \quad \ldots(3.9)$$

1 mol of NH_4Cl
= 14 + 4+ 35.5 = 53.5 g
∴ Molar mass of NH_4Cl
= 0.0535 kg

Note that $s = 4.185 \text{ J k}^{-1} \text{ kg}^{-1}$

Therefore, this value ΔH value is the integral enthalpy of the solution of a solute in a specific mole ratio of the solute to the solvent.

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 kg of water requires $\frac{0.0535 \times 0.200}{1.8} = 0.0059445$ kg of NH_4Cl

$= 5.9445$ g of NH_4Cl

3.3 REQUIREMENTS

Apparatus			Chemicals
Thermos flask	—	1	Solid Ammonium Chloride
Glass stirrer	—	1	Water
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	

3.4 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 Experiment 1a. Place it in a thermos flask. 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. 3.4 and consequently the enthalpy of solution for the dissolution of one mole of solute using Eq. 3.9.

You can record your observations as shown below:

3.5 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/^oC of water		Time/s	Temperature/^oC 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 $= m_2 - m_3$ =…….g

Volume of water in calorimeter $= V$ =……. cm^3

Mass of water $= m_w$ =…….g = $\frac{\ldots\ldots}{1000}$ kg

Temperature-time data for pure water and for solution:

Time/s	Temperature/^oC of water		Time/s	Temperature/^oC of solution
……	……	……	……	……
……	……	……	……	……
……	……	……	……	……
……	……	……	……	……
……	……	……	……	……
……	……	……	……	……
……	……	……	……	……
……	……	……	……	……

Time of mixing = ……s

3.6 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.

3.7 RESULT

The integral enthalpy of solution of ammonium chloride was found to be ……. $J\ mol^{-1}$.

EXPERIMENT 4

DETERMINATION OF ENTHALPY OF HYDRATION OF ANHYDROUS COPPER SULPHATE

Structure

4.1 Introduction
Expected Learning Outcomes
4.2 Principle
4.3 Requirements
4.4 Procedure
4.5 Observations
4.6 Calculations
4.7 Result

4.1 INTRODUCTION

In the previous experiment you have learnt about the determination of integral enthalpy of solution i.e., the enthalpy change associated with the dissolution of 1 mole of a solute in a definite amount of the solvent so as to get a solution of desired solute: solvent mole ratio. The integral enthalpy of solution is found to depend on the nature of the solute and the mole ratio of the solute to the solvent. In this experiment we would use integral enthalpies of solution of anhydrous copper sulphate and copper sulphate pentahydrate to determine the enthalpy of hydration of anhydrous copper sulphate. In the next experiment, you would study the variation of the solubility of benzoic acid in water with temperature and use it to determine the associated enthalpy changeviz., dissolution enthalpy of benzoic acid.

Expected Learning Outcomes

After studying about and performing this experiment, you should be able to:

- explain the principle of determination of enthalpy of hydration of anhydrous copper sulphate;
- determine the heat capacity of a calorimeter (beaker) for a given volume;
- calculate the amounts of anhydrous copper sulphate and copper sulphate

pentahydrate required to prepare an aqueous solution of a given solute:solvent mole ratio;

- ❖ determine the integral enthalpies of solution for anhydrous copper sulphate and copper sulphate pentahydrate for a solute: solvent mole ratio of 1:400; and
- ❖ use the data on integral enthalpies of solution of anhydrous copper sulphate and copper sulphate pentahydrate to determine the enthalpy of hydration of anhydrous copper sulphate.

4.2 PRINCIPLE

The enthalpy of hydration of anhydrous copper sulphate corresponds to the enthalpy change associated with the hydration of anhydrous copper sulphate to give copper sulphate pentahydrate. In other words, this corresponds to the enthalpy change associated with the following reaction,

$$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_2O \quad \ldots(4.1)$$

In order to determine the enthalpy change for the above reaction we make use of two concepts viz., the integral enthalpy of solution and Hess's law of constant heat summation. You would recall from the previous experiment that the integral enthalpy of solution refers to the enthalpy change associated with the dissolution of 1 mole of a solute in a definite amount of the solvent so as to get a solution of a given solute: solvent mole ratio. If we take 1 mole each of anhydrous copper sulphate and copper sulphate pentahydrate and determine their integral enthalpies of solution for the solute: solvent mole ratio of 1:400, the corresponding thermochemical equations would be

$$CuSO_4(s) + 400H_2O(l) \rightarrow CuSO_4.400H_2O \quad \Delta H_1 \ldots(4.2)$$

$$CuSO_4.5H_2O(s) + 400H_2O(l) \rightarrow CuSO_4.405H_2O \quad \Delta H_2 \ldots(4.3)$$

You would remember from Unit 3 of the BCHCT-133 course that at large mole ratio of the solvent to the solute, the enthalpy of dilution for adding a few moles of solvent is very low and we can assume that the enthalpy change for the reaction given in Eq. 4.3 and Eq. 4.4 (given below) are equal, i.e., $\Delta H_2 = \Delta H_3$

$$CuSO_4.5H_2O(s) + 395H_2O(l) \rightarrow CuSO_4.400H_2O \quad \Delta H_3 \ldots(4.4)$$

Now, you need to recall Hess's law of constant heat summation about which you have learnt in your earlier classes as well as in Course BCHCT-133. According to this law, *"the enthalpy change associated with a given chemical reaction is the same whether it occurs in a single stage or in many stages"*. It implies that the net enthalpy change for a reaction depends only on the initial and final states, and not on the intermediate states through which the system passes. An important consequence of the Hess's law is that the thermochemical equations can be added and subtracted, like algebraic equations. Using this law, we subtract

Eq. 4.4 from Eq. 4.2. This gives the expression for hydration of anhydrous copper sulphate.

$CuSO_4(s) + 400H_2O(l) \rightarrow CuSO_4.400H_2O \qquad \Delta H_1$

$CuSO_4.5H_2O(s) + 395H_2O(l) \rightarrow CuSO_4.400H_2O \qquad \Delta H_3$

$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_2O \qquad \Delta H = \Delta H_1 - \Delta H_3$

As we argued above, $\Delta H_3 = \Delta H_2$, so by replacing ΔH_3 by ΔH_2 the enthalpy of hydration of anhydrous copper sulphate can be given as

$$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_2O \qquad \Delta H = \Delta H_1 - \Delta H_2 \quad \ldots(4.5)$$

In other words, it is equal to the difference in the integral enthalpies of solution of anhydrous copper sulphate and copper sulphate pentahydrate for same solute: solvent mole ratio. Thus, we can say that the enthalpy of hydration of anhydrous copper sulphate can be determined by using the integral enthalpies of solution of anhydrous copper sulphate and copper sulphate pentahydrate for the same solute: solvent mole ratio.We have taken the solute: solvent mole ratio as 1:400, one can take any high mole ratio. However, you must remember that for low solute: solvent mole ratios our assumption ($\Delta H_2 = \Delta H_3$,) may not be valid.

In an alternative method, for anhydrous copper sulphate we take the solute: solvent mole ratio as 1: 400 whereas for copper sulphate pentahydrate we take it to be 1: 395. The calculations become simpler. Some of you can try this method and compare your results with fellow learners.

4.3 REQUIREMENTS

Apparatus		Chemicals
Thermos flask	1	Anhydrous copper sulphate
Glass Stirrer	1	Copper sulphate pentahydrate
Thermometer 110°C (1/10°C)	1	Water
Stopwatch	1	
Beaker 400 cm^3	1	
Beaker 250 cm^3	1	
Measuring cylinder 100 cm^3	1	
Weighing bottle	1	
Analytical balance	1	
Weight box	1	
Wash bottle	1	

4.4 PROCEDURE

There are following four steps of the experiment:

A. Determination of heat capacity of the calorimeter (beaker) for a volume of 200 cm^3

B. Determination of integral enthalpy of solution for anhydrous copper sulphate for a solute: solvent mole ratio of 1:400

C. Determination of integral enthalpy of solution for copper sulphate pentahydrate for a solute: solvent mole ratio of 1:400

D. Calculation of the enthalpy of hydration of anhydrous copper sulphate

Let us learn about the procedure for these.

A. Determination of heat capacity of the calorimeter (beaker) for a volume of 200 cm^3

Follow the instructions given as under and record your observations in the Observation Tables 1 and 2 given below (Section 4.5).

1. Take a thermos flask having two holes in its lid. Insert the thermometer through one of these holes and the stirrer through the other hole.
2. Take a clean beaker of 400 cm^3 capacity; add 100 cm^3 of distilled water to it with the help of measuring cylinder and place the beaker inside the thermos flask
3. Place the lid on the thermos flask and measure the temperature of water at an interval of half a minute each for about four minutes. Record your observations in Observation Table 1.
4. Take a beaker of 250 cm^3 capacity; add100 cm^3 of hot distilled water (having a temperature of about 20 ^oC higher than the room temperature) to it with the help of a measuring cylinder. Start the stopwatch and measure the temperature of hot water at an interval of half a minute each for about four minutes. Record your observations in Observation Table 1.
5. Open the lid of the thermos flask, quickly transfer the hot water to it and replace the lid.
6. Note the time of mixing of hot and cold water, stir the contents and continue measuring the temperature of the mixture of water every half minute (Caution: Do not put off the stopwatch, the readings of the hot water and the mixture are to be taken continuously). Record your observations in Observation Table 1.
7. Plot graphs between the temperatures (y-axis) of water (cold, hot and mixture) as a function of time (x-axis). Use same set of axes to draw the graphs in the same figure.
8. Mark the time of mixing on the figure. Determine the temperatures of cold water, hot water and the water mixture at the time of mixing of hot and cold water using the graphs and calculate the heat capacity of the calorimeter by using Eq. 4.6.

Repeat step 1− 6 with the same beaker of 400 cm^3 capacity and record your observations in Observation Table 2; repeat steps 7and 8 with the new set of data.

B. Determination of integral enthalpy of solution for anhydrous copper sulphate for a solute: solvent mole ratio of 1:400

As you have learnt in the previous experiment that to determine the integral enthalpy of solution of a solute we need to first calculate the mass of the solute required to be dissolved in a given volume of the solvent so as to get the desired

solute: solvent mole ratio. Since we have determined the heat capacity of the calorimeter for a volume of 200 cm^3 of water we would calculate the mass of solute to be dissolved in 200 cm^3 of water. To calculate the mass of anhydrous copper sulphate (M=159.6 g mol^{-1}) required to dissolve in 200 cm^3 of water so as to get a solution having solute:solvent mole ratio of 1:400, we proceed as follows:

Molar mass of anhydrous copper sulphate = 159.6 g mol^{-1}

Molar mass of water = 18 g mol^{-1}

Mass of anhydrous copper sulphate (1mole) required for 400 moles (400 mol × 18 g mol^{-1}= 7200 g) of water = 159.6 g

Mass of anhydrous copper sulphate required for 1 g of water $= \frac{159.6}{7200}$ g

Mass of anhydrous copper sulphate required for 200 g (200 cm^3× 1 g cm^{-3}) of water

$$= \frac{159.6}{7200} \times 200 = 4.44 \text{ g}$$

After calculating the required mass of anhydrous copper sulphate, you can determine the integral enthalpy of solution for anhydrous copper sulphate by following the instructions given below in sequential order

1. Weigh the required amount of anhydrous copper sulphate in a weighing bottle and record your observations at B under Section 4.5 (Observations).
2. Take a thermos flask having two holes in its lid. Insert the thermometer through one of these holes and the stirrer through the other hole.
3. Take the 400 cm^3 beaker for which the heat capacity has been determined in part A; add 200 cm^3 of distilled water to it with the help of a measuring cylinder and place the beaker inside the thermos flask
4. Place the lid on the thermos flask and measure the temperature of the distilled water at an interval of half a minute each for about four minutes. Record your observations in Observation Table 3.
5. Open the lid of the flask; quickly add the weighed anhydrous copper sulphate to the beaker, replace the lid, note the time of mixing of anhydrous $CuSO_4$ to water and stir the mixture.
6. Continue measuring the temperature of the mixture every half a minute for about another four minutes and record your observations in Observation Table 3.
7. Plot graphs between the temperatures (y-axis) of water and the solution of anhydrous copper sulophate, as a function of time (x-axis). Use same set of axes to draw the graphs in the same figure.
8. Indicate the time of mixing on the figure and determine the temperature of water and of the solution of anhydrous copper sulphate at the time of mixing from the graphs.

Use this data along with the heat capacity of the calorimeter to calculate integral enthalpy of solution for anhydrous copper sulphate for a solute: solvent mole ratio of 1:400.

C. Determination of integral enthalpy of solution for copper sulphate pentahydrate for a solute: solvent mole ratio of 1:400

Here, we need to calculate the mass of copper sulphate pentahydrate (M = 249.7 g mol^{-1}) required to dissolve in 200 cm^3 of water so as to get a solution having solute:solvent mole ratio of 1:400. For this we proceed as follows:

Molar mass of copper sulphate pentahydrate = 249.7 g mol^{-1}

Molar mass of water = 18 g mol^{-1}

Mass of copper sulphate pentahydrate required for 400 moles

(400 mol × 18 g mol^{-1} = 7200 g) of water = 249.7 g

Mass of copper sulphate pentahydrate (1mole) required for 1 g of water

$$= \frac{249.7}{7200} \text{ g}$$

Mass of copper sulphate pentahydrate required for 200 g

(200 cm^3 × 1 g cm^{-3}) of water $$= \frac{249.7}{7200} \times 200 = 6.936 \text{ g}$$

After calculating the required mass of copper sulphate pentahydrate, you can determine the integral enthalpy of solution for copper sulphate pentahydrate by following the instructions given below in sequential order.

1. Weigh the required amount of copper sulphate pentahydrate in a weighing bottle and record your observations at C under Section 4.5 (Observations).
2. Take a thermos flask having two holes in its lid. Insert the thermometer through one of these holes and the stirrer through the other hole.
3. Take the 400 cm^3 beaker for which the heat capacity has been determined in part A; add 200 cm^3 of distilled water to it with the help of a measuring cylinder and place the beaker inside the thermos flask
4. Place the lid on the thermos flask and measure the temperature of the distilled water at an interval of half a minute each for about four minutes. Record your observations in Observation Table 4.
5. Open the lid of the thermos flask; quickly add the weighed copper sulphate pentahydrate to the beaker, replace the lid, note the time of mixing of $CuSO_4 \cdot 5H_2O$ to water and stir the mixture.
6. Continue measuring the temperature of the mixture (solution of $CuSO_4 \cdot 5H_2O$) every half a minute each for another four minutes and record your observations in Observation Table 4.
7. Plot graphs between the temperature (y-axis) of water and solution, as a function of temperature (x-axis). Use same set of axes to draw the graphs in the same figure.

8. Indicate the time of mixing on the figure and determine the temperature of water and of the solution of copper sulphate pentahydrate at the time of mixing from the graph.

   Use this data along with the heat capacity of the calorimeter to calculate integral enthalpy of solution for copper sulphate pentahydrate for a solute: solvent mole ratio of 1:400.

D. Calculation of the enthalpy of hydration of anhydrous copper sulphate

As discussed above, the enthalpy of hydration of copper sulphate can be calculated by the following formula

$$\Delta H = \Delta H_1 - \Delta H_2 \qquad \ldots(4.5)$$

Where, ΔH_1 and ΔH_2 respectively are the integral enthalpies of solution for anhydrous copper sulphate and copper sulphate pentahydrate for a solute: solvent mole ratio of 1:400. These are obtained in the part B and C respectively.

4.5 OBSERVATIONS

A. Determination of heat capacity of the calorimeter (beaker) for a volume of 200 cm^3

Volume of cold water = ____ cm^3

Volume of hot water = ____ cm^3

Set – I

Observation Table 1

Time-temperature data for cold, hot and mixed water as a function of time

Time / min	Temperature / °C		
	Cold water	Hot water	Mixture
0.5			---
1.0			---
1.5			---
2.0			---
2.5			---
3.0			---
3.5			---
4.0			---
4.5	---	---	
5.0	---	---	
5.5	---	---	
6.0	---	---	
6.5	---	---	
7.0	---	---	
7.5	---	---	
8.0	---	---	

Time of mixing: ……min.

Set – II

Observation Table 2

Time-temperature data for cold, hot and mixed water as a function of time

Time /min	Temperature/°C		
	Cold water	Hot water	Mixture
0.5			---
1.0			---
1.5			---
2.0			---
2.5			---
3.0			---
3.5			---
4.0			---
4.5	---	---	
5.0	---	---	
5.5	---	---	
6.0	---	---	
6.5	---	---	
7.0	---	---	
7.5	---	---	
8.0	---	---	

Time of mixing: …… min.

B. Determination of integral enthalpy of solution for anhydrous copper sulphate for a solute: solvent mole ratio of 1:400

Mass of empty weighing bottle = m_1 = ….g

Mass of weighing bottle + anhydrous $CuSO_4$ = m_2 = ….g

Mass of weighing bottle after transferring anhydrous $CuSO_4$ = m_3 = ….g

Mass of anhydrous $CuSO_4$transferred (m) = $m_2 – m_3$ = ….g

Volume of water in calorimeter = V = ….cm^3

Observation Table 3

Time-temperature data for water and solution of anhydrous $CuSO_4$

Time /min	Temperature/ °C	
	Cold water	Solution of $CuSO_4$
0.5		---
1.0		---
1.5		---
2.0		---
2.5		---
3.0		---
3.5		---

4.0	---	
4.5	---	
5.0	---	
5.5	---	
6.0	---	
6.5	---	
7.0	---	
7.5	---	
8.0	---	

Time of mixing: …… min.

C. Determination of integral enthalpy of solution for copper sulphatepentahydrate for a solute: solvent mole ratio of 1:400

Mass of empty weighing bottle = m_1 = ….g

Mass of weighing bottle + $CuSO_4 \cdot 5H_2O$ = m_2 = ….g

Mass of weighing bottle after transferring $CuSO_4 \cdot 5H_2O$ = m_3 = ….g

Mass of $CuSO_4 \cdot 5H_2O$ transferred (m) = $m_2 - m_3$ = ….g

Volume of water in calorimeter = V =….cm^3

Observation Table 4

Time-temperature data for water and solution of $CuSO_4 \cdot 5H_2O$

Time /min	Temperature/°C	
	Cold water	Solution of $CuSO_4 \cdot 5H_2O$
0.5		---
1.0		---
1.5		---
2.0		---
2.5		---
3.0		---
3.5		---
4.0	---	
4.5	---	
5.0	---	
5.5	---	
6.0	---	
6.5	---	
7.0	---	
7.5	---	
8.0	---	

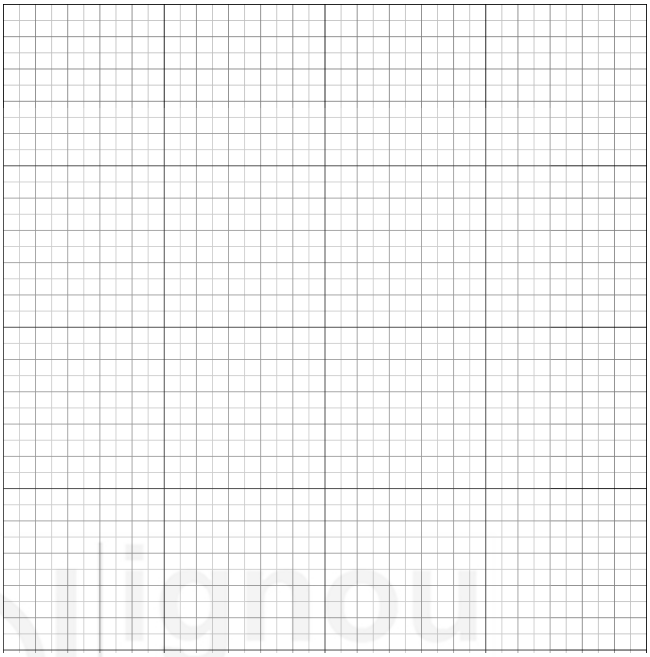
Time of mixing: …… min.

4.6 CALCULATIONS

Perform the calculations based on the observations recorded above. You need to perform the calculations stepwise. Let's begin with step 1.

A. Determination of heat capacity of the calorimeter (beaker) for a volume of 200 cm^3

i. Use data recorded in Observation Table 1 to plot graphs between the temperature and time for cold water, hot water, and their mixture in the graph provided below. Indicate the time of mixing on the graph. Use same set of axes to plot the graphs in the same figure and also mark the time of mixing on the figure.



ii. Use the graphs to find out the temperatures of cold water, hot water, and their mixture at the time of mixing. Record the same here

Temperature of cold water at the time of mixing = ___°C

Temperature of hot water at the time of mixing = ___°C

Temperature of mixture of cold and hot water at the time of mixing = ___°C

iii. Calculate the heat capacity of the calorimeter by using the following formula that you have learnt in Experiment 1.

$$C_P(\text{calorimeter}) = 4.185\ V d_w \left[\frac{T_h - T_m}{T_m - T_c} - 1\right] \text{J K}^{-1} \qquad \ldots(4.6)$$

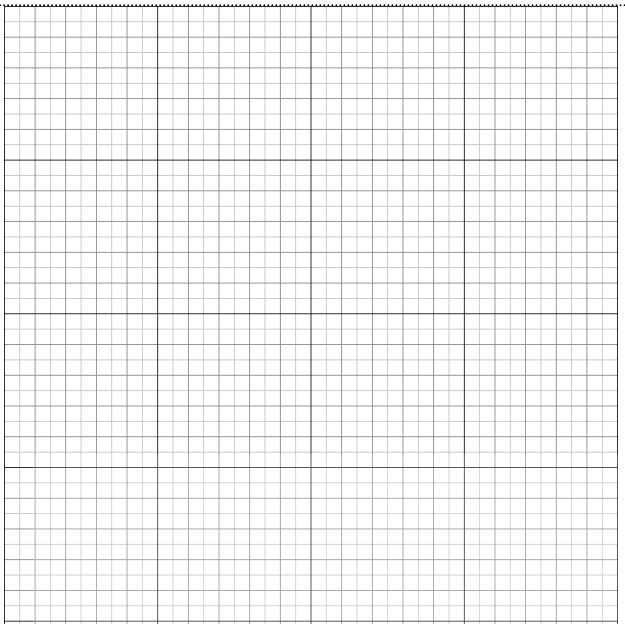
Where, T_c, T_h and T_m are the temperatures of cold water, hot water and their mixture respectively at the time of mixing.

V= total volume of water

d_w = the density of water at room temperature (*Your counselor would provide you the value of d_w at the temperature of the laboratory*)

Substitute the values of different terms in the Eq. 4.6 and calculate the value of heat capacity of the calorimeter (beaker) for a volume of 200 cm^3.

Repeat the steps i), and ii) for the data of second set recorded in Observation Table 2. Plot the graphs for second set in the graph given.



Calculate the value of heat capacity for second set of data by using the same formula as in set-1.

Set-1: The heat capacity of the calorimeter is found to be= …….J K^{-1}

Set-2: The heat capacity of the calorimeter is found to be= …….J K^{-1}

The two values calculated for the heat capacities of the calorimeter should be equal or close to each other. You can take average of the two values as the correct value of the heat capacity of the calorimeter. In case the two values happen to be quite different from one another then perform one more set of the determination and take the average of two values close to each other.

B. Determination of integral enthalpy of solution for anhydrous copper sulphate for a solute: solvent mole ratio of 1:400

You have learnt in Experiment 3 that the integral enthalpy of solution for a solute can be obtained by using the following formula,

$$\Delta H_{sol} = [m_1 s + C_p(c)]\,(T_2 - T_1)\frac{M}{m_2} \qquad \ldots(4.7)$$

where,

T_1= temperature of the water at the time of mixing

T_2 = temperature of the solution at the time of mixing

m_1 = the mass of solvent taken

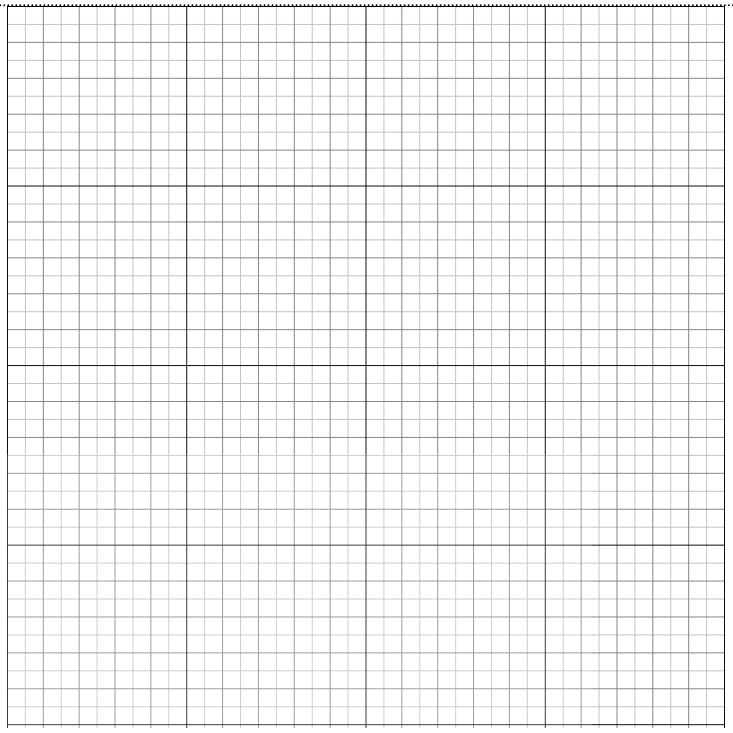
m_2 = the mass of solute taken

M = molar mass of the solute

C_p(c) = heat capacity of the calorimeter

s = specific heat of water, = 4.185 J K^{-1}

i. Using data recorded in Observation Table 3, plot graphs between the temperature and time for cold water and the solution of anhydrous copper sulphate in the graph provided below. Indicate the time of mixing on the graph.



ii. Use the graphs to find out the temperatures of cold water, and the solution of anhydrous copper sulphate at the time of mixing. Record the same here

Temperature of cold water at the time of mixing T_1 = ___°C

Temperature of solution of anhydrous copper sulphate at the time of mixing T_2 = ___°C

iii. Calculate the integral enthalpy of solution for anhydrous copper sulphate by using the following formula as given above.

$$\Delta H_1 = [m_1 s + C_p(c)]\,(T_2 - T_1)\frac{M}{m_2} \qquad \ldots(4.7)$$

Substitute the values of different terms in the above formula and calculate the integral enthalpy of solution for anhydrous copper sulphate for a solute: solvent mole ratio of 1:400

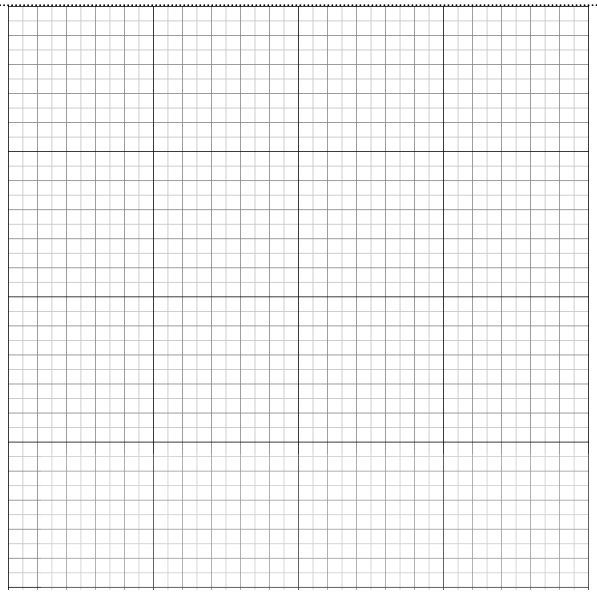
The integral enthalpy of solution for anhydrous copper sulphate for a solute: solvent mole ratio of 1:400 is found to be, ΔH_1 = ... *k*J mol^{-1}

C. Determination of integral enthalpy of solution for copper sulphate pentahydrate for a solute: solvent mole ratio of 1:400

i. Using data recorded in Observation Table 4 plot graphs between the temperature and time for cold water and the solution of copper sulphate pentahydrate in the graph provided.

ii. Use the graphs to find out the temperatures of cold water, and the solution of copper sulphate pentahydrate at the time of mixing. Record the same here.
Temperature of cold water at the time of mixing T_1 = ___°C

Temperature of solution of copper sulphate pentahydrate at the time of mixing T_2 = ___°C



iii. Calculate the integral enthalpy of solution for copper sulphate pentahydrate by using the following formula as given above.

$$\Delta H_2 = [m_1 s + C_p(c)]\,(T_2 - T_1)\frac{M}{m_2} \qquad \ldots(4.7)$$

Substitute the values of different terms in the above formula and calculate the integral enthalpy of solution for copper sulphate pentahydrate for a solute: solvent mole ratio of 1:400.

The integral enthalpy of solution for anhydrous copper sulphate pentahydrate for a solute: solvent mole ratio of 1:400 is found to be, ΔH_2 = ... *k*J mol^{-1}

D. Calculation of the enthalpy of hydration of anhydrous copper sulphate

As explained above, the enthalpy of hydration of copper sulphate can be calculated by the following formula

$$\Delta H = \Delta H_1 - \Delta H_2 \qquad \ldots(4.5)$$

Where, ΔH_1 and ΔH_2 respectively are the integral enthalpies of solution for anhydrous copper sulphate and copper sulphate pentahydrate for a solute: solvent mole ratio of 1:400. Substitute the values of ΔH_1 and ΔH_2 (as determined in steps B and C) in the above formula and calculate the enthalpy of hydration of anhydrous copper sulphate

The enthalpy of hydration of anhydrous copper sulphate is found to be:
ΔH = ... kJ mol^{-1}

4.7 RESULT

The enthalpy of hydration of anhydrous copper sulphate is found to be:
ΔH = ... kJ mol^{-1}

EXPERIMENT 5

DETERMINATION OF DISSOLUTION ENTHALPY OF BENZOIC ACID BY STUDYING TEMPERATURE DEPENDENCE OF ITS SOLUBILITY

Structure

5.1 Introduction
Expected Learning Outcomes
5.2 Principle
5.3 Requirements
5.4 Procedure
5.5 Observations
5.6 Calculations
5.7 Result

5.1 INTRODUCTION

In the previous experiment you have learnt about the determination of enthalpy of hydration of anhydrous copper sulphate by determining the integral enthalpies of solution of the anhydrous copper sulphate and copper sulphate pentahydrate for solute: solvent mole ratio of 1:400. In the present experiment we would take up the determination of dissolution enthalpy of benzoic acid by using solubility measurements as a function of temperature. This would involve using van't Hoff equation about which you have learnt in your previous classes. In the next experiment you would learn about measurement of pH of aerated drinks, fruit juices, soaps and shampoos.

Expected Learning Outcomes

After studying about and performing this experiment, you should be able to:

- explain the principle of determination of dissolution enthalpy of benzoic acid from the measurement its solubility at different temperatures;
- give van't Hoff equation and state different terms in it;

- modify the van't Hoff equation to relate temperature variation of solubility and enthalpy of dissolution;
- prepare a standard solution of oxalic acid;
- standardise a solution of NaOH by titrating against a standard solution of oxalic acid;
- measure the solubility of benzoic acid at different temperatures by titrating its saturated solutions at different temperatures against a standard solution of sodium hydroxide; and
- calculate the dissolution enthalpy of for benzoic acid by using the solubility data at different temperatures.

5.2 PRINCIPLE

You know that when we dissolve a solute in a solvent to make solution the amount of solute dissolving in a given amount of solvent depends on the nature of solute, solvent and temperature. The amount of solute that dissolves in 100 cm^3 of the solvent at a given temperature is called its solubility. The number of moles of a substance that dissolve in 1 dm^3 of a solvent is called its molar solubility and the number of moles of solute that are dissolved per kg of the solvent is termed as its molal solubility. Benzoic acid has very low solubility in water. If we take a certain amount of water, say at room temperature and add sufficient benzoic acid to it so as to obtain a saturated solution then there will be equilibrium between the dissolved and undissolved (solid) benzoic acid. It means that in such a saturated solution the rate at which benzoic acid is dissolving and the rate at which it is crystallizing from the solution are equal. This dissolution equilibrium can be represented as

$$C_6H_5COOH\,(s) + H_2O\,(l) \rightleftharpoons C_6H_5COOH\,(aq) \quad \ldots(5.1)$$

The corresponding equilibrium constant can be written as

$$K_{diss} = [C_6H_5COOH\,(aq)] \quad \ldots(5.2)$$

Where, $[C_6H_5COOH\,(aq)]$ is the molar concentration of dissolved benzoic acid at the temperature of the solution. As the equilibrium given in Eq. 5.1 is a heterogeneous equilibrium the concentration of solid benzoic acid and the solvent water would not appear in the expression of equilibrium constant. Thus, we can say that the solubility of benzoic acid i.e., the concentration of benzoic acid in its saturated solution is a special case of equilibrium constant.

You have learnt that the temperature dependence of equilibrium constant is given in terms of van't Hoff equation. In the present case of dissolution equilibrium the equation would be

$$\frac{d\ln K_{diss}}{dT} = \frac{\Delta H_{diss}}{RT^2} \quad \ldots(5.3)$$

As mentioned above, the right side of the Eq.(5.2) is the molar solubility (S) of benzoic acid; we can rewrite Eq. (5.2) as,

$$K_{diss} = S \quad \ldots(5.4)$$

The van't Hoff equation (given below) relates the temperature dependence of equilibrium constant and enthalpy

$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2}$$

substituting it in Eq. 5.3 we get,

$$\frac{d\ln S}{dT} = \frac{\Delta H_{diss}}{RT^2} \quad \ldots(5.5)$$

Here, ΔH_{diss} is the dissolution enthalpy, R is the molar gas constant, and T is the temperature in Kelvin scale. If we assume that the dissolution enthalpy is constant over the experimental temperature range (room temperature ± 20 K) we can integrate the equation in the temperature range T_1 to T_2 wherein the solubility varies from S_1 to S_2. On integrating Eq. 5.5 we get,

$$\int_{S_1}^{S_2} d\ln S = \int_{T_1}^{T_2} \frac{\Delta H}{R} \times \frac{dT}{T^2} \quad \ldots(5.6)$$

as ΔH and R are constant, we can write

$$\int_{S_1}^{S_2} d\ln S = \frac{\Delta H}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} \quad \ldots(5.7)$$

On integrating the equation and applying limits,

$$ln\frac{S_2}{S_1} = -\frac{\Delta H}{R}\left[\frac{1}{T}\right]_{T_1}^{T_2} = -\frac{\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \quad \ldots(5.8)$$

$$\Rightarrow \quad \ln\frac{S_2}{S_1} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad \ldots(5.9)$$

$$\Rightarrow \quad \log\frac{S_2}{S_1} = \frac{\Delta H}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] = \frac{\Delta H}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \quad \ldots(5.10)$$

$$\Rightarrow \quad \Delta H = 2.303\,R\left[\frac{T_1 T_2}{T_2 - T_1}\right]\log\frac{S_2}{S_1} \quad \ldots(5.11)$$

Thus, by measuring the solubilities (S_1 and S_2) of a substance at two different temperatures viz., T_1 and T_2 we can determine the dissolution enthalpy, ΔH_{diss} by using Eq. 5.11.

In order to determine the solubility of benzoic acid at different temperatures, we prepare saturated solutions of benzoic acid at different temperatures. Then we pipette out a known volume of the supernatant liquid from the saturated solutions and determine the concentrations of the withdrawn liquids by titrating against a standard solution of NaOH.

5.3 REQUIREMENTS

Apparatus		**Chemicals**
Volumetric flask, 100 cm^3	1	Benzoic acid
Analytical balance	1	Oxalic acid
Weighing bottle	1	Sodium hydroxide
Weight box	1	Phenolphthalein

Beaker, 250 cm^3	2	Distilled water
Burette	1	
Burette stand	1	
Pipette 10 cm^3	1	
Conical flask 100 cm^3	5	
Thermometer 110°C (1/10°C)	1	
Measuring cylinder 100 cm^3	1	
Funnel	1	
Glass Stirrer	1	
Spatula	1	
Wash bottle	1	
Dropper	1	
Porcelain tile	1	

5.4 PROCEDURE

The experiment has the following four steps

A. Preparation of a standard solution of oxalic acid

B. Standradisation of a solution of sodium hydroxide by titrating against standard solution of oxalic acid

C. Determination of solubility of benzoic acid at different temperatures

D. Calculation of the enthalpy of dissolution of benzoic acid from the data so obtained

Let us learn about the procedure for these

A. Preparation of a standard solution of oxalic acid

Follow the instructions given as under and record your observations in the Observation Tables in Section 5.5

1. As you know, to prepare a standard solution of a substance we need to first calculate the amount of the substance required for preparing the required volume of the solution of desired concentration. We wish to prepare 100 cm^3 of 0.05 M solution of oxalic acid.

   The mass of oxalic acid (M = 126 g mol^{-1}) required to prepare 100 cm^3 of 0.05 M solution of oxalic acid would be:

$$m(\text{in g}) = \frac{0.05 \times 100 \times 126}{1000} = 0.63\,\text{g}$$

2. Weigh about 0.65 g of oxalic acid on a rough weighing balance and transfer it to a clean dry weighing bottle.

To prepare V cm^3 of a standard solution of molarity M for a substance having a molar mass of M, the mass (m) of the solute required is given by the following formula

$$m(\text{in g}) = \frac{M \times V \times M}{1000}$$

3. Accurately weigh the weighing bottle with oxalic acid and record your observations under (a) in Section 5.5.

4. Transfer the oxalic acid to a clean volumetric flask of 100 cm^3 capacity through a glass funnel.

5. Accurately weigh the weighing bottle containing oxalic acid left (if any) and find the exact mass of oxalic acid transferred by subtracting this mass from the mass of the weighing bottle plus oxalic acid.

6. Dissolve oxalic acid in about 30-40 cm^3 of distilled water taken in the volumetric flask. Once dissolved, make up the volume up to the mark with distilled water. This can be done initially by pouring distilled water with a wash bottle (till the level reaches the neck of the flask) and then by adding distilled water dropwise with the help of a pipette or a clean dropper.

7. Stopper the flask tightly and shake well before use to obtain a homogeneous solution.

B. Standardisation of a given solution of sodium hydroxide by titrating against standard solution of oxalic acid

1. Prepare a solution of sodium hydroxide by dissolving about 0.4 g of NaOH in 200 cm^3 of distilled water taken in a beaker.

2. Rinse and fill up a clean burette with sodium hydroxide solution with the help of a funnel and mount it on the burette stand. Note the reading on the burette and record it in the Observation Table 1 under the initial reading column.

3. Carefully pipette out 10 cm^3 of the standard oxalic acid solution and transfer to a clean 100 cm^3 conical flask. Add two to three drops of phenolphthalein indicator to it.

Concordant reading: two identical readings of the volume of titrant used in a titration

4. Titrate the solution with constant swirling against a white background (you may use a white porcelain tile for this purpose) till a persistent pink colour is obtained that does not fade on shaking. Record the reading in the Observation Table1 under the final reading column.

5. Repeat the titration to get at least two concordant readings and record the same in the Observation Table1

C. Determination of solubility of benzoic acid at different temperatures

1. Take four 100 cm^3 conical flasks and label them as 10 °C, 20 °C, 30 °C, and 40 °C respectively

2. Take a 250 cm^3 beaker, add about 60-70 cm^3 of distilled water to it and heat it to about 45-50 °C.

3. Slowly add sufficient amount of crystals of benzoic acid with the help of a spatula to the hot distilled water with continuous stirring so as to obtain a saturated solution

4. Allow the solution to cool on its own, keep monitoring the temperature while stirring. When the temperature approaches 40 °C stop stirring and as it becomes 40°C, quickly pipette out 10 cm^3 of the supernatant liquid and transfer it to the conical flask labeled as 40 °C. (To avoid crystals of benzoic acid to get sucked into the pipette, wrap a small piece of filter paper to the tip of the pipette and tie it with a thread. Remove the filter paper before transferring the solution to conical flask)

5. Repeat the step 4 for 30 °C, 20 °C and 10 °C temperatures. In order to go below the room temperature you may keep the beaker in an ice bath.

6. Titrate the pipetted solutions with standardised sodium hydroxide solution using phenolphthalein as indicator. The procedure is as under,

   i. Rinse and fill up the burette with standardised sodium hydroxide solution with the help of a funnel and mount it on the burette stand. Note the reading on the burette and record it in the Observation Table 2 under the initial burette reading column.

   ii. Take the first conical flask and add two to three drops of phenolphthalein indicator to it and warm the solution in water bath to ensure that the solution becomes clear.

   iii. Titrate the solution with constant swirling against a white background (you may use a white porcelain tile for this purpose) till a persistent pink colour is obtained that does not fade on shaking. Record the burette reading in the Observation Table 2 under the final reading column.

   iv. Similarly, repeat the titration with the remaining conical flasks containing the benzoic acid solutions withdrawn at different temperatures and record the initial and final burette readings in the Observation Table 2.

Warming the solution before titration ensures that any solid benzoic acid obtained due to cooling of solution is dissolved

D. Calculation of the enthalpy of dissolution from the data so obtained

As shown in Section 5.2, the dissolution enthalpy of benzoic acid can be calculated by using the following formula.

$$\Rightarrow \qquad \Delta H = 2.303\, R\left[\frac{T_2 - T_1}{T_1 T_2}\right]\log\frac{S_2}{S_1} \qquad \ldots(5.11)$$

where, S_1 and S_2 are the solubilities of benzoic acid at the temperatures, T_1 and T_2 respectively.

5.5 OBSERVATIONS

a) Preparation of a standard solution of oxalic acid

Mass of empty weighing bottle	=	m_1	= …. g
Mass of weighing bottle + oxalic acid	=	m_2	= …. g

Mass of weighing bottle after transferring oxalic acid = m_3 = …. g

Mass of oxalic acid transferred (m) = $m_2 - m_3 = m$ = …. g

Molar mass of oxalic acid = M = 126 g mol^{-1}

Volume of the oxalic acid solution prepared = V = …. cm^3

➔ Molarity of oxalic acid solution = $M_O = \frac{m \times 1000}{126 \times 100} = \frac{10m}{126}$ = ... M

b) Standardisation of sodium hydroxide solution by titrating against standard solution of oxalic acid

Volume of standard solution of oxalic acid, V_O = ____ cm^3

Solution taken in the burette : Sodium hydroxide

Indicator used : Phenolphthalein

Observation Table 1
Standardisation of sodium hydroxide solution

S.No.	Volume of standard oxalic acid solution / cm^3	Burette reading		Titre value / cm^3 (Final-initial burette reading)
		Initial	Final	
1				
2				
3				
		Concordant value		

Volume of NaOH used (concordant value)= _____ cm^3

c) Determination of concentrations (solubilities) of benzoic acid at different temperatures by titrating against standardised solution of sodium hydroxide

Volume of benzoic acid solution taken, V_B = ____ cm^3

Solution taken in the burette : Sodium hydroxide

Indicator used : Phenolphthalein

Observation Table 2
Titration of different benzoic acid solutions with standardised solution of sodium hydroxide

Temp. of drawing the sample / °C	Volume of benzoic acid solution / cm^3	Burette reading		Titre value / cm^3 (Final-initial burette reading)
		Initial	Final	
40				
30				
20				
10				

5.6 CALCULATIONS

Perform the following calculations based on the observations recorded above.

1. Molarity of the standard solution of oxalic acid

The molarity of standard solution of oxalic acid can be calculated by substituting the value of *m*, the mass of oxalic acid used to prepare the solution in the following formula:

$$M_o = \frac{m \times 1000}{126 \times 100} = \frac{10\,m}{126} = M_o = \text{.....} \text{ M}$$

Molarity of oxalic acid solution= M_o =…….M.

2. Standardisation of sodium hydroxide

Volume of standard solution of oxalic acid used = V_o …….cm^3

Volume of NaOH used (concordant value from Observation Table1) = V_N …….cm^3

The concentration of the given sodium hydroxide solution can be determined as follows.

The reaction involved in the titration:

$$2NaOH + (COOH)_2 \rightarrow (COONa)_2 + H_2O$$

Molarity equation: $M_N V_N = 2M_O V_O$

The molarity of sodium hydroxide= $M_N = \frac{2\,M_o V_o}{V_N}$ =.....M

Molarity of the prepared solution of sodium hydroxide= M_N =..... M

3. Determination of concentration (solubility) of benzoic acid at different temperatures

At 40°C:

Volume of NaOH used (from Observation Table 2) =V_N …….cm^3

The molarity of NaOH as determined in part 2 = M_N = …..M

Volume of benzoic acid solution taken = V_B= …….cm^3

The reaction involved in the titration:

$$C_6H_5COOH + NaOH \rightarrow C_6H_5COONa + H_2O$$

Molarity equation: $M_B V_B = M_N V_N$

$$\Rightarrow M_B = \frac{M_N V_N}{V_B} M$$

Calculate the concentration of the benzoic acid solution by substituting the values,

The concentration (solubility) of benzoic acid solution withdrawn at 40°C =……mol dm^{-3}

At other temperatures: Similarly calculate the concentrations (solubilities) of other solutions of benzoic acid and compile your data in the following table

Temp. T /°C	**Temp. T** /K	**Concentration (solubility) of benzoic acid / mol dm^{-3}**
40	313	
30	303	
20	293	
10	283	

4. **Calculation of dissolution enthalpy for benzoic acid:** Take the solubilities of benzoic acid at any two temperatures from the table above and use Eq. (5.11) given below to calculate the dissolution enthalpy of benzoic acid.

$$\Rightarrow \qquad \Delta H = 2.303\, R\left[\frac{T_1 T_2}{T_2 - T_1}\right]\log\frac{S_2}{S_1} \qquad \ldots(5.11)$$

Repeat the calculation with other combinations of temperatures and obtain the corresponding solubilities and compile them in the following table.

Temp. T_1 /K	**Temp. T_2** /K	**Dissolution enthalpy** /kJ mol^{-1} $\Rightarrow \Delta H = 2.303\, R\left[\frac{T_1 T_2}{T_2 - T_1}\right]\log\frac{S_2}{S_1}$
303	313	
293	303	
283	293	
283	313	

Average value of the dissolution enthalpy = ΔH = ... kJ mol^{-1}

5.7 RESULT

The dissolution enthalpy for benzoic acid is found to be, ΔH = ... kJ mol^{-1}

EXPERIMENT 6

MEASUREMENT OF pH OF AERATED DRINKS, FRUIT JUICES, SOAPS AND SHAMPOOS USING pH-METER

Structure

6.1 Introduction
Expected Learning Outcomes
6.2 Principle
6.3 Requirements
6.4 Procedure
6.5 Observations
6.6 Result

6.1 INTRODUCTION

In the previous experiment you have learnt about the determination of dissolution enthalpy of benzoic acid by using its solubility measurements as a function of temperature. In this experiment you would learn about and make measurements of the pH of aerated drinks, fruit juices, soaps and shampoos. You have learnt about the concept of pH in your earlier classes as well as in the course BCHCT-133 and are aware that pH is a measure of the concentration of hydrogen (hydronium) ions in an aqueous solution. It is an important parameter that concerns us in many of our day to day activities. The soaps we use for washing or for bathing; shampoos we use on our hair; detergents for washing clothes; the face creams etc. have a certain value of pH. One of the important considerations for their quality is their pH; it has to be such that these are safe for our body. Similarly, the acidity of fruit juices or aerated drinks we consume can also affect us by acting on the enamel of our teeth. Consumption of highly acidic drinks can severely damage the enamel and affect our health.

In this experiment you would learn about the measurement of pH of different solutions by using an instrument called pH meter. In this context you would learn about the concept of pH, the principle of pH meter and glass electrode. In the next experiment

you would learn about the preparation of buffer solutions, measurement of their pH values using pH meter and comparing the observed values with the theoretical values.

Expected Learning Outcomes

After studying about and performing the experiment, you should be able to:

- ❖ define pH and explain the principle of pH meter used for measuring the pH of aqueous solutions;
- ❖ describe a combination glass electrode and explain its working principle;
- ❖ state the importance of using pH meter;
- ❖ process the given sample of fruit juice, aerated drink, soap or shampoo to make it suitable for pH measurement with pH meter;
- ❖ calibrate the pH meter using standard buffer solutions; and
- ❖ make measurement of pH of a solution using pH meter.

6.2 PRINCIPLE

You have learnt in the Unit 7 of BCHCT-133 course that a Danish botanist S.P.L. Sorensen introduced the concept of pH, in 1909. He was concerned about representing the concentrations of H^+ and OH^- ions in the aqueous solutions of acids and bases that vary over a very wide range. This required using negative powers of 10 and it was quite inconvenient to handle these numbers.

He proposed a practical scale called **pH scale** to quantitatively express the concentration or 'potential' of H^+ ions in the aqueous solutions of acids and bases; especially in dilute solutions (< 0.01 M). He defined pH as the negative logarithm (to the base 10) of the molar concentration of hydrogen (we now use hydronium) ions in solution. That is,

$$pH = -\log_{10}[H^+] \text{ or } -\log_{10}[H_3O^+] \quad \ldots(6.1)$$

The basic logic of the scale was that by taking logarithm the numbers expressed as negative powers of 10, representing concentration of hydrogen ions become simple negative numbers (e.g., $\log_{10} 10^{-3} = -3$), which are relatively easier to handle. However, to make it even better, the expression was multiplied by −1 so that the concentrations of hydrogen ions in dilute aqueous solutions of acids and bases could be expressed in terms of simple positive numbers.

Thus, to know the pH of a given solution we need to measure the concentration of hydrogen ions in it. Now the question comes is how do we measure the concentration of hydrogen ions in an aqueous solution? One simple answer could be to titrate the solution with a standard solution of a base / acid. However, this seemingly simple answer involves elaborate experimentation and also may not be an appropriate answer due to the following reasons.

- The sample being measured may be deeply coloured e.g., an industrial effluent and we may not have a suitable indicator for the determination of the end point of the titration.

- The sample being measured gets consumed in the process of titration and we may not be able to afford it in case of biological samples as these generally are not available in large amounts and are difficult to obtain.
- It is quite time consuming process; we need a quick determination

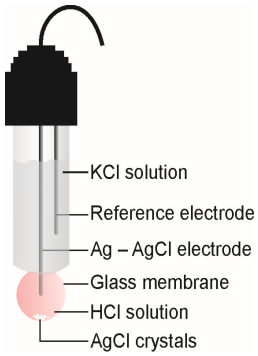
Such a quick determination of pH can be done with the help of an instrument called pH meter. The measurement of pH of a solution with pH meter is based on the measurement of the potential of an electrode that is reversible to the hydrogen ion concentration (and hence pH) of the solution. A combination glass electrode is most commonly employed for this purpose. The electromotive potential of the combination glass electrode is measured by the pH meter and is electronically converted to the pH of the solution. The pH meters are so designed that the scale directly indicates the pH of the solution. In order to understand the principle of pH meter we need to recall the principle of glass electrode about which you have learnt in your earlier classes.

An alternative way of quick measurement of pH of a solution is by using the pH paper or Universal indicator solution. However, these provide only a rough estimate of the pH value.

A glass electrode consists of a glass tube having a bulb of thin glass membrane (that is permeable to H^+ ions) at one end. The bulb is filled with a solution of a constant pH (e.g., 0.1 M HCl) and a reversible electrode like Ag - AgCl electrode (silver wire coated with silver chloride) dipped in it. When this glass electrode is dipped in an aqueous solution whose pH is to be determined, a potential is developed across the glass membrane. This potential depends on the difference in the concentrations of hydrogen ions across the glass membrane. The glass electrode having Ag - AgCl electrode can be represented as

A calomel electrode can also be used in place of Ag - AgCl electrode.

$$Ag|\ AgCl\ |\ Cl^-,\ |\ H^+(0.1M)\ |glass\ membrane|\ H^+(Unknown) \quad \ldots(6.2)$$



a glass electrode

And the emf of the glass electrode is given by the following Nernst equation

$$E = E^{o}_{glass} - \frac{RT}{nF}\ln[H^+] \quad \ldots(6.3)$$

Substituting the values of R, *T*, F and n; at 298 K the Eq. (6.3) becomes

$$E = E^{o}_{glass} - 0.0592\ pH \quad \ldots(6.4)$$

As you know that we cannot measure the potential of a single electrode, we need to combine it with a standard reference electrode. Here, we use a calomel electrode as a reference. The cell so obtained can be represented as

$$Ag|\ AgCl\ |\ Cl^-,|\ H^+(0.1M)\ |glass\ membrane|\ H^+(Unknown)::\ calomel\ electrode \quad \ldots(6.5)$$

or

$$Ag|\ AgCl\ |\ Cl^-,|\ H^+(0.1M)\ |glass\ membrane|\ H^+(Unknown)::\ KCl(satd.)|\ Hg_2Cl_2|\ Hg(l) \quad \ldots(6.6)$$

The cell potential of this combination is given as

$$E_{cell} = E_{calomel} - E_{glass} \quad \ldots(6.7)$$

$$E_{cell} = E_{calomel} - (E^{o}_{glass} - 0.0592\ pH) \quad \ldots(6.8)$$

The emf of standard calomel electrode is = 0.241 V

It is experimentally found that the potential of a glass electrode varies with the activity of hydrogen ions in the solution and there is a change of 0.0591 V per pH unit at 25 °C.

Substituting in Eq. (6.8) we get,

$$E_{cell} = 0.241 - (E^{o}_{glass} - 0.0592\ pH) \quad ...(6.9)$$

On simplification we get,

$$pH = \frac{E_{cell} - 0.241 + E^{o}_{glass}}{0.0592} \quad ...(6.10)$$

Thus, we see that there is a direct relationship between the pH and E_{Cell}. So the measurement of pH essentially comes down to measuring the potential of the cell given in Eq. (6.5). However, due to high resistance of glass membrane we cannot use an ordinary potentiometer for measuring the potential. The pH meter uses an electronic voltmeter to measure this E_{Cell} and by electronically processing the data converts it into pH that is displayed by an LED on the instrument.

Fig. 6.1: A typical laboratory pH meter assembly

There are two possibilities to create the cell given in Eq. (6.6). In one of the ways we use two electrodes (calomel or some other reference electrode and a glass electrode) as described above. In the second way we use a combination glass electrode that combines the glass electrode and the calomel electrode in a single unit. Most of the modern pH meters employ combination glass electrodes as the process of measurement of pH becomes convenient.

You may be thinking that we mentioned above that Eq. (6.10) relates pH and E_{cell} but conveniently ignored the term, E^{o}_{glass}. You are right; we purposely ignored this to take it up now. E^{o}_{glass} is a constant that depends on the nature of the glass used for making the glass membrane and also the potential of Ag-AgCl electrode. Since different manufacturers may use different type of glass so this parameter would be different for different electrodes. In fact it is a characteristic of the glass electrode / combination glass electrode being used. Therefore, we need to determine it for the electrode being used in the measurement of pH. For this we take a buffer solution of known pH and measure E_{cell} for it. For example, if we take a buffer solution having a pH of 4.0 then we can write Eq. (6.10) as

$$4.0 = \frac{E_{cell} - 0.241 + E^{o}_{glass}}{0.0592} \quad ...(6.11)$$

Simplifying, we get

$$E^{o}_{glass} = 0.4598 - E_{cell} \quad ...(6.12)$$

Substituting the measured value of E_{cell} we can get the value of E^{o}_{glass}. In any measurement of pH with pH meter using glass electrode / combination glass electrode the first step is to measure the E_{cell} for a buffer of known pH which provides the value of E^{o}_{glass} -a characteristic of the electrode being used. This process is called **calibration** of pH meter. Once calibrated, the pH meter can be used for any number of measurements. However, the glass membrane does get affected by the time and storage conditions, it is therefore, desired to calibrate the pH meter every time before making pH measurements.

We can use Eq. (6.9) to establish a relationship between the pH values of known (buffer solution) and unknown solutions and the corresponding E_{cell} values.

$$E_{cell}(buffer) = 0.241 - (E^{o}_{glass} - 0.0592 \text{ pH (buffer)}) \quad ...(6.13)$$

$$E_{cell}(sample) = 0.241 - (E^{o}_{glass} - 0.0592 \text{ pH (sample)}) \quad ...(6.14)$$

Subtracting Eq. (6.14) from Eq. (6.13) we get,

$$E_{cell}(buffer) - E_{cell}(sample) = 0.0592 \text{ [pH (buffer)-pH (sample)]} \quad ...(6.15)$$

You may note that by this way we do not need to calculate E^{o}_{glass}; it gets eliminated. Further, you must remember that in the expressions given above we have assumed the temperature to be 298K. At other temperatures the numbers in the equations given above will change. The modern pH meters have provision to apply temperature corrections also however; it is beyond the scope of this course.

6.3 REQUIREMENTS

Apparatus		Chemicals / materials
Measuring cylinder 100 cm^3	1	Standard buffer solutions*
Beaker 100 cm^3	5	Fruit juice samples
Beaker 50 cm^3	2	Aerated drink sample
Glass Stirrer	1	Soap sample
pH meter	1	Shampoo sample
Combination glass electrode	1	**In case the standard buffer solutions are not available, the laboratory staff will use buffer tablets to prepare the solutions and provide the same.*
Wash bottle	1	
Blade / knife	1	

6.4 PROCEDURE

The experiment has the following steps

A. Preparation of the samples of given materials for pH measurement
B. Calibration of the pH meter
C. Measurement of pH of prepared samples by pH meter

Let us learn about the procedure for these steps

A. Preparation of samples of given materials for pH measurement

The preparation of sample for measurement of pH is different for different types of materials. Prepare the samples as given below:

I. **Aerated drinks:** The aerated drinks do not require any formal preparation. You can transfer about 20 cm^3 of the aerated drink in a 50 cm^3 beaker and proceed for the measurement of pH.

II. **Fruit juices:** in case of the measurement of pH of a fruit juice sample you may use a packaged fruit juice. For this, shake the juice well to make it homogenous and transfer about 20 cm^3 of it to a 50 cm^3 beaker for measurement. However, in case you are arranging for a fresh fruit juice, get it without any additive or dilution. Again, shake well before making measurement of pH.

III. **Soap solution**: Take 20 cm^3 of hot boiling water in a 50 cm^3 beaker and to this add 2.0 g of scrapped soap (you may use a blade or a knife to scrape the soap). Stir gently to dissolve the soap, and allow it to cool to room temperature before making the measurement. The sample for detergent can also be prepared in the same way.

IV. **Shampoo solution**: Transfer 2.0 cm^3 of the shampoo to a 50 cm^3 beaker and add distilled water to it to make the volume up to 20 cm^3. Stir gently without making lather and keep the solution undisturbed for about 30 minutes before measuring the pH

B. Calibration of the pH meter

There are a large number of manufacturers of pH meters used in the laboratories. All the pH meters used in the laboratories have their own operation / instruction manual. You are required to refer to the instruction manual of the pH meter being used by you and study its operation. Your counselor would help you in learning the way to measure pH with the pH meter available in your laboratory. However, a general procedure for the calibration of pH meter is given below.

While measuring pH ensure that the bulb of the glass / combination electrode is completely dipped into the solution. If not fully dipped add some more solution

i. Connect the combination glass electrode to the pH meter; switch on the pH meter and allow it to stabilize for about 15 minutes.

ii. Take the standard buffer solution of pH=7.0 in a clean beaker and place the glass electrode in this solution. Gently stir the solution and note the pH as described in the operational manual of the pH meter. It is expected to be 7.0. If it is not seven, adjust it to 7.0 with the calibration knob on the pH meter.

iii. Wash the electrode with distilled water and wipe off the water adhering to it by using a tissue paper. For washing the electrode hold it over a waste container or the washbasin and rinse the electrode thoroughly with distilled water using a wash bottle.

iv. Repeat step (ii) with the standard buffer of pH 4.0.

v. Repeat step (ii) to (iv) till you get consistent values with the standard buffer solutions of pH 4.0 and 7.0. You may take the help of your counselor or the laboratory assistant for this.

Once calibrated the pH meter is ready for the measurement.

Alternatively, you may use standard buffer solutions of pH 7.0 and 9.2 for the calibration of the pH meter

C. Measurement of pH of the given sample solution

i. Take the sample whose pH is to be measured in a clean beaker and place the washed and dried glass electrode in this solution. Take care that the bulb of the electrode is fully dipped into the solution and it does not touch the base or the walls of the beaker.

ii. Gently stir the solution and note the pH as described in the operational manual of the pH meter. (Some times the value may fluctuate, note the reading when it is stable)

iii. Record your observations in the Observation Table 1 given below.

6.5 OBSERVATIONS

Record your observations here. Write the name of the sample used in column 1 and the measured value of the pH in column 2.

Observation Table 1

Measured pH values of different sample solutions prepared

S.No	Sample	Measured pH value
1		
2		
3		
4		
5		

6.6 Result

The pH values of different samples are found as given below:

S.No	Sample	Measured pH value
1		
2		
3		
4		

EXPERIMENT 7

PREPARATION & MEASUREMENT OF pH VALUES OF BUFFER SOLUTIONS AND THEIR COMPARISON WITH THEORETICAL VALUES

Structure

7.1 Introduction
Expected Learning Outcomes
7.2 Principle
7.3 Requirements
7.4 Procedure
7.5 Observations
7.6 Calculations
7.7 Result

7.1 INTRODUCTION

In the previous experiment you have learnt about and made measurements of the pH of aerated drinks, fruit juices, soaps and shampoos.You have also learnt about the concept of pH and the principle of pH meter used for measuring the pH of different solutions. In this experiment you would learn about the preparation of buffer solutions and measurement of their pH values. You have learnt in your earlier classes that buffer solutions are the ones that resist the change in their pH value on adding small amounts of solutions of strong acids or bases or on slight dilution. Buffer solutions are used in many chemical and biochemical experiments. In this experiment you would also undertake the calculation of theoretical pH values of the prepared buffers solutions using Henderson-Hasselbalch equation and compare them with the experimentally observed values. In the next experiment, you would learn about the determination of melting and boiling points of organic compounds.

Expected Learning Outcomes

After studying about and performing this experiment, you should be able to:

- ❖ define buffer solutions and give examples of different types of buffer solutions;
- ❖ state the Henderson-Hasselbalch equation for the pH of acidic and basic buffer solutions;
- ❖ prepare series of acidic and basic buffer solutions of different pH values;
- ❖ calibrate the pH meter and measure the pH of the prepared buffer solutions;
- ❖ calculate the theoretical (expected) pH values of the prepared buffer solutions by using Henderson-Hasselbalch equation; and
- ❖ compare the calculated and experimental pH values of the prepared buffer solutions.

7.2 PRINCIPLE

You have learnt in the Unit 8 of BCHCT-133 course that a buffer solution is defined as a solution that resists the change in its pH on adding small volumes of strong acid / base or on slight dilution. A buffer solution consists of a mixture of a weak acid or a weak base and a salt having an ion common with it. The buffer solutions containing a weak acid and its salt containing a common ion are called **acidic buffer solutions** e.g. acetic acid and sodium acetate, (CH_3COOH + CH_3COONa). On the other hand the buffer solutions containing weak base and its salt having a common ion are called **basic buffer solutions** e.g. ammonium hydroxide and ammonium chloride,(NH_4OH + NH_4Cl).

The pH of acidic buffer solution depends on the relative concentrations of the weak acid and its salt in the buffer mixture. These are related in terms of the following Henderson-Hasselbalch equation.

$$pH = pK_a + \log\frac{[salt]}{[acid]} \quad \ldots(7.1)$$

$pK_a = -\log K_a$

Where, pK_a is the negative logarithm (to the base 10) of the acid dissociation constant of weak acid, K_a. So we see that for a given acidic buffer the pH depends on the ratio of concentrations of the salt and the weak acid and the pK_a value. In other words, we can say that by varying the relative concentrations of the weak acid and its salt in acidic buffer system we can control its pH value. Similarly, the expression for the pOH of a basic bufferis

$$pOH = pK_b + \log\frac{[salt]}{[base]} \quad \text{or} \quad pH = 14 - pK_b + \log\frac{[salt]}{[base]} \quad \ldots(7.2)$$

$pK_b = -\log K_b$

Where, pK_b is the negative logarithm (to the base 10) of the acid dissociation constant of weak acid, K_b. Here again we can vary the concentrations of the weak base and its salt to vary the pOH (and hence pH) of the buffer solution. In the light of these, we will prepare different buffer solutions by suitably varying the concentrations of different components of the buffer systems. The Eq. (7.1) and Eq. (7.2) can be used to calculate the theoretical (expected) pH values of the prepared buffer solutions. These values can then be compared with the experimentally determined pH values.

7.3 REQUIREMENTS

Apparatus		Chemicals
pH meter	1	Standard buffer solutions*
Combination glass electrode	1	0.2 M Acetic acid*
Beaker 50 cm^3	10	0.2 M Sodium acetate*
Burettes	4	0.2 M Ammonium hydroxide*
Burette stand and clamp	4	0.2 M Ammonium chloride*
Funnels	2	
Wash bottle	1	* These solutions would be prepared by the laboratory staff and provided to you
Glass Stirrer	1	

7.4 PROCEDURE

The experiment has the following steps:

A. Preparation of a series of acetic acid- sodium acetate buffer solutions

B. Preparation of a series of ammonium hydroxide- ammonium chloride buffer solutions

C. Calibration of the pH meter

D. Measurement of pH values of the prepared buffer solutions

E. Calculation of expected pH values of the buffer solutions and their comparison with the experimental values

Let us learn about the procedure for these steps:

A. **Preparation of a series of acetic acid- sodium acetate buffer solutions**

Follow the procedure given below to prepare a series of acetic acid- sodium acetate buffer solutions of different pH values

i. Take a clean burette and rinse it with the given solution of 0.2 M acetic acid.

ii. Fill the burette with 0.2 M acetic acid solution by using a funnel and clamp the burette on the burette stand. Label the burette as 0.2 M acetic acid.

iii. Similarly take another clean burette, rinse it with the solution of 0.2 M sodium acetate.

iv. Fill the burette with 0.2 M sodium acetate solution by using a funnel and clamp the burette on the burette stand. Label the burette as 0.2 M sodium acetate.

v. Take five beakers each of 50 cm^3 capacity and label them as A-1 to A- 5.

vi. Carefully transfer 16 cm^3 of 0.2 M acetic acid and 4 cm^3 of 0.2 M sodium acetate solutions from the respective burettes to beaker labeled as A-1 and mix the solution.

vii. Similarly transfer acetic acid and sodium acetate solutions to the other four beakers as per the Observation Table 1 given under observations (Section 7.5) and stir each solution.

B. **Preparation of a series of ammonium hydroxide-ammonium chloride buffer solutions**

Follow the procedure given below to prepare a series of ammonium hydroxide- ammonium chloride buffer solutions of different pH values

i. Take a clean burette and rinse it with the given solution of 0.2 M ammonium hydroxide.

ii. Fill the burette with 0.2 M ammonium hydroxide solution by using a funnel and clamp the burette on the burette stand. Label the burette as 0.2 M ammonium hydroxide.

iii. Similarly take another clean burette, rinse it with the solution of 0.2 M ammonium chloride.

iv. Fill the burette with 0.2 M ammonium chloride solution by using a funnel and clamp the burette on the burette stand. Label the burette as 0.2 M ammonium chloride.

v. Take five beakers each of 50 cm^3 capacity and label them as B-1 to B- 5.

vi. Carefully transfer 16 cm^3 of 0.2 M ammonium hydroxide and 4 cm^3 of 0.2 M ammonium chloride solutions from the respective burettes to beaker labeled as B-1 and mix the solution.

vii. Similarly transfer 0.2 M ammonium hydroxide and 0.2 M ammonium chloride to the other four beakers as per the Observation Table 2 given under observations (Section 7.5) and stir each solution.

C. Calibration of the pH meter

The general procedure for the calibration of pH meter is given below. You may need to consult the operational manual of the pH meter being used.

i. Connect the combination glass electrode to the pH meter; switch on the pH meter and allow it to stabilize for about 15 minutes.

ii. Take the standard buffer solution of pH=7.0 in a clean beaker and place the glass electrode connected to the pH meter in this solution. Gently stir the solution and note the pH as described in the operational manual of the pH meter. It is expected to be 7.0.

iii. If it is not seven adjust it to 7.0 with the calibration knob on the pH meter.

iv. Wash the electrode with distilled water and wipe off the water adhering to it by using a tissue paper. Repeat step (ii) with the standard buffer of pH 4.0.

v. Repeat step (ii) to (iv) till you get consistent values with the standard buffer solutions of pH 4.0 and 7.0. You may take the help of your counselor or the laboratory assistant for this.

Once calibrated the pH meter is ready for the measurement

While measuring pH ensure that the bulb of the glass / combination electrode is completely dipped into the solution. If not fully dipped add some more solution

Alternatively, you may use standard buffer solutions of pH 7.0 and 9.2 for the calibration of the pH meter

D. Measurement of pH of the buffer solutions

i. Take the buffer solution labeled as A-1 in a clean beaker of 50 cm^3 capacity and dip the glass electrode into it. Take care that the bulb of the electrode is fully dipped in the solution and it does not touch the base or the walls of the beaker.

ii. Gently stir the solution; note the pH value from the pH meter and record it in the Observation Table 1 given below.

iii. Wash the bulb of the glass electrode with distilled water poured with a wash bottle. Gently wipe the electrode bulb.

iv. Repeat the same procedure with the other buffer solutions of A- series.

v. Similarly, measure the pH of buffer solutions of B-series and record your observations in Observation Table 2.

7.5 OBSERVATIONS

Record your observations here

Observation Table 1

Volume of acetic acid and sodium acetate solutions required for preparing series of acetic acid –sodium acetate buffer solutions and measured pH values of the solutions so obtained

S. No.	Volume of 0.2 M acetic acid /cm^3	Volume of 0.2 M sodium acetate/cm^3	Measured pH Value
A-1	16	04	
A-2	12	08	
A-3	10	10	
A-4	08	12	
A-5	04	16	

Observation Table 2

Volume of ammonium hydroxide and ammonium chloride solutions required for preparing series of ammonium hydroxide –ammonium chloride buffer solutions and measured pH values of the solutions so obtained

S. No.	Volume of 0.2 M Ammonium hydroxide/cm^3	Volume of 0.2 M Ammonium chloride/cm^3	Measured pH Value
B-1	16	04	
B-2	12	08	
B-3	10	10	
B-4	08	12	
B-5	04	16	

7.6 CALCULATIONS

The pH values of the acidic buffer solution can be calculated by using Eq.(7.1). For acetic acid-sodium acetate buffer the equation becomes

$$\text{pH} = \text{p}K_\text{a} + \log\frac{[\text{sodium acetate}]}{[\text{acetic acid}]}$$

The pKa value for acetic acid is 4.76; substituting in the equation we get,

$$\text{pH} = 4.76 + \log\frac{[\text{sodium acetate}]}{[\text{acetic acid}]}$$

The expected (theoretical) pH value of the prepared buffer solutions can be calculated by substituting the concentrations of sodium acetate and acetic acid in the expression. For example, the theoretical pH value for the buffer solution labeled as A-1 would be

$$\text{pH} = 4.76 + \log\frac{[4]}{[16]} = 4.76 + \log\frac{1}{4} = 4.76 - \log 4 = 4.76 - 0.60 = 4.16$$

$$\log\frac{1}{x} = -\log x$$

You may note here that in this calculation we have just used the volumes of the salt solution and acid solutions used to prepare the buffer. This is justified because in this expression we need to use the ratio of their concentrations and not absolute concentrations. As the stock solution of the two components had same concentration (0.2 M), we can just take the volumes of these solutions used to represent their concentrations. However, if the concentrations of the stock solutions were different, we would need to calculate the concentrations of the two components in the buffer mixture.

Similarly calculate the expected pH values for the other buffer solutions of A series and record them in the Observation Table 3 given below. For comparison the measured pH values can be taken from Observation Table 1.

Observation Table 3

Expected and observed pH values of the prepared acetic acid and sodium acetate buffer solution (A–series)

S. No.	Expected pH value	Measured pH Value (From Observation Table 1)
A-1		
A-2		
A-3		
A-4		
A-5		

Similarly the pH values of B series of buffer solutions can be calculated by using the following expression assuming the temperature to be 298 K and taking the value of pK_w to be 14.

$$\text{pH} = 14 - \text{p}K_\text{b} + \log\frac{[\text{salt}]}{[\text{base}]}$$

$$\text{p}K_\text{W} = \text{pH} + \text{pOH}$$

The pK_b value for ammonium hydroxide is 4.76. Substituting it in the equation and simplifying we get,

$$pH = 14 - 4.76 + \log\frac{[\text{ammonium chloride}]}{[\text{ammonium hydroxide}]}$$

$$pH = 9.24 + \log\frac{[\text{ammonium chloride}]}{[\text{ammonium hydroxide}]}$$

Here again the stock solutions of the buffer components have same concentration so we can just use the volumes of the two components used for preparing the buffer solution to calculate the ratio of their concentrations. Calculate the pH values of the prepared buffer solutions and record them in the Observation Table 4 given below. For comparison the measured pH values can be taken from Observation Table 2.

Observation Table 4

Expected and observed pH values of the prepared ammonium hydroxide – ammonium chloride buffer solutions (B–series)

S. No.	Expected pH value	Measured pH Value (From Observation Table 2)
B-1		
B-2		
B-3		
B-4		
B-5		

7.7 Result

The calculated and measured pH values of the prepared buffer solutions are as under.

S. No.	Expected pH value	Measured pH Value
A-1		
A-2		
A-3		
A-4		
A-5		
S. No.	**Expected pH value**	**Measured pH Value**
B-1		
B-2		
B-3		
B-4		
B-5		

UNIT 2

TECHNIQUES IN ORGANIC LABORATORY

Structure

2.1 Introduction

Expected Learning Outcomes

2.2 Techniques of Heating, Cooling and Filtration

Heating Methods

Heating Under Reflux

Cooling Methods

Stirring

Filtration

2.3 Techniques of Separation and Purification

Solvent Extraction

Recrystallisation

Sublimation

Distillation

Chromatography

2.4 Tests for Purity

Melting and Boiling Point

2.5 Glassware: Precautions in Use and Cleaning

2.6 Laboratory Safety

2.7 Laboratory Note-Book

Sample Note-Book Format

2.8 Answers

2.1 INTRODUCTION

In this lab course you have performed a number of physical chemistry experiments, which were based on the physical chemistry concepts dealt in the theory course of this semester. From Experiment 8 onwards you would be doing experiments based on organic chemistry concepts. These concepts are mainly related to the preparation and purification of organic compounds.

The first unit of this block is meant to introduce some of the common experimental techniques, which you would use for carrying out experiments in the organic chemistry laboratory. The apparatus required for various techniques will be described and the theory of some of the techniques will be briefly discussed along with the related experiments. You will learn how to use simple laboratory techniques such as heating, cooling, stirring and filtrations. You will also study briefly the separation and purification techniques such as extraction, recrystallisation, distillation and chromatography. Determination of the physical constants such as melting and boiling points to check the purity of organic

compounds is mentioned in this unit and discussed in detail along with the Experiments 8 and 9. Finally, we would tell you how you should record your work in the laboratory note-book. After this unit you will study the details of the experiments that you will perform in the laboratory.

Expected Learning Outcomes

After studying this unit you should be able to:

- describe basic laboratory operations such as heating, cooling, stirring and filtration;
- explain the basic concepts involved in separation and purification techniques;
- select and use appropriate apparatus and techniques for various types of organic experiments;
- state the various precautions needed in the use and cleaning of glass apparatus and for laboratory safety; and
- describe how to maintain laboratory record for the experiments.

2.2 TECHNIQUES OF HEATING, COOLING AND FILTRATION

The organic reactions do not undergo completion with ease and have to be heated at higher temperatures or may be subjected to other type of operations. Heating, cooling, stirring and filtration are the important operations widely used both in preparatory and quantitative organic chemistry. Let us study these simple laboratory techniques in the following subsections.

2.2.1 Heating Methods

Heating of organic compounds is an important, common and essential activity for various reasons. Heating increases the rate of chemical reactions. You would recall that organic reactions are molecular reactions. Unlike most of the inorganic reactions, which are ionic and often instantaneous, organic reactions are slow and incomplete at room temperature. An organic reaction mixture has, therefore, often to be heated to make the reaction go. Heating is also required in purification of liquids by distillation and in the dissolution of solids during recrystallisation and also in the determination of melting and boiling points of organic compounds for testing their purity.

In an organic laboratory the following heating devices are generally used:

i) Bunsen burner
ii) Water bath
iii) Oil bath
iv) Sand bath

Let us understand the use and the precautions that should be taken in using these devices.

i) Bunsen burner

Since nearly all the organic substances are inflammable, care and good judgment should always be taken when considering the use of these devices. Direct heating on a burner flame should be avoided as far as possible. However, if a burner has to be used, say, while taking a melting or boiling point, all inflammable and volatile materials should be removed away from the burner. In case direct heating has to be done, it is advisable to use wire gauze. This makes heating more uniform.

ii) Water bath

A water bath should be used to provide uniform heating. For temperature up to 100°C, a water bath is generally employed. You may be using an electrically heated water bath or a common copper water bath, which can be heated on a burner. A common type of electrically heated water bath is shown in Fig. 2.1. Water bath is covered with rings, which can be adjusted according to the size of the vessel to be heated. The water bath is safe for flammable liquids but care has to be taken to prevent you from getting burnt by the hot steam.

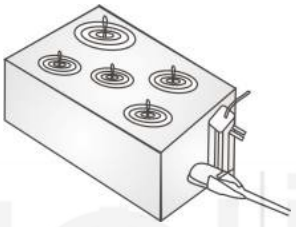


Fig. 2.1: Electrically heated water bath.

iii) Oil bath

Like water bath an oil bath is used to provide uniform heating. The difference being that an oil bath is used when heating is carried out above 100°C. The oil bath can be made by filling a copper bath with a liquid like paraffin oil (Fig. 2.2). Silicone oil is good quality oil but it is expensive. All the oils have a tendency to give fumes at high temperature therefore; the reactions in an oil bath should be carried out in a fume hood.

Fig. 2.2: Copper bath.

iv) Sand bath

The sand bath is also used for uniform heating and used to achieve high temperatures. A sand bath is a shallow iron plate filled with sand. It is heated by means of a burner. It is one of the safest devices to be used as per the requirement. However, if the reaction is such that there is a possibility of toxic vapours coming out of the reaction, the reaction should be carried out in fume hood as in the case of an oil bath.

2.2.2 Heating Under Reflux

When a solution is heated and boiled in such a manner that the vapours produced during heating undergo condensation and return back to the solution

from where these vapours are produced, the process is repeated many times during the ongoing reaction and called **refluxing** of the solution or the reaction mixture. A reaction mixture has to be often heated under reflux to prevent loss of volatile reagents and solvents. The other purpose of refluxing is to speed up the reaction.

In the process of refluxing, generally a round-bottom flask is fitted with a water condenser and heated on a water bath or an oil bath as shown in Fig. 2.3. The liquid should be made to boil gently and condense back into the flask. The reaction flask should never be filled more than 1/2 to 2/3. In case of very high boiling solvents an air condenser may be used.

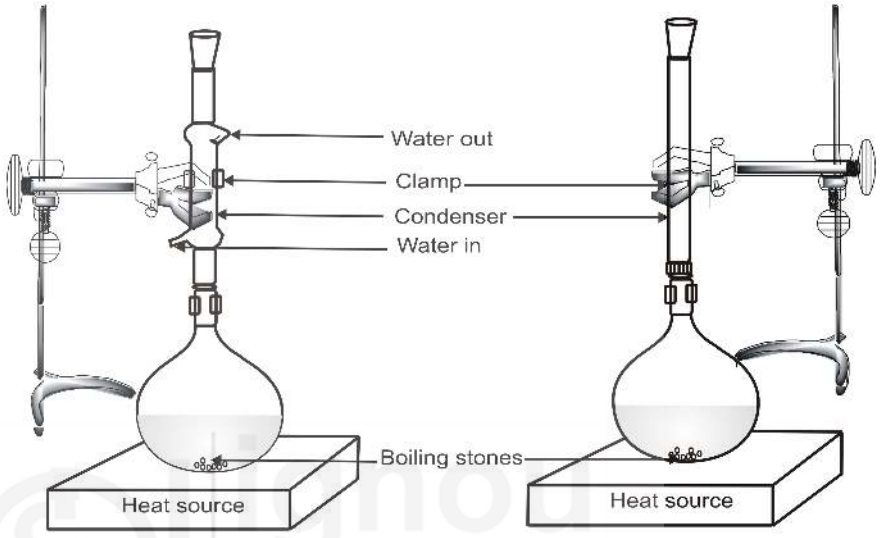


Fig. 2.3: Heating a reaction mixture under reflux:
(a) with a water condenser.
(b) with an air condenser.

2.2.3 Cooling Methods

The way heating is necessary for an organic reaction to proceed, for some of the reactions the reaction mixture may have to be kept at room temperature to get the desired product. Sometimes we have to keep temperatures below the room temperature for carrying out reactions, which are strongly exothermic, i.e. the ones that release a lot of energy on mixing. Finely crushed ice is used for maintaining the temperature at 0-5^{o}C. In order to maintain the temperature below 0^{o}C, a mixture of common salt and crushed ice is used. This is called the freezing mixture and gives a temperature in the range of -5 or > -20°C.

2.2.4 Stirring

In the context of organic reactions, stirring is meant to be shaking of the reaction mixture with the help of a glass rod or other means for various purposes. It is done to dissolve the contents of the reaction mixture or sometimes it may be the requirement of the reaction. In case of heterogeneous reaction mixtures, yields can be considerably improved by stirring. Stirring can be done with electromechanical or electromagnetic stirrers too. The latter may have a hotplate also and provide both for heating and stirring (Fig. 2.4).

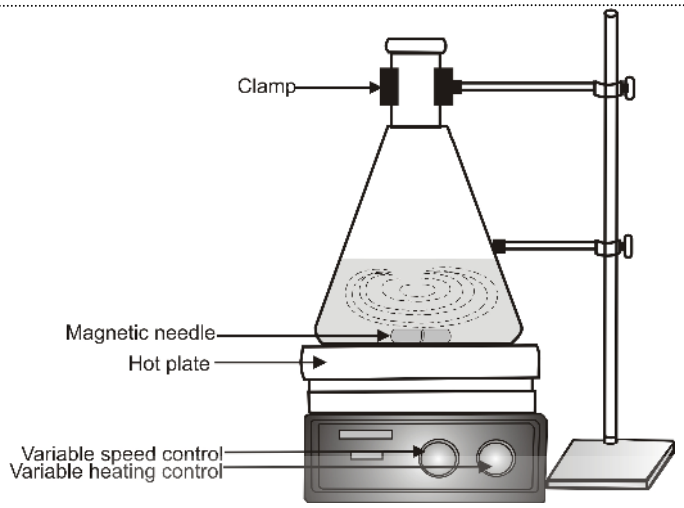


Fig. 2.4: Schematic diagram of a stirrer hot plate.

2.2.5 Filtration

In an organic laboratory, filtration is a commonly used technique. It is essential to filter any solid separated after the reaction is over or when a compound is required to be recrystallised for purification. Filtration can be carried out either under atmospheric pressure called the **gravity filtration** (ordinary filtration) or under reduced pressure called **suction filtration**. Ordinary filtration is considerably accelerated when a **fluted filter paper** is used because it increases the surface area and thus the rate of filtration. We have shown in Fig. 2.5 how to fold the filter paper to make it fluted.

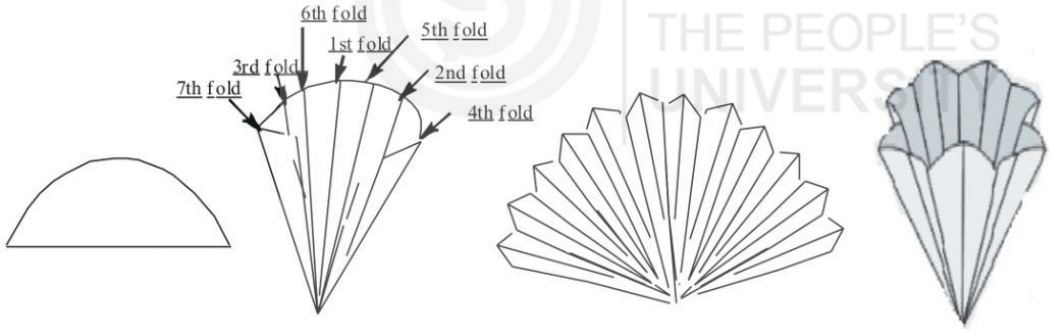


Fig. 2.5: Folding the filter paper to make a fluted the paper.

You may also ask your counsellor to demonstrate the foldings done for making a fluted filter paper. The filter paper should fit the funnel properly and before filtration it should be wetted by the pure solvent. ***The level of the liquids, to be filtered, should always be lower than the paper edge.***

For rapid filtration, we use sunction filtration. In this, the filtration flask is attached to a water pump/vacuum pump, which sucks out air, thus reducing the pressure inside the filtration flask. The liquid is forced down by the atmospheric pressure. A suction filtration unit consisting of a porcelain Buchner funnel, a filtration flask and a water pump/vacuum pump is shown in Fig. 2.6. A filter paper circle, cut correct to size is fitted in the Buchner funnel. The filter paper is wetted with solvent, and suction put on before pouring in the solution to be filtered. The size of the funnel used in filtration, ordinary or under suction should be according to the amount of the substance to be filtered.

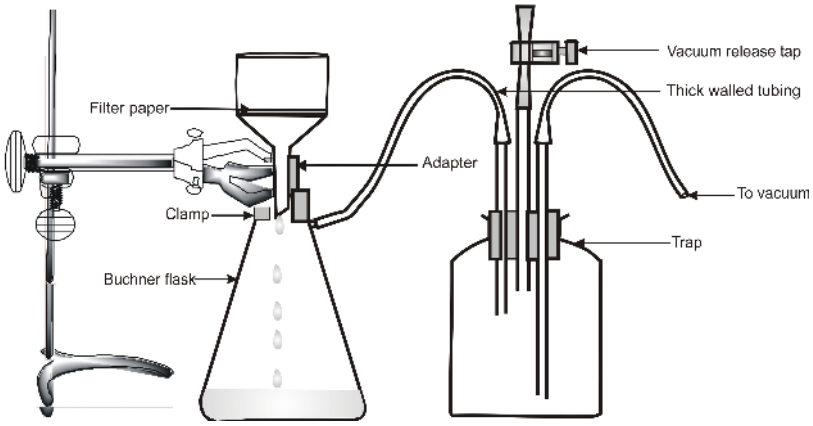


Fig. 2.6: Suction filtration using a Buchner funnel.

SAQ 1

Give reasons why suction filtration is to be preferred to gravity filtration.

After learning the common operational techniques involved in the initial stages of carrying out an organic reaction we will discuss about the techniques involved after the reaction time is over. Thus these techniques involve separation of the product formed and purification of the product separated as it might contain impurity (ies). This is described in the next section.

2.3 TECHNIQUES OF SEPARATION AND PURIFICATION

So far we have studied common operational techniques. You might know that organic reactions are rarely straight forward i.e. there are side reactions leading to by-products. There can be formation of a mixture of products. Also very often the reactions do not undergo completion and the unreacted starting materials remain with the products formed. Therefore it becomes essential to isolate and purify the desired product after carrying out a reaction. In this section, we first discuss separation and purification techniques for the prepared product, and then we discuss about some tests for confirming the purity of the product. The important techniques of purification are solvent extraction, recrystallisation, sublimation and distillation. We will start with solvent extraction in the next subsection.

2.3.1 Solvent Extraction

Solvent extraction is a separation technique, which makes use of the differential solubility of a given solute in **two** immiscible solvents to separate it from a given mixture. One of the common solvents is water and the other solvent is an organic solvent immiscible with water. Extraction is based on the principle of **phase distribution** that you have studied in your theory course. An organic compound being more soluble in organic solvents will preferably go into the organic layer.

For extraction, the aqueous mixture is taken in a separatory funnel. A small volume of an immiscible solvent, like diethyl ether or n-hexane, is added. Care should be taken that the separatory funnel is not more than 3/4th full. The

funnel is stoppered and gently shaken to mix the contents thoroughly **(Fig 2.7a**). Since the solvents are generally volatile, it is necessary to vent the funnel by inverting it and opening the stopcock **(Fig. 2.7b).** The funnel is then made to stand on an iron ring and the layers allowed to separate (**Fig. 2.7c**). The aqueous layer being heavier will generally be the lower layer. It can be drawn off by opening the stopcock and then pouring the organic layer in another container.

Chloroform and carbon tetrachloride are heavier than water; therefore, these form a lower layer in the separatory funnel.

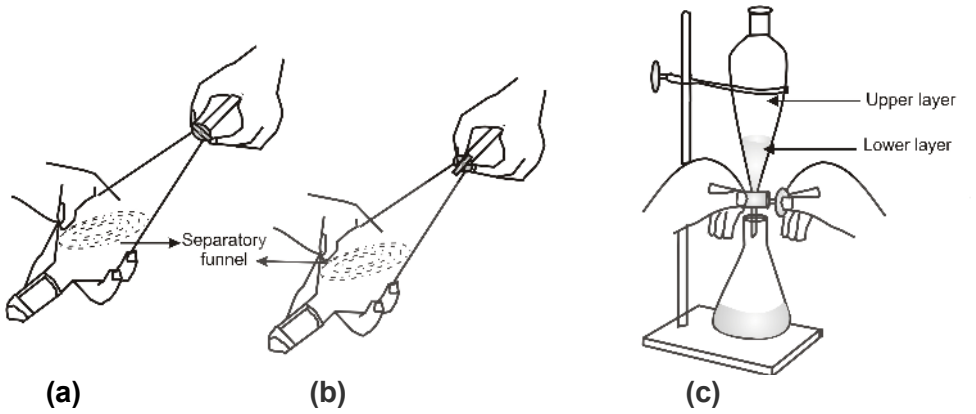


Fig.2.7: Holding a separatory funnel:
(a) during shaking (b) during venting (c) while draining the lower layer

The process may be repeated twice and the three lots of extract combined. A larger number of extractions with small volumes of the solvent is able to extract more of the substance than a single extraction with a large volume. It may be necessary to wash the extract with dilute acid/alkali and then with plain water before it is dried over a suitable drying agent. A larger number of extractions should be dried over a basic substance like anhydrous K_2CO_3 or solid NaOH and acid sensitive substance over Na_2SO_4. Anhydrous $MgSO_4$ is a good general purpose drying agent.

In the following subsection let us read about crystallisation as one of the separation and purification technique.

2.3.2 Recrystallisation

In an organic reaction when a solid is separated after working up of the reaction as per the procedure, it is said to have **crystallised** and the process of formation of the solid or the crystals is called **crystallisation**. The solid separated may have some impurities because of which it may not be that crystalline. It has to be subjected to further purification using **recrystallisation** or **chromatographic** technique. You will study about the former in Experiment 8. Here we would restrict to the introduction of recrystallisation.

Recrystallisation is one of the most effective purification technique for solids. It takes advantage of the fact that nearly all solids are more soluble in a hot than in a cold solvent. Before carrying out recrystallisation, it is useful to have an idea about the degree of purity of the substance and the nature of impurities. If the impurities in the impure solid dissolve and remain dissolved when the solution is cooled, the crystals will ideally be pure. On the other hand, the impurities can remain undissolved in the hot solution in which case, these can be filtered off; the solution is concentrated and allowed to crystallise. As mentioned earlier Experiment 8 is based on this technique. Let us understand another technique of purification in the following subsection.

2.3.3 Sublimation

Sublimation is an alternative to recrystallisation for purifying some solids. The criteria for effective purification by sublimation are as follows:

(i) The compound to be purified must have a relatively high vapour pressure.

(ii) The impurities must have vapour pressure substantially lower than the compound to be purified.

The technique involves placing the impure solid in a sublimation chamber or dish as shown in **Fig. 2.8 (a) by the name 'purpose built sublimator'** and heating it to a temperature higher than that of the cold surface on which it is to be collected, but lower than its melting point. Under these conditions, the solid will be vapourised and the vapours will condense on the cold surface. The crystals that form on the cold surface are usually very pure, since impurities do not vapourise.

Sublimation may be carried out in a simple apparatus consisting of a china dish in which the sample is heated, and an inverted glass funnel to collect the sublimate. A piece of filter paper with a few holes ensures that the sublimate does not fall back into the dish, a loose cotton plug on the stem of the funnel prevents vapours from escaping.

To increase the rate of sublimation, the process may be carried out under reduced pressure, for this purpose, a simple apparatus may be set up shown in **Fig. 2.8 (b) by the 'name improvised sublimator'**. The sample is put in the outer tube, which is heated. Cold water is circulated through the inner tube or 'cold finger' to ensure complete condensation.

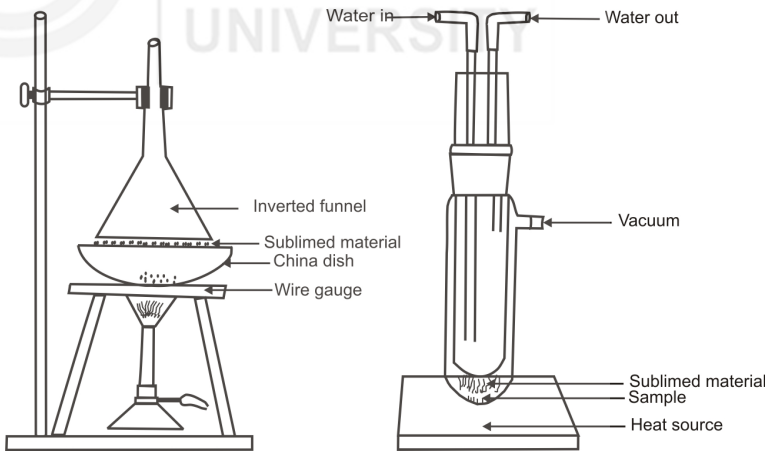


Fig. 2.8: Apparatus for sublimation using (a) purpose built sublimator (b) improvised sublimator

In the next subsection you will study about a purification technique meant for separating and purifying a mixture of liquids.

2.3.4 Distillation

Distillation is an important method used for purifying organic liquids. In very simple terms, it is a process of vapourising a liquid in one vessel and condensing the vapour into another. In very precise manner distillation is the process of heating a liquid to its boiling point, condensing the vapour by cooling

and collecting the liquid called distillate done in a number of ways depending on the type of impurities. These are explained in brief below:

1. **Simple Distillation**: It involves vapourisation and condensation only one time. It is useful for purifying a liquid with, non-volatile impurities or impurities with higher or lower boiling point than the product liquid.
2. **Fractional Distillation**: It involves the process of vapourisation and condensation several times. It is useful for separating miscible liquids having similar boiling points and volatility i.e. the mixture of liquids with boiling points less than 80°C apart.
3. **Vacuum Distillation**: This distillation is done under high pressure for the liquids that either have very high boiling points or decompose at atmosphere pressure on heating.

Apparatus Used for Distillation

The apparatus used for a simple distillation is shown in Fig. 2.9. An appropriate size of a round bottom flask should be chosen to contain the liquid for distillation the liquid should be only half filled in it. The thermometer is inserted from one side of the still head. The condenser is attached to the round bottom flask to which the rubber tubings are attached at both the ends in the outer jacket. The cold tap water in the condenser should enter from the lower end and go out from the upper end. This ensures continuous presence of water in the condenser jacket. At the end of the condenser a collecting flask is attached in which the pure distilled liquid is collected.

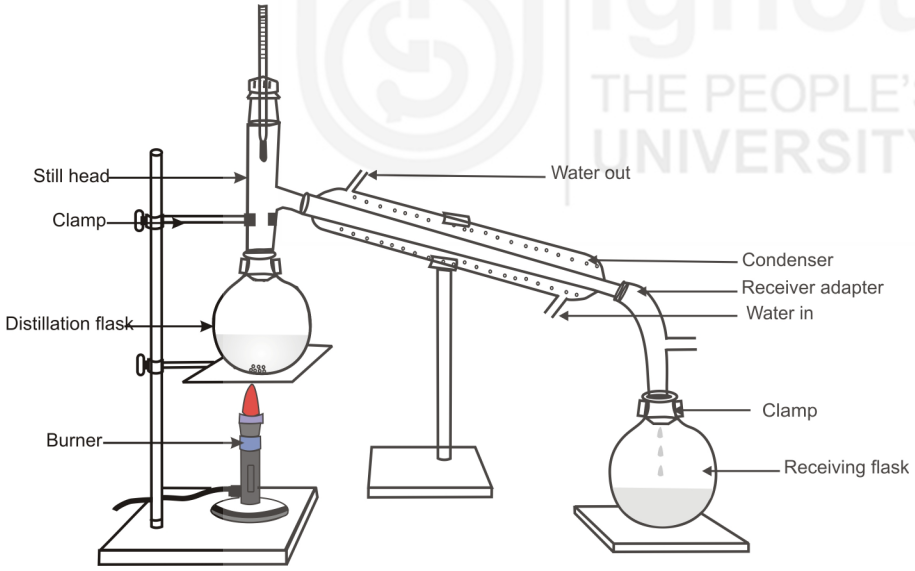


Fig. 2.9: Apparatus for simple distillation.

For heating, a water bath (up to 100°C) or an oil bath (up to 200°C) can be used. To avoid bumping, **pumice stones** also called the **boiling stones** may be added to the distillation flask. The pumice stones provide a sharp surface upon which bubbles naturally form. These promote smooth generation of bubbles helpful in preventing bumping and formation of large bubbles.

Simple distillation is not effective for separating liquids with difference of boiling points less than 25°C. In order to achieve such separations fractional distillation is carried out. The apparatus generally used for fractional distillation is shown in Fig. 2.10.

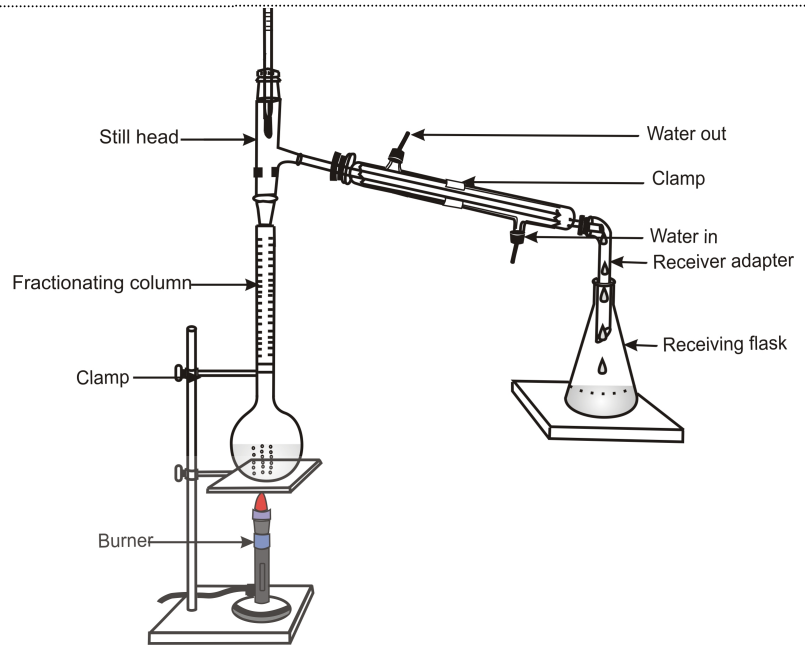


Fig. 2.10: Apparatus for fractional distillation.

The set up is like that for a simple distillation but as you can observe a fractionating column is attached to the flask, which is not required in case of simple distillation. Various types of fractionating columns are available, which differ in their effectiveness of separation. The most commonly used is a fractionating column which provides a large surface area for continuous heat exchange between the hot vapours rising upwards and the cooled liquid coming downward. This results into a repeated evaporations and condensation leading to separating the two compounds in the mixture.

For distillation under reduced pressure, the apparatus is fitted as shown in Fig. 2.11 attached to a vacuum pump. A water pump generally gives a pressure of about 10-15 torr and reduces the boiling point by about 100°C, an oil rotatory pump reduces the pressure to about 0.1 torr and further lowers the boiling point by 60°C. A thin stream of air introduced into the distillation flask through a capillary tube prevents bumping in this case.

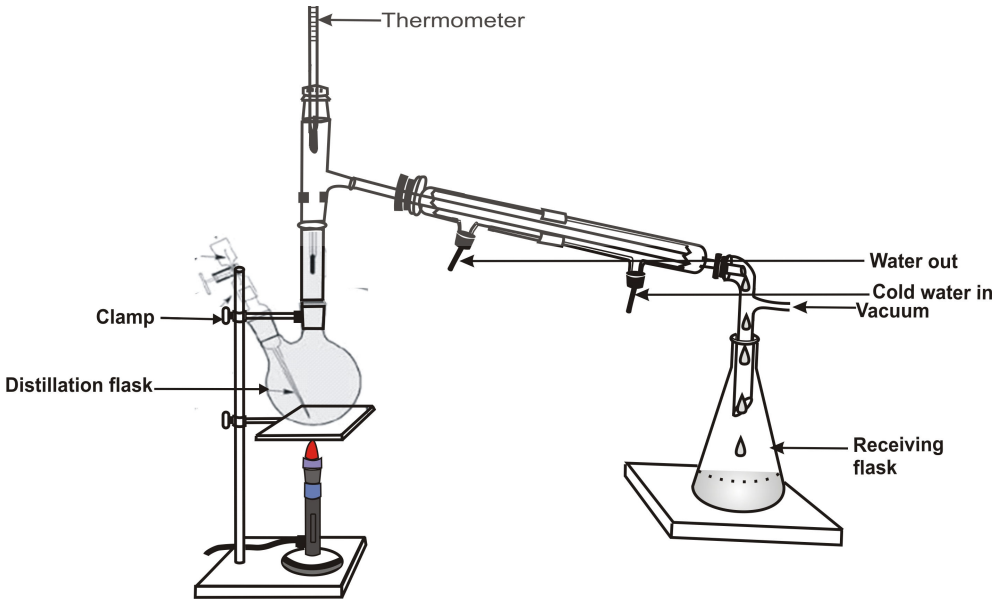


Fig. 2.11: Apparatus for vacuum distillation.

Let us now understand an important technique that was initially used for the separation of coloured compounds. It is called chromatography. You would recall the experiments you performed in Semester I based on paper chromatography. A detail of chromatographic principle and the method of identification of organic compounds were given in Experiment 9 of that laboratory course. In the present laboratory course the other type of chromatographic technique is explained, which is related to the separation and purification of the product formed.

2.3.5 Chromatography

You have read that chromatographic separation depends on the differences in the partition coefficient of the components of a mixture between two immiscible phases. One of these is the mobile phase, which moves relative to the other, the stationary phase. The substances being separated are transported with the mobile phase.

According to the physical states of the mobile and stationary phases, various chromatography methods are classified as adsorption, liquid-liquid partition, gas-solid and gas-liquid chromatography. You are aware that all the techniques are carried out in organic chemistry laboratories as a routine. For processes like gas chromatography, fairly sophisticated commercial instruments are available. For the purpose of identification and purification, thin layer chromatography is relevant for undergraduate chemistry level therefore we will discuss this type in detail. However, there is no experiment based on this technique in this course.

Thin Layer Chromatography

Thin layer chromatography abbreviated as TLC and also called analytical TLC is based on the principle of adsorption. It can be used for:

- checking purity
- preliminary tests before separation
- qualitative comparison with known substances
- monitoring a reaction

The method of using this technique involves a number of steps. These are explained below.

Preparation of the Plate

It is good to work in small scale to prevent the wastage of chemicals and other resources. For preparing the plates for the purpose of identification of compounds, microscopic slides like the ones used in a biosciences laboratory can be used. The plates have to be thoroughly cleaned and dried. The stationary phase is alumina or kiesel gel applied in thickness of about 0.2 mm from slurry of the adsorbent in carbon tetrachloride (about 30 g in 100 ml of CCl_4) by dipping the plate in the slurry and allowing to drain. A binder like calcium sulphate is added to kiesel gel / alumina which helps in binding the adsorbent to the glass plate.

Silica Gel with binder for the TLC is available in the market.

The plates are then put in a rack and activated by heating in an oven at 100^0 C for an hour or so. The TLC plates can also be prepared using aluminium or plastic sheets, the aluminium based being very common as the stationary phase is well bound and available commercially.

Application of the Substance

A dilute (1%) solution of the substance in the least polar, suitable, low boiling solvent is applied to the plate with a thin capillary in the form of a spot at one end as shown in Fig. 2.12(a) and the solvent allowed to evaporate completely.

Developing the Chromatogram

The plate is made to stand in a chromatographic chamber with the lower end with the spot, dipping in the eluent and allowing to develop (Fig. 2.12(b)). The chromatographic chambers are small jars with fitting stoppers. When the solvent front has advanced a suitable distance, the plate is removed, the solvent front marked and the plate allowed to dry (Fig. 2.12(c)).

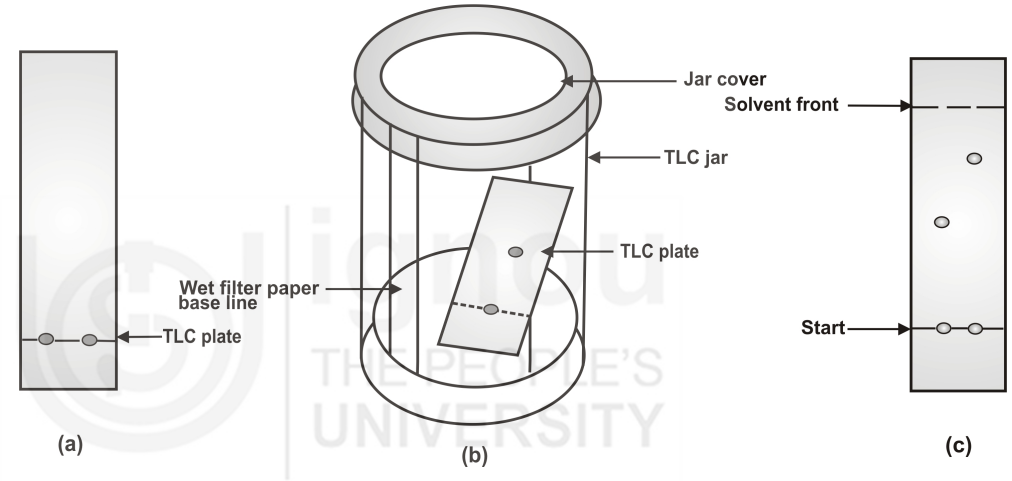


Fig. 2.12: A TLC plate spotted with the sample: a) before development; b) developing a TLC plate; c) after development.

Detection

Coloured spots are, of course, immediately visible. Colourless spots can be made visible by:

- standing the plate under ultraviolet light if the substance absorbs ultraviolet, e.g., aromatic compounds glow in ultraviolet light.
- standing the plate in iodine vapour in a chromatographic jar, organic compounds generally give coloured spots with I_2.
- spraying with 1:1 H_2SO_4- water mixture and then heating strongly to carbonise the compounds. You should be careful with H_2SO_4 spray; it is preferably done in a fume hood.
- spraying with suitable reagents which give coloured spots with the substances under observation, for example ninhydrin in case of amino acids.

Recording

The chromatogram is recorded using a tracing paper. Starting position, solvent from and the spots are clearly marked. The details about the type of plate, eluent and method of development are also recorded.

R_f value of a substance is calculated by the relationship:

$$R_f = \frac{\text{Distance of spot centre start}}{\text{Distance of solvent front start}}$$

The R_f value depends on the conditions under which the chromatogram was run, namely, type of plate, eluent, temperature, etc. Its reproducibility is about $\pm$ 20%. However, it is best to run the probable reference compound on the same plate for comparison.

You can check the understanding of chromatographic technique by attempting the following SAQ and then proceed further to learn how to check the purity of the compound purified by the methods explained so far.

SAQ 2

Two components, A and B were separated by TLC. When the solvent front had moved off a distance of 10 cm above the level of the original sample spot, the spot of A was 7.0 cm and that of B was 4 cm above the original spot. Calculate the R_f for A and B.

2.4 TESTS OF PURITY

You have learnt that organic reactions are always accompanied with some impurity or with starting materials left due to incomplete reactions. In any case the product formed has to be purified for further reactions. More important is to ensure the purity of the product. There are physical, chemical and instrumental methods to ascertain that. The age-old methods used till today are by checking the melting point and boiling point of solid and liquid compounds respectively. You will be studying the concepts of ascertaining purity under Experiment 9, where you will perform experiments related to these. Let us understand in brief about the basics of melting and boiling point in the following subsection.

2.4.1 Melting and Boiling Points

Melting point is defined as the temperature at which the solid and liquid phases of the substance are in equilibrium at a pressure of one atmosphere. The melting point is a unique property of a compound, which is independent of source and method of purification. A pure compound usually melts within a range of 1-2^{o}C, not more. The presence of impurity in a compound lowers its melting temperature. The melting point of a solid is determined by capillary method using a melting point apparatus. The details of the capillary method are explained under Experiment 8 where you will perform an experiment and determine the melting point of the compound given.

Boiling point can also be taken as a test for the purity of a liquid. It is defined as the temperature at which the liquid starts boiling and the liquid and the

gaseous phases are at equilibrium. A pure liquid will have a certain definite boiling point only at a particular pressure, as the boiling point is affected both by impurities and by the ambient or external pressure. Impurities generally raise the boiling point. Since boiling point is the temperature at which the vapour pressure of a liquid becomes equal to the ambient pressure, the boiling point of a liquid will be higher at higher pressure, and the liquid will boil at a lower temperature if the pressure is reduced.

When 5 ml or more of the liquid is available, its boiling point can be determined by slowly distilling it from a small flask. For smaller quantities, a micro method has to be used. One such method which you would be using is called the **Siwoloboff's method** which will be described in detail in the experiment on determination of boiling point of the liquids given in Experiment 9. Now you will briefly learn how to use and clean the glassware used in a chemistry laboratory.

2.5 GLASSWARE: PRECAUTONS IN USE AND CLEANING

Organic preparations involve the use of glassware of various types. It is very important that the glassware you use in the laboratory is perfectly clean as dirty glassware could contaminate your reaction product. Also you have to be careful in handling the glassware lest you hurt yourself. You would like to recall Unit 1 of the Semester-I laboratory course. Following safety precautions may be kept in mind regarding the proper and safe use of glassware.

The primary rule in handling and using laboratory glassware is, ***never apply pressure or strain to any piece of glassware.*** This applies to insertion of glass tube or thermometers into rubber or cork stoppers or fitting corks on condensers, funnels, etc. A convenient method of inserting glass into corks is to lubricate glass with a little water or water containing soap or glycerol. Glass piece must be grasped very close to the cork when trying to insert it. It is wise to wrap a piece of cloth around the glass and cork; this would prevent a serious cut even if the glass breaks.

Chromic acid can be prepared by dissolving potassium dichromate in concentrated sulphuric acid.

The glassware must be washed immediately after use. Most chemical residues can be removed by washing the glassware with soap or common laboratory detergent. Common organic solvents like alcohol or acetone can be used for washing off substances insoluble in water. Stubborn residues may need more powerful cleaning solutions, like chromic acid, or a mixture of alcohol with solid potassium hydroxide, etc. We would advise you to consult your counsellor before using these strong cleaning solutions, which require special care in handling.

Glassware often needs drying when it is used in an organic preparation. Glassware, other than standard or graduated glassware can be dried by a hot air blower or in a hot air oven. Graduated glassware should never be heated; it can be rinsed with alcohol or acetone and allowed to drain. Stoppers and interchangeable joints should be properly greased in order to avoid sticking.

Let us briefly understand the laboratory safety in general that was discussed in Unit 1 of first semester laboratory course.

2.6 LABORATORY SAFETY

Chemistry laboratories are potentially dangerous because they contain inflammable liquids, poisonous chemicals and fragile glassware. When high-pressure cylinders of gases are used, these also pose a potential danger. Therefore, proper precautions must always be taken and safe experimental procedures must be followed while working in a chemistry laboratory. If this is not done, a chemistry laboratory is more dangerous than a kitchen or a bathroom.

Some important general safety considerations are given below. Any special precaution or safety measures are given in the particular experiments. You should read all these carefully and follow them faithfully.

1. The first thing to be familiar with is the layout of the laboratory especially where fire extinguishers, fire blanket or the first aid box is.
2. Never work alone in the laboratory.
3. Check the glassware before using. It should not have any cracks.
4. Almost all organic liquids are inflammable and therefore should never be heated on a naked flame. You may use water or an oil-bath.
5. All the chemicals must be handled with caution. As far as possible direct contact with skin must be avoided. Rubber or plastic gloves can be worn while handling especially toxic compounds. Avoid inhaling vapour of any compound. ***Never taste anything.***
6. A fume hood must be used for handling dangerous substances or for carrying out reaction in which noxious gases are evolved.
7. Ask your counsellor for safe disposal of chemicals and glassware. Never pour solvents and other chemicals into the sink, put them into special containers for waste. Also do not throw used filter paper or broken glassware into the sink, put them in dustbins.

In the laboratory you will perform a number of experiments. You know from your previous experience that all the experiments have to be written and get checked by the counsellor. Therefore a note-book is used for this lab course also. Let us recall all that is required to maintain a lab note-book.

2.7 LABORATORY NOTE-BOOK

One of the most important characteristics of a scientist is the habit of keeping good record of the work that has been done. The record should reflect all the planning that has gone in as well as the observations at various stages of the experiment. A chemist must observe things like whether there was a colour change when the reactants were mixed or a gas evolved, was the reaction exothermic etc., and record them. These observations may appear insignificant but prove helpful in correct interpretation of an experimental result.

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

1. Record all observations and data in the note-book at the time they are obtained. Never use scraps of paper for noting things like weights of reactants taken, melting or boiling points, etc. they might get lost or mixed up.
2. The record should be so thorough and well organised that on reading, it should be possible for anyone to understand what has been done and repeat it. It may not be necessary to copy out the exact procedure, since this is given in your laboratory manual. However, results should be summarised, conclusions drawn for each experiment and explanation provided if the results vary from those expected.
3. Laboratory note-book is complete log of all operations. Dates, times and other information must be entered regularly.
4. A bound note-book should be used for laboratory record. Special laboratory note-books are available, often with numbered pages, one side being blank and the other ruled.
5. All entries must be made in ink. If a mistake is made, it should be crossed out and correctly ruled.
6. The first page of the note-book can be used as the title page, a few pages can be left for the table of contents.

Types of Organic Experiments

There are two broad classes of experiment in organic chemistry. Investigative experiments called qualitative organic analysis like identifying the functional group (s) in a compound or the compound itself. These types of experiments have been covered in the first semester lab course. Preparative experiments involve conversation of one compound into another. These experiments require slightly different type of note-book format. Here we will discuss the format we are going to use for preparative experiments.

Preparative Type of Experiments and Laboratory Notebook

Successful laboratory work requires preparation for the experiment in advance. You must read the theory and experimental procedure before coming to the lab, so that you understand what you are doing and are also able to plan the experiment properly; and finish it in the allotted time.

Some of the information required to be noted for preparative organic experiment is as follows:

1. **Title**
2. **Introduction**

   Give brief description of the experiment
3. **Main Reaction (s)**

   Write equations for the conversation of starting compounds, i.e., reactants into products. The equations should be balanced so that it is possible to calculate the theoretical yield of the product.
4. **Table of Reactants and Products**

   A convenient method for summarising the amount of reactants to be taken and the product formed is setting up a Table of Reactants and Products. It may contain the following:

(i) The name and structure of each starting material and product.

(ii) The molecular weight of each of the above

(iii) The weight in grams of each starting material taken

(iv) The moles of each starting material as calculated from (ii) and (iii)

(v) Theoretical mole ratio for the reactants and products, which can be calculated from the balanced equation for the reaction.

(vi) Physical properties of the reactants and products like melting point, boiling point, density, colour, etc.

5. **Yield Data**

The maximum expected yield of the product, called the theoretical yield, can be calculated from the table of Reactants and Products. In an organic preparation a reactant may sometimes be taken in excess of that indicated by the balanced equation. From the number of moles of each reactants used and the mole ratio of reactants indicated in the balanced equation, the reactant that is the limiting reagent can be determined. The reaction stops when the limiting reagent is consumed, no matter how much of the reactants remain. This, in a way, ensures as complete a conversation of the key reactant as may be possible under the reaction. The theoretical yield in such cases can be calculated from the number of moles of the product expected from the number of moles of the limiting reagent and the balanced chemical equation. The theoretical yield in grams can be calculated by multiplying the theoretical yield in moles of the product by its gram molecular weight.

Percentage yield, which is a way of expressing the efficiency of a reaction can be calculated from the actual and theoretical yield.

$$\text{Percent yield} = \frac{\text{actual yield in grams}}{\text{theoretical yield in grams}} \times 100$$

Percent yield is often rounded off to whole numbers. Percent yields of 80% and above are considered excellent for organic reactions.

6. **Observed Properties of the Product**

Physical properties of the product obtained from the experiment like melting point, boiling point, colour, odour, crystalline form, etc. should be compared with ones reported.

A sample note-book format for organic preparation experiments is given here. Preparation of acetanilide from aniline using a mixture of acetic anhydride and sodium acetate as the acetylating reagents is taken as example. You may follow it for reporting the experiments done by you.

2.7.1 Sample Note-Book Format

Title: Preparation of Acetanilide

Introduction: Acetanilide is prepared by acetylation of aniline with acetic anhydride. Aniline is dissolved in diluted hydrochloric acid and acetylated with acetic anhydride in the presence of aqueous sodium acetate.

Main reaction: The reaction involved is given below.

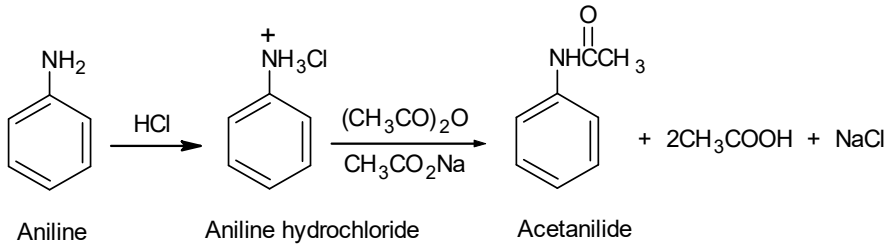


Table of Reactants and Products

Sl. No.	Compound	Mol. Wt.	Weight used	Moles used	Molar Ratio	Other data
1.	Aniline	93	6.8g (6.6 cm^3)	.73	1	Liquid b.p.184°C
2.	Conc. Hydrochloric acid	36.5	6.1 cm^3 (1.69 *M* HCl)	0.073	1	
3.	Acetic anhydride	102	6.8g(8.5 cm^3)	0.09	1.2	Liquid b.p. 139.5°C
4.	Sodium acetate	82	11 g	0.134	1.8	Solid
5.	Acetanilide	135			1	

Yield

Say the yield is 6 g from the equation it can be seen that one mole of aniline will give one mole of acetanilide, i.e., 93 g of aniline will given 135 g of acetanilide or 6.8 g should give 9.87 g.

So, the percent yield = 6.8/9.87× 100 = 60.8%

Observed Properties of the Product

Acetanilide separates out in almost pure form and the m.p. is 113°C.

2.8 ANSWERS

Self-Assessment Questions

1. Vacuum filtration is faster than gravity filtration, because the vacuum filtration is done by the application of reduced pressure whereas gravity filtration is as a result of the force of gravity which is not very high.

2. R_f value of a substance can be calculated by the relationship;

$$R_f = \frac{\text{Distance of spot on centre from start}}{\text{Distance of solvent front from start}} = \frac{l_1}{l_2}$$

In case of A, l_1 = 7 cm and l_2 = 10 cm, therefore

$$R_f = \frac{7}{10} = .7$$

In case of B, l_1 = 4 cm and l_2 = 10 cm, therefore

$$R_f = \frac{4}{10} = 0.4$$

EXPERIMENT 8

PURIFICATION OF ORGANIC COMPOUNDS BY RECRYSTALLISATION AND DISTILLATION

Structure

8.1 Introduction

Expected Learning Outcomes

8.2 Recrystallisation

Solvent for Recrystallisation

Principle of Dissolution and Recrystallisation

Steps of Recrystallisation

8.3 Experiment 8 (a): To Recrystallise Benzoic Acid Using Hot Water

Requirements

Procedure

Result

8.4 Distillation

8.5 Experiment 8 (b): To Separate a Mixture of Hexane and Toluene by Distillation

Requirements

Procedure

Result

8.6 Answer

8.1 INTRODUCTION

In the first unit of this block you were familiarised with some of the techniques and the relevant apparatus required for the purification of organic compounds. You will be making use of almost all of those in this and the other experiments of this block. The details of the purification techniques are given along with the present experiments for a theoretical background and proper understanding.

You have studied in your theory courses and the previous unit that organic reactions, whether synthesised in laboratory or obtained from natural sources, are always accompanied with a number of side products and sometimes the starting materials. Therefore, it becomes essential to isolate the product and purify it. A number of techniques were explained in the previous unit. Out of the various techniques explained in brief you would be using the recrystallisation and the distillation techniques in the given experiments for purifying the solid

and liquid products respectively. Thus in the first experiment you will recrystallise the given organic compound using hot water for its purification. In the second experiment you will distill the mixture of two liquids to get a pure liquid. We have explained the concept, the process of recrystallisation and the procedure to carry out the same. Similarly the concepts involved in simple and fractional distillation processes are explained for purifying and separating the given mixture of liquids.

In the next set of experiments the melting and boiling point determination will be explained as criteria of purity of solids and liquids respectively.

Expected Learning Outcomes

After performing the experiments you should be able to:

- define recrystallisation and explain the process of purification by recrystallisation;
- explain the nature and type of solvent used for purification by recrystallisation;
- recrystallise benzoic acid using hot water;
- describe the simple and fractional distillation techniques of purification; and
- purify the given mixture of hexane and toluene by simple distillation.

8.2 RECRYSTALLISATION

In Unit 1 of this course you have studied the general concept involved in the interchangeably used terms crystallisation and recrystallisation . Before we describe the concept in detail, let us recall the difference between these frequently used two terms. The product obtained as a result of organic reaction is separated as an amorphous solid after the work up. The process involved is called **crystallisation** and the product as the crystallised product. When this crystallised product is made to dissolve in a solvent to get pure crystals, the process is called **recrystallisation**. Thus, recrystallisation may be defined as the process of formation of solid crystals generally from a solution. The solution is obtained by dissolving the impure compound into a solvent. The choice of an appropriate solvent is very significant and critical in this process. There is no rule to choosing a right solvent but some general principles are very helpful. Let us learn about the same in the following subsection.

8.2.1 Solvent for Recrystallisation

It is always better to try recrystallisation of a compound on a small scale first. It means that only part of the impure compound should be taken to try the recrystallisation. The following points can be used as general guidelines:

1. The compounds tend to be more soluble in chemically similar solvents. A polar compound will dissolve better in a polar solvent, similarly a nonpolar compound will prefer a nonpolar solvent.

2. A good solvent would mean that the compound is soluble in hot and nearly insoluble in cold solvent.

3. Very good solvents require very high concentration of solute for recrystallisation i.e. the compound is adequately soluble in the given solvent.

4. Polar solvents tend to produce better crystals than nonpolar or hydrocarbon solvents, e.g., ethanol is a polar solvent while benzene is nonpolar.

5. A good solvent should have different solubilities for the compound and the impurity. It will be difficult to separate the two with similar solubilities.

6. The solvent should not react with the compound to be recrystallised. As is understandable, it will lead to a different and new product, which is not desired.

7. A good recrystallisation solvent would be partially volatile so that it is easily removed while recovering the pure compound.

8. A good recrystallisation solvent chosen is generally nonflammable, nontoxic and less expensive.

Table 8.1 gives a list of common solvents with their boiling points arranged in order of increasing polarity and the class of compounds for which they can be used.

Table: 8.1: Some Common Solvents, their Boiling Points and Polarity

S. No.	Efficient Solvents	Boiling Point (°C)	Class of substance to be crystallised	Polarity of Solvent
1.	Pentane, Hexane, Petroleum ether, Benzene (flammable, toxic vapours)	80	Hydrocarbons	Hydrophobic (lipophilic) nonpolar
2.	Diethyl ether (highly flammable)	34.6	Ethers	
3.	Chloroform (toxic)	61	Halohydrocarbons	
4.	Acetone (flammable)	56	Tertiary amines	
5.	Ethyl (or methyl) acetate (flammable)	78	Ketones and Aldehydes, Esters	
6.	Ethanol	78	Phenols, Alcohols	
7.	Methanol	65	Carboxylic acids	
8.	Water	100	Sulphonic acids Organic salts	Hydrophilic-Polar

Mixed Solvents

Sometimes it is difficult to find one solvent alone of right choice i.e. the compound does not either dissolve sufficiently or dissolves too readily. Then one has to work with a mixture of solvents called **mixed solvents**. How is a mixed solvent chosen?

If the solvent is such that the compound dissolves too quickly in it, another solvent having very low dissolving tendency for this particular compound can be added to the first one. If the compound dissolves properly in the first solvent and the solubility in the second is too low then a solvent with better dissolving property can be added to it so that a good combination may lead to recrystallisation effectively. The solvent pairs used as mixed solvents should be miscible with each other. Some of the common solvent pairs of mixed solvents are listed in Table 8.2.

Table 8.2: Some of the common solvent pairs for mixed solvent recrystallisation

Solvent 1	Solvent 2
Water	Ethanol / Methanol / Acetic Acid / Acetone
Methanol	Dichloromethane
Acetone	Diethyl ether
Diethyl ether	Hexane / Methanol
Ethyl acetate	Cyclohexane
Ethanol	Petroleum ether
Chloroform	Petroleum ether

8.2.2 Principle of Dissolution and Recrystallisation

It is important to know the principle involved in the solubility of the compound in a solvent and also the recrystallisation process. Let us understand these in the following paragraphs.

Principle of Dissolution

Solvation is the process of interaction of the solute entities with the solvent molecules, giving stability to the former.

The process of dissolution of the compound starts by breaking of its crystal lattice. The energy required for breaking the lattice is obtained during the process of **solvation** by solvent molecules. If the solvation energy happens to be higher than the lattice energy of the compound, the compound dissolves and the constituent species get into the solution. The lattice energy of a compound can be assessed by its melting point. Higher the melting point, higher will be the lattice energy of the compound. Thus the higher the melting point, the less soluble the compound is in a given solvent.

The principle of **'*like dissolves like*'** is also followed here and is dependent on the relative polarities of the compound and the solvent. It means that a compound will be soluble in the solvent of similar nature. We can say that the solubility of the organic compounds depends a lot on the nature of the functional groups of the compounds. The compounds with polar groups will show better

solubility in polar solvents and the compounds with nonpolar groups will be more soluble in nonpolar solvents. For example, groups like OH, NH, CONH, COOH, etc. will be more soluble in solvents like water, methanol and ethanol. The hydrocarbons and their halogenated derivatives are nonpolar and dissolve in nonpolar solvents like, chloroform, carbon tetrachloride, hexane and petroleum ether.

Principle of Recrystallisation

The process of recrystallisation begins when the hot solution is kept for cooling undisturbed. The tiny particles of the compound in the form of ions, atoms or molecules start arranging themselves in a characteristic pattern leading to the formation of a crystal. This is the process of initiation of recrystallisation and called **nucleation**. Gradually the crystals grow in size and number with time, eventually leading to fully recrystallised compound. If the cooling of the solution is done fast, the number of nucleation sites increase and the crystals grow smaller in size. Alternatively, slow cooling leads to better and pure crystal growth.

Nucleation is the first step in the process changing from one state to the other.

Now we shall look into step-by-step process of recrystallisation in the next subsection.

8.2.3 Steps of Recrystallisation

In its simplest form the general scheme of recrystallisation follows three broad steps: **dissolution**, **cooling** and **filtration**. These may be depicted as shown in Fig. 8.1.

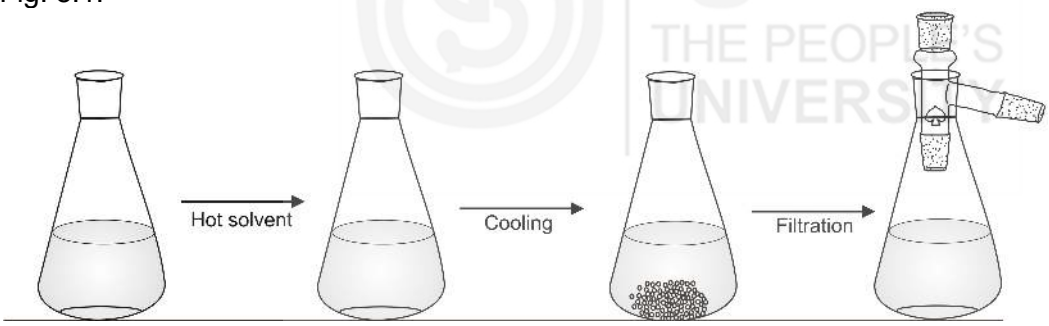


Fig. 8.1: General steps of recrystallisation.

However, the complete sequence of steps involved in recrystallisation is explained below:

1. Selection of a Solvent

First of all suitable solvent is chosen by doing a solubility test. A small amount of the compound is taken in a test tube in which a solvent is added. If the compound readily dissolves, the solvent is not considered appropriate. Another test tube containing solid is heated with some other solvent after it has not dissolved in cold. In case most of the compound dissolves in heating gently and then completely dissolves on continuous heating, the solvent may be considered right. If the compound readily dissolves in hot solvent; another solvent may be added that does not have solubility for the compound. This is based on the concept of mixed solvents as explained earlier.

The selection criteria for the solvent may be summarised as follows:

1. Compound must be insoluble in the solvent at room temperature.
2. Compound should be soluble on boiling the solvent.
3. The boiling point of the solvent should be lower than the melting point of the compound.
4. An adequate amount of crystals should be obtained on cooling of the solvent.

2. Dissolution

Once the choice of a suitable solvent has been made, the impure substance is dissolved in it. It may be noted that purer the substance and larger the crystals, the more slowly it will dissolve. Large crystals may have to be crushed before dissolving. The volume of the solvent is taken to get a **supersaturated** solution of the substance i.e. a minimum possible volume of the solvent should be used. The impure or crude substance must be weighed before dissolving; this will enable you to calculate the yield of the pure product.

Supersaturated solution: A solution that contains more solute than the solvent can have under the given conditions.

3. Decolourisation: Removing Coloured Impurities

In case the solution is strongly coloured by impurities, **activated carbon** / charcoal may be added to decolourise it. For this the material is first dissolved and then the solution heated with 2-4% its weight of charcoal for about 10 minutes. Decolourisation of the crystals is done in an Erlenmeyer flask, which is convenient to heat. The solution is then cooled and filtered by gravity filtration. If required, the treatment can be repeated with fresh carbon.

Activated carbon or charcoal: preheated material to increase the activity.

4. Filtration

Filtration serves to remove dust and insoluble impurities. After decolourisation, the hot solution can be filtered through a fluted filter paper, which has been preheated by pouring through it a small volume of the hot solvent. As mentioned earlier, this is called simple or gravity filtration. To prevent premature crystallisation, a slight excess of the solvent may be used. Still if any substance is left on the filter paper, it can be removed later. The method of making a fluted filter paper and gravity filtration has been explained in subsection 2.2.5 of the previous unit. After filtration the hot solution is kept aside without disturbing it.

5. Recrystallisation

You have to first observe the formation of crystals in the solution kept for cooling. In case it is taking long for the crystals to appear, recrystallisation from a supersaturated solution can be induced by:

- slowly cooling the hot solution to room temperature or below by keeping in a refrigerator.
- slowly adding a miscible solvent in which the compound has a poor solubility, until the solution starts getting cloudy. The solution is then warmed to clear the turbidity and allowed to cool slowly. As you have studied in subsection 8.2.1, this is called the mixed solvents technique. You have read that the typical mixed solvents are ethanol-water, benzene-petroleum ether, etc.

Sometimes you might like to speed up the process of recrystallisation, this may be facilitated by:

- adding of a **seed** crystal: This can be done by adding a pinch of solid compound into the solution kept for recrystallisation.
- scratching the side of the vessel with a glass rod: If the crystals do not form spontaneously these may be induced to form by scratching the inside wall of the flask with a glass stirring rod just below the surface of the solvent.

6. Separation of Crystals

Crystals are separated from the mother liquor by filtration preferably under suction; sometimes the crystals can be removed by centrifugation, especially in case the quantity is very small. You might know that centrifugation involves separation by the process of high speed spinning of the solution with recrystallised product. The crystals are washed with cold and pure solvent to remove the mother liquor sticking to the crystals.

Mother liquor: the liquid left after filtration of the crystals. It is the liquid in which the solid was dissolved earlier.

7. Drying

Solid organic compounds must be dried because the presence of moisture or organic solvents may affect their melting point, quantitative elemental analysis and even spectra. A solid that has been recrystallised from a volatile solvent can be usually dried by allowing it to air dry at room temperature. If the solid gets collected on a Buchner funnel under suction, most of the solvent would be sucked off and drying will become easier.

For more effective drying, desiccators with suitable desiccants like silica gel, phosphorous pentaoxide or fused calcium chloride may be used. To remove hydrocarbon solvents, a block of solid paraffin is helpful. Samples for quantitative elemental analysis are usually dried in vacuum desiccator. Over drying should, if at all, be carried out at temperatures well below the melting point of the substance.

Now you can attempt to answer the following SAQs.

SAQ 1

List four criteria that should be used in selecting a solvent for recrystallisation.

SAQ 2

The following solvent selection data was collected for an impure solid. Based on these results, what solvent would you use to recrystallise this solid?

Solvent	Solubility at room temperature	Solubility when heated	Crystals formed when cooled
Methanol	insoluble	insoluble	none
Chloroform	insoluble	soluble	very few
Cyclohexane	insoluble	soluble	many
Toluene	insoluble	soluble	very few

SAQ 3

Compound X is quite soluble in toluene, but only slightly soluble in petroleum ether. How could these solvents be used in combination in order to recrystallise X?

8.3 EXPERIMENT 8(a): TO RECRYSTALLISE BENZOIC ACID BY USING HOT WATER

In this experiment you will learn the concept of recrystallisation by taking a sample of benzoic acid and recrystallising it with hot water. The sample would be provided by the counsellor to you. You have to follow the steps given in the procedure and report the result after checking the melting point of the recrystallised product.

8.3.1 Requirements

Apparatus	**Chemicals**
Erlenmeyer flask	Benzoic acid sample
Bunsen burner	Water
Measuring cylinder	Carbon/Charcoal
Vacuum filtration apparatus	Grease
Watch glass	Pumice stones
Spatula	
Büchner funnel	
Funnel	
Stirring rod	
Whatmann filter paper	

8.3.2 Procedure

Follow the steps given below to recrystallise the sample of benzoic acid given to you.

1. Weigh about 1.00 g of benzoic acid from the sample given to you for recrystallization and transfer it to a 125-mL Erlenmeyer flask.
2. Add about 20 mL distilled water, using a graduated cylinder, to the flask and bring the mixture to the boiling point by heating on a hot plate or over a Bunsen burner as is available to you.

Precaution*: Do not forget to add pumice stone to the boiling liquid, as it would help in a smooth boiling.*

3. Keep stirring the solution taken in the flask and keep boiling gently to dissolve benzoic acid completely.

4. Remove the flask from the burner and observe the solution. If you see some amount of benzoic acid undissolved, add some more of hot or cold water with heating and shaking continued. Addition of water has to be slow so that water added is just enough to get a saturated solution of benzoic acid.

5. Check the clarity of the solution, if coloured even slightly, add a pinch of charcoal and heat the solution again. Gravity filter the clear solution through a Whatman filter paper.

If the solution is not coloured this step should be skipped.

6. After step 4 add about 10-15mL of water and leave the flask standing undisturbed on a flat platform. Let it cool on its own.

7. You might observe the formation of crystals of benzoic acid in about 10 minutes time.

8. If you do not see or see only a few crystals then scratch the sides of the flask above the level of the solution with the sharp end of a glass rod. This may let small crystals drop into the solution and *"seed"* the solution. As mentioned before seeding is one of the ways to facilitate recrystallisation. Alternatively the solution may be cooled in the ice bath. You can ask your counsellor to help you in carrying out step 8.

A seed crystal can develop a nucleation helpful for the recrystallisation process.

9. After the recrystallisation is complete, filter the crystals through a vacuum filtration set up as shown in Unit 2, Subsection 2.2.3. Keep the crystals for air-drying.

10. After ensuring that the crystals have dried up, weigh these and confirm the purity by determining the melting point.

*Calculate the percent amount recovered using the following formula***.**

$$\%\,\text{Recovered} = \frac{\text{Weight of benzoic acid obtained after recrystallisation}}{\text{Weight of benzoic acid before recrystallisation}} \times 100$$

8.3.3 Result

The sample of benzoic acid was recrystallised with hot water.

Melting point of the compound was found to be = ------- ^{0}C

The yield of the recrystallised compound was found to be = ----- g

SAQ 4

What are the purposes of the following in recrystallisation of solids?

i) Boiling stones/Pumice stones

ii) Activated carbon

iii) Seed crystals

After learning and performing the experiment to purify a solid compound by recrystallisation, you will learn to purify an impure liquid by distillation. The experiment based on the distillation technique is discussed in the following section. Before performing the experiment let us revise the concept of distillation.

8.4 DISTILLATION

Let us revise what we have studied about distillation in the previous unit. Liquids can be purified by distillation, a process that involves vaporising a liquid and condensing the vapour as a distillate. Simple distillation can help removal of non-volatile impurities or when the difference in boiling points of components is 80^0 or more. Fractional distillation can be used to separate components of a mixture of liquids with relatively smaller difference in boiling points. In case a liquid decomposes at or near the boiling point, distillation can be carried out under reduced pressure. It is called the vacuum distillation. You have studied in detail about the distillation assemblies used for all the types in Sec. 2.3.4 of Unit 2 of this course.

The experiment based on the distillation technique is discussed in the following section.

8.5 EXPERIMENT 8 (b): TO SEPARATE A MIXTURE OF HEXANE AND TOLUENE BY DISTILLATION

You would have understood the concept of distillation as explained in the previous unit and revised in section 8.4 as above. The mixture of two liquids given in this experiment consists of hexane with a boiling point of 68°C and toluene with a boiling of 110.6°C. On the basis of the facts studied you would be able to appreciate that it is possible to separate the two liquids by simple distillation procedure. You are given the requirements and the procedural details in the following subsections to perform the experiment.

8.5.1 Requirements

Apparatus	Chemicals
Round bottom flask	Hexane
Distillation head	Toluene
Adopter	Water
Condenser	Grease
Erlenmeyer flask	Pumice stones
Iron stands	
Clamps	
Wire gauze	
Measuring cylinder	
Thermometer	

8.5.2 Procedure

Follow the steps given below to carry out the experiment.

1. Set up the distillation assembly with the help of your counsellor ensuring that all the joints are very well greased. Check that the thermometer is placed well in the jacket meant for it.
2. Take the mixture of hexane (~ 20 mL) and toluene (~ 20mL) in the round bottom flask used in the distillation assembly. The size of the flask should be chosen in such a manner that it should not be more than half full with the solvent mixture.
3. Allow the water to flow in the outer jacket of the condenser before starting to heat the liquid mixture in the flask.
4. Start heating gently the mixture of liquids using a flame or a hot plate or a water bath. A water bath is used for low boiling liquids. In the present case one of the components i.e. toluene has a b.p. higher than 100°C, therefore you will have to use a Bunsen burner or a hot plate or a heating mantle.

   Do not forget to add pumice stone to the flask while heating.

5. Note the temperature of the boiling liquid mixture after some liquid has been collected in the collecting flask. Keep collecting till about 20 mLof the liquid has collected. Observe the temperature at this stage. It should correspond to the b.p. of hexane i.e. 68°C.
6. Transfer the fraction collected at the first boiling temperature achieved and around an amount of 20 mL.
7. Continue heating the remaining liquid and note the temperature. You will find the temperature rising suddenly till it has reached about 110°C.
8. Collect the distilled liquid at 110°C in the flask till all possible liquid is finished.
9. Transfer the fraction collected second time. This would be the toluene fraction.
10. Report the result with the temperatures for the two fractions collected. These temperatures will represent the boiling points.

8.5.3 Result

The b.p. of the first fraction collected =……°C

The b.p. of the second fraction collected =……°C

You can try to answer the following SAQs to check the understanding of the purification of liquids by distillation.

SAQ 5

Why is it important that cooling water enters at the lower end and exits at the upper end of the condenser jacket, and not vice versa?

SAQ 6

During a distillation why should the flask be filled to only half or two thirds of its capacity?

8.6 ANSWERS

Self-Assessment Questions

1. There are four important criteria that are used in selecting a solvent for a crystallisation.

   (i) Substances tend to be more soluble in chemically similar solvents.

   (ii) Good crystallisation would imply that the substance is very soluble in hot and insoluble in cold Solvents.

   (iii) Very good solvents require very high concentration of solute for crystallisation.

   (iv) Polar solvents tend to produce better crystals than hydrocarbon solvents.

2. Cyclohexane is a good solvent. As evident from the table that solid is very soluble in hot and insoluble in cold cyclohexane and this solvent system gives the best yield.

3. The compound should be first dissolved in toluene by heating. Petroleum ether may be added drop-wise for crystals to appear on cooling.

4. i) Boiling stones: to avoid bumping of the solution

   ii) Activated carbon: to remove of the colour of the solution

   iii) Seed crystals: to initiate crystal formation

5. It is to ensure continuous condensation of vapours coming from the mixture of liquids taken in the flask and kept for boiling.

6. It is to avoid the boiling over of liquid and not the vapours from the flask to the collecting flask. On heating this may lead to impure liquid collection.

EXPERIMENT 9

CRITERIA OF PURITY: DETERMINATION OF MELTING AND BOILING POINTS

Structure

9.1 Introduction

Expected Learning Outcomes

9.2 Melting Point

Measuring the Melting Point: Capillary Method

9.3 Experiment 9 (a): To Determine the Melting Points of the Given Solid Compounds

Requirements

Procedure

Result

9.4 Boiling Point

9.5 Experiment 9 (b): To Determine the Boiling Point of the Given Liquid Compounds

Requirements

Procedure

Result

9.6 Answers

9.1 INTRODUCTION

You performed the experiments to purify a solid and a liquid product by crystallisation and distillation respectively. In the present experiments you will learn about very important criteria of purity. These are useful in confirming whether the compound is pure or not. The two criteria are melting point and boiling point for solid and liquid products respectively. You must have studied in the theory courses that these physical properties are characteristic of a compound and help in the identification of the same.

You will learn the theoretical concepts involved in these criteria and then find out the melting point of a solid and the boiling point of a liquid.

Expected Learning Outcomes

After performing the experiments you should be able to:

- ❖ define melting point and describe the method of its determination;
- ❖ explain the effect of impurity on the melting point of a solid substance;
- ❖ determine the melting points of the given pure organic solids;
- ❖ define boiling point and describe the method of its determination;
- ❖ explain the effect of impurity on the boiling point of a liquid; and
- ❖ determine the boiling points of the given liquids.

9.2 MELTING POINT

You must have read in your previous classes and Unit 2 of this block that melting point of a pure substance is used as a test of its purity. Melting point is an important property that helps also to identify a compound. You have read the basic definition and significance of melting point in determining the identity and purity of a compound. How is the identity determined?

The identity of a certain compound can be confirmed by mixing it with a sample of the known compound and then obtaining the melting point of the mixture. If the two compounds are not the same, the melting point would generally be lowered and the melting point range broadened. Let us understand the concept as follows.

Mixed Melting Point

The fact that an additional substance lowers the melting point of a pure organic substance is utilised in mixed melting point test for the identification of organic compounds. For this, the melting point of an authentic sample of the compound is compared with that of a mixture of the authentic sample with another compound. In case both are identical, there would be no lowering in the melting point of the mixture. When these are different, the melting point of the mixture might get lowered by several degrees. It is often possible to attach the two capillary tubes, one containing the authentic sample and other, the mixture, on either side of the thermometer and take their melting points simultaneously. This would give a comparative account of melting points simultaneously.

Let us understand the method of taking melting point using a capillary tube.

9.2.1 Measuring the Melting Point: Capillary Method

Melting points are usually determined in capillary tubes open to the air. A capillary tube is a thin glass tube of 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 Bunsen burner flame for a few seconds while rotating it. The molten glass would seal the capillary. Formation of large beads should be avoided.

The capillary tube can be heated in a liquid bath or on an electrically heated metal block. You would be using the **Thieles melting point bath**, which is a tube with a closed bent side arm, Fig. 9.1. On heating the bent side arm, the

heated liquid circulates and raises 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 up to 220°C. Above this temperature is starts fuming and gets discoloured. Silicone oils, though more stable, are expensive.

The thermometer is fitted through a cork. A section of the cork is cut away, so that the thermometer scale is visible and also to allow the air to escape on heating. The temperature at which the sample melts completely is noted down as the melting point of the sample compound.

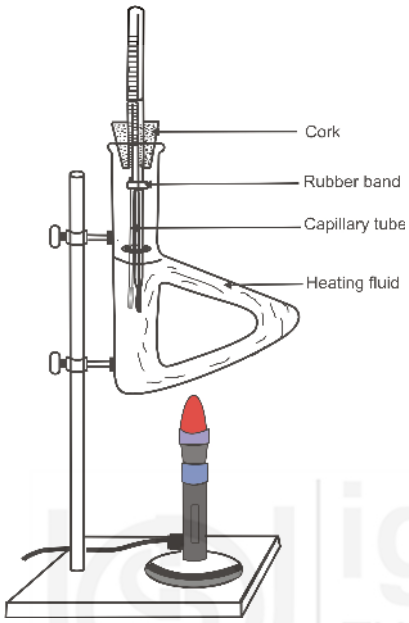


Fig. 9.1: Thiele's melting point apparatus

Melting point can also be determined using an apparatus which is heated electrically. This type of melting point apparatus is shown in Fig. 9.2. The apparatus is used for determination of melting points up to 350ºC. The aluminum block in the apparatus has holes to introduce the capillary tube and a thermometer. The temperature is regulated by energy regulator fitted to the unit. The sample gets uniformly heated and can be seen through a lens provided in the upper part of the unit.

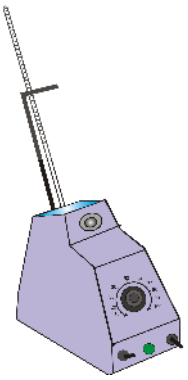


Fig. 9.2: Electrically heated melting point apparatus

You can ask your counsellor if a melting point apparatus as explained above is available in the laboratory. The counsellor can demonstrate the determination of melting point using this apparatus.

Now that you have got familiarised with the method and apparatus used to determine the melting point, you can perform the experiment given in the next section.

9.3 EXPERIMENT 9 (a): TO DETERMINE THE MELTING POINTS OF THE GIVEN SOLID COMPOUNDS

You have read the capillary method of determining the melting points of solid compounds in the previous section. Your counsellor will give you two compounds for determining the melting point as per the method explained. The requirements and the procedure are given below.

9.3.1 Requirements

- Melting point apparatus with thermometer
- Capillary Tubes
- Bunsen burner
- Compounds for melting point determination

9.3.2 Procedure

Follow the steps given below for determining the melting points of the compounds given.

1. Assemble the melting point apparatus i.e. the Thiele tube with the help of clamp attached to an iron stand. The apparatus should have enough of mineral oil/or any other oil to cover the top of the side arm outlet. Take capillary tubes for filling the solid whose melting point is to be determined.

2. Follow the procedure of filling the capillary tube as explained below:

   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 mound. 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 working bench. 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.

3. 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. For this purpose, the capillary tube is moistened with the bath liquid. The surface tension of the liquid enables the capillary tube to become attached to the thermometer by capillary action. The thermometer, with the capillary tube attached, is then inserted into the bath. Care is taken that the open end of the tube is well above the level of the liquid. Allow for expansion of the liquid on heating.

4. The melting point apparatus (Fig. 9.1) is heated with a small flame; comparatively rapidly till the temperature is about 15°C below the melting point of the substance, and then slowly such that the rise of temperature is about 2°C per minute. The temperature at which the substance starts to melt and that at which it has completely liquefied, i.e. the melting range is noted. As said above, for a pure compound it should not exceed 0.5-1°C.

   Any softening, sintering, evolution of gas or any other signs of decomposition have to be carefully noted.

   In case of an unknown compound, an approximate melting point may be taken first.

5. Record the temperature at the beginning and the end of the melting range.

6. Leave the apparatus for cooling by 10-15°C below the expected melting point of the other solid and repeat the whole procedure and report the result.

9.3.3 Result

Melting point of compound 1 was found to be = ……°C

Melting point of compound 2 was found to be = ……..°C

You can try to answer the following SAQs to assess the understanding of the significance and the method of taking melting point.

SAQ 1

For the following melting points, indicate what might be concluded regarding the purity of the sample.

a) 130° – 132° C

b) 56° – 60°C

c) 147°C (decomposes)

d) 173.5° -174.5°C

SAQ 2

Read the following statements critically and indicate whether each is true or false, and if false, explain why.

a) An impurity always lowers the melting point of an organic compound.

b) A sharp melting point for a crystalline organic substance always indicates a pure single compound.

c) If the addition of a sample of compound A to compound B does not lower the melting point of B, B must be identical to A.

d) If the addition of a sample of compound A lowers the melting point of compound B, B and A cannot be identical.

9.4 BOILING POINT

You have read in Unit 2 that boiling point is another very important test to check the purity of liquids. In fact, like melting point this property can be used for the identification of compounds. In very simple terms boiling point abbreviated as b.p. is the temperature at which the liquid changes into gas. Unlike melting point, it is difficult to have a single and sharp temperature for b.p. It is observed generally in the range of 2-3^{o}C.

The boiling point is a characteristic property of a liquid. It depends upon the structural features of the liquid compound. The following factors influence the boiling point.

1. **Polarity**; **Nature of intermolecular forces**: The interactions in a compound are due to polar covalent bonds or formal charges and non-covalent interactions that include dipole-dipole interaction, H-bonding and van der Waals forces. The liquid molecules are held together by close non-covalent interactions. When the liquid is heated these interactions are broken and the liquid starts getting converted to gaseous state. Thus increased H-bonds, polar covalent bonds or formal charges in a molecule tend to increase the boiling point.

2. **Molar mass:** A compound having higher molecular mass has more atoms that can be involved in non-covalent interactions. The larger the number of non-covalent interactions, more the energy required to break the non-covalent interactions to transform the compound from the liquid phase to the gas phase. Thus higher the molar mass, higher is the boiling point.

3. **Shape of the molecule**; **Presence of branching**: Molecules with similar molecular formula and functional groups vary in their boiling points depending on whether these are straight chain or branched. It has been observed that straight chain compounds have higher boiling points as compared to branched chain compounds. Branching blocks molecules from packing together too closely and results in weak non-covalent interactions. This makes the molecules require less energy for the phase change i.e. from liquid to gas phase.

It was mentioned in Unit 2 that the distillation method is used to determine the boiling point when there is an amount of more than 5mL of the liquid. For less amounts some micro-methods are used out of which the **Siwoloboff's method** is the most reliable and common. The method makes use of a boiling point apparatus based on the Theile tube as used in the case of melting point determination. The method is described below.

Siwoloboff's Method

In this method, two tubes are required, an ordinary melting point capillary tube, 90-110 mm long and a wider tube, 3-5 mm in diameter and 80-100 mm long. The capillary tube is sealed at one end and the seal is made in it by holding it in a flame. The wider tube is also sealed at one end. The capillary tube is placed in the wider tube with open end down as shown in Fig. 9.3.

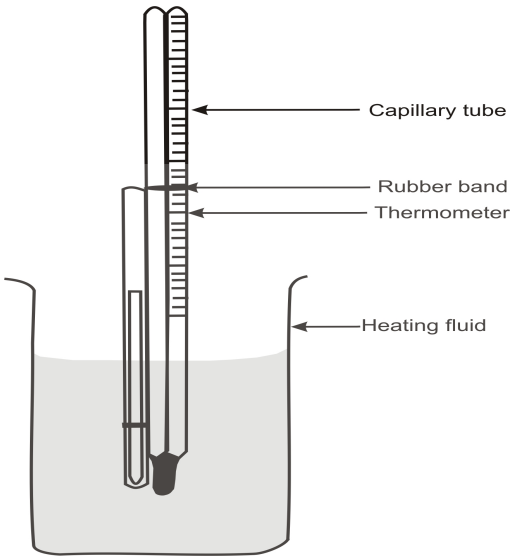


Fig. 9.3: Assembly of boiling point apparatus.

Then using a pipette, the liquid for which the boiling point has to be determined is put into the wider tube such that its level is about 2 mm above the seal in the capillary tube. The tube is attached to the thermometer keeping the liquid at level with the mercury bulb of the thermometer. A rubber band may have to be used for the purpose. The thermometer with attached tubes is inserted into a heating bath.

Care is taken that the rubber band is well above the level of the liquid, as rubber gets attacked by liquid paraffin.

The bath is heated until a rapid and continuous stream of bubbles comes out of the capillary tube. Before this occurs, some bubbles evolving in an erratic fashion may be seen. This is due to the air trapped in the capillary tube. There would be a marked change from slow evolution of air bubbles to the rapid evolution of bubbles resulting from the liquid boiling as its boiling point is reached. However, **this is not the boiling point of the liquid.** At this stage, the heating source is removed and the bath allowed to cool slowly. As the rate of bubbling decreases, the liquid starts to rise into the capillary tube. This temperature is noted. **It is the boiling point of the liquid.** If the liquid rises sufficiently slowly, it may be possible to note the temperature at which the liquid starts to rise, and that at which the capillary is full, i.e. the boiling point range of the liquid.

The capillary tube is removed and the liquid shaken out from the small end. The capillary is then replaced in the sample tube and the process of heating and cooling repeated. A more accurate determination may be possible this time. Observed boiling points should be reproducible to within 1-2^{o}C.

You would like to know the physical basis of this technique. It is explained as follows:

Before the liquid is heated, the capillary tube is filled with air. As the bath is heated, the air in the capillary tube is driven out and is replaced with the vapour of the liquid. On further heating until the liquid starts boiling vigorously, the actual boiling point of the liquid has exceeded, the air in the capillary tube has replaced completely with the vapour of the liquid. On cooling at a particular temperature the vapour pressure of the liquid rises in the capillary tube. This temperature is the boiling point of the liquid.

After getting familiarised with the method of determining the boiling point of liquids in micro amounts, you can now perform the experiment given in the next section.

9.5 EXPERIMENT 9 (b): TO DETERMINE THE BOILING POINTS OF THE GIVEN LIQUID COMPOUNDS

You are given two liquids for their boiling point determination. Follow the procedure and report the result.

9.5.1 Requirements

- Boiling point apparatus
- Bunsen burner
- Iron stand with clamp
- Capillary tubes
- Thermometer
- Two liquid compounds

9.5.2 Procedure

Follow the steps given below for this experiment.

1. Take a small volume (≈ 5 ml) of the liquid in a small test tube as provided by your counsellor.
2. Place a capillary tube, sealed at one end, with open-end down into the liquid contained in the test tube.
3. Attach a thermometer to the tube with a rubber band, and clamp the apparatus to an iron stand.
4. Immerse the assembly in a water bath (or an oil bath for samples with boiling point higher than 100^{o}C). Observe the temperature carefully.
5. With increase in temperature you will see a rapid evolution of bubbles from the end of the tube. Continue heating for about 5-10 seconds.

Make sure that all of the air has been expelled from the capillary, and the vapors of the liquid remains in the capillary.

6. Remove the burner or the hot plate, but do not take the assembly out of water bath (or oil bath), and carefully watch the capillary.

   You might see the bubbles continuously coming out until the pressure exerted by the vapor of the liquid becomes equal to the atmospheric pressure.

7. Again observe the status of bubbles. The bubbles will slow down with lowering of temperature and at some point, the liquid will rise into the capillary.

8. Read the thermometer value and record the temperature when the bubbles stop.

   The temperature observed when this happens should be the observed boiling point of the liquid.

9. Compare the temperature noted by you with the literature value of the boiling point for the liquid used. The difference should not be more than 2-3°C.

10. Repeat the procedure with the other liquid. Allow the hot bath to cool at least 15 - 20°C below the suspected boiling point before repeating the experiment. Report the result in your note-book.

Each time you perform the procedure, you must use a new capillary.

9.5.3 Result

Boiling point of compound 1 was found to be = ……°C

Boiling point of compound 2 was found to be = ……°C

You can try to answer the following SAQs to check your understanding of testing the purity of organic compounds.

SAQ 3

Which of the compounds, ethanol (CH_3CH_2OH) or methanol (CH_3OH) should have the higher boiling point and Why?

SAQ 4

What is the effect of a small amount of impurity on the boiling point of an organic compound?

SAQ 5

What are the purposes of boiling point determination?

9.6 ANSWERS

Self-Assessment Questions

1. A pure crystalline compound has, in general, a definite and sharp melting point, i.e., the melting range or the difference between the temperature at which the collapse of crystals is first observed and the temperature at which the sample becomes completely liquid, does not exceed 0.5°C –1.0°C. In our case only melting point 173.05°C–174.5°C fit in this criterion. It is therefore, the melting point of pure compound.

2. a) True b) True c) True d) False

   If A and B are two different compounds, the melting point of the mixture may get depressed by several degrees.

3. Ethanol will have a higher boiling point as it has more mass as compare to methanol.

4. Impurity increases the boiling point of the compound.

5. The two main purposes are to:

   - Separate liquids from a mixture of the liquids.
   - Check the purity of the compound.

EXPERIMENT 10

BROMINATION OF ANILINE

Structure

10.1 Introduction

Expected Learning Outcomes

10.2 Planning an Organic Synthesis

10.3 Experiment: Bromination of Aniline

Requirements

Procedure

10.4 Experiment Report – 10: Preparation of 2,4,6-Tribromo-Aniline

10.5 Terminal Questions

10.6 Answers

10.1 INTRODUCTION

In Unit 1, we described various laboratory methods-used in an organic laboratory. In the Experiments 10-15, we shall describe how the preparatory experiments are carried out. This will permit you the practice and development of manipulative techniques commonly used in organic chemistry.

Preparative Organic Chemistry is a quest for new compounds or attempts at conversion of known compounds to other products with some specific properties. It may often be difficult to bring about a desired chemical transformation. However, it is equally and sometimes, even more difficult to isolate and purify the product. So, an organic chemist has to call upon all the knowledge, skill and ingenuity at his/her command while preparing or purifying a compound. No wonder, then, that, preparative organic chemistry bas been described as 'veritable mixture of science, art and craft'. In this experiment we will give you some general hints on Organic Synthesis. We hope these will enable you to organise your work better and improve your performance. Finally, we shall give the preparation of 2,4,6-tribromoaniline using aniline and bromine. Along with the procedural detail of the experiment you will also learn briefly about the electrophilic substitution reactions of aromatic compounds.

Expected Learning Outcomes

After reading the procedural details and performing this experiment you should be able to:

- describe various criteria which have to be kept in mind while choosing a particular procedure for the synthesis of a compound;
- plan an experiment, choosing a convenient scale and appropriate apparatus for carrying out the reaction, its work up, purification and identification of the product;
- carry out the preparation of 2,4,6-tribromoaniline using aniline and bromine;
- explain electrophilic substitution reactions;
- calculate yield of final product; and
- determine the melting point of crystallised product.

10.2 PLANNING AN ORGANIC SYNTHESIS

As discussed in the previous unit, before you take up any preparation, you would have to choose a method for it. The choice of an appropriate method from amongst the many alternatives available will depend one or more of the following criteria which are self-explanatory :

- availability of good literature procedure or recipe,
- availability of starling materials and reagents .
- feasibility of the procedure and the precautions needed,
- time, labour and cost involved.

You should read carefully the procedure you choose, including any footnotes or precautions. As far as possible, try to understand the reaction pathway so that you are able to cope with the crucial phases of the reaction as well as avoid side-reactions leading to lower yields and impure product.

Before starting an experiment, considerable planning bas to be done. The four stages or the experimental process which need consideration are :

- reaction,
- work-up or isolation,
- purification,
- characterisation .

As you may have learnt organic reactions are very sensitive to conditions like concentration, medium, temperature, etc., under which they are carried out. Some reactions are very sensitive to even the traces of moisture, so the solvents, reagents and the apparatus have to be rigorously dried. In addition, the endothermic reactions will need heating, he exothermic ones cooling; and a heterogeneous mixture will need to be stirred. We would advise you to plan for all these contingencies before starting a reaction. Next, optimal conditions for work-up isolation and purification have to be chosen. It helps a great deal if you know the properties like the physical state, mp, bp, solubility, respectively, etc. of the reactants, the product and the by-products of the reaction.

should be able to

Once a pure product is obtained, it has to be characterised by its mp, bp, ir, tlc or other spectroscopic methods etc. These values are compared with reported values in the case of a known compound. In case the compound is unknown, it is purified till, say, there is no further change in its mp, tlc orir. Planning also has to be done for the maximal use of time and scale.

TIME

An estimate of the duration of each step in the procedure should be made. Stage(s) where the process can be interrupted, if necessary, should be identified. You should always plan to start a reaction at a time such that you can either work up the product or leave it at a convenient stage at the time you have to leave the lab.

SCALE

A suitable scale has to be chosen which makes handling easy. While doing this, the volume of solvents, the size of the reaction vessel and other apparatus used in work-up has to be kept in mind.

A lot of preliminary work has to be done before a can be started. Purity of all reagents and solvents need to be checked (In earlier part of this course, we have described the methods of checking the purity of the reagent). Apparatus has to be set up. In choosing a reaction vessel care should be taken to see that it is never more than I /2 or 2/3 full. Remember liquids expand when heated. As mentioned above, adequate arrangements have to be made for heating, cooling or stirring a reaction mixture. We have already encountered with these simple laboratory techniques in earlier experiments of this course. A drying tube may be used to avoid leakage of moisture into the reaction mixture. **All organic solvents are inflammable and, therefore, should never be heated on a naked flame.**

In this experiment and in subsequent experiments, we will describe how the preparatory experiments are carried out. This will permit you the practice and development of manipulative techniques which you have studied in Unit 1 and in earlier experiments of this course.

10.3 EXPERIMENT: BROMINATION OF ANILINE

This experiment is actually based on electrophilic substitution reactions of aromatic compounds. Therefore, first you will recapitulate theory of electrophilic substitution reactions of aromatic compounds and then the procedural detail of the preparation of 2,4,6-tribromoaniline on bromination of aniline.

Electrophilic Substitution

Electrophilic substitution reactions are typical reactions of aromatic compounds. Electrophilic aromatic substitutions include a wide variety of reactions like nitration, sulphonation, Friedel-Crafts' alkylation and acylation, halogenation and so on. These substitutions, therefore, form a route of access to various aromatic compounds by permitting introduction of certain substitutes which can then be transformed or replaced by the desired ones.

However, the various aromatic compounds differ in the case of facility with which they undergo electrophilic substitution. It has been found that a substituent group present in the benzene ring affects both the reactivity of the ring towards electrophilic attack and the orientation of the incoming substituent. The reactivity of an aromatic compound towards an electrophile is reflected in the severity of conditions for the reaction and the time it would take.

Orientation determines whether the substituent already present would direct the incoming substituent to *ortho/para* or the *meta* position.

On this basis the substituents have been broadly classified as follows:

1. Activating groups which facilitate further substitution and are ortho/para directing. These are electron donating groups
   - Strongly activating
   - $-NH_2(-NHR, -NR_2)$
   - $-OH$
   - Moderately activating
   - $-OCH_3(-OC_2H_5$, etc.)
   - $-NHCOCH_3$
   - Weakly activating
   - $-C_6H_5$
   - $-CH_3(-C_2H_5$, etc.)
2. Deactivating groups which make further substitution difficult and are *meta* directing. These are electron attracting groups.

   $-NO_2$ $-SO_3H$

   $-N(CH_3)_3$ $-CHO, -COR$

   $-CN$

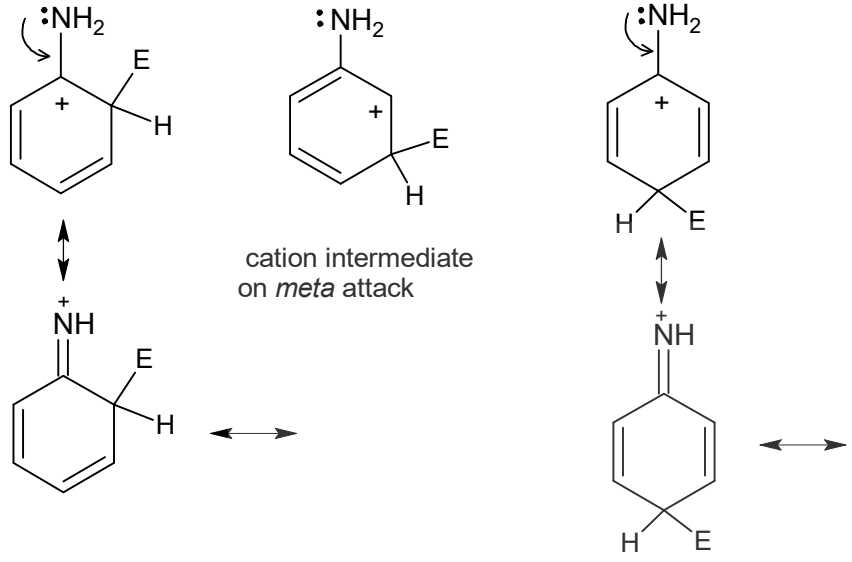
   $-COOH (-COOR)$
3. Deactivating groups which are ortho/para directing.

   $-F,$ $-Cl,$ $-Br,$ $-I$

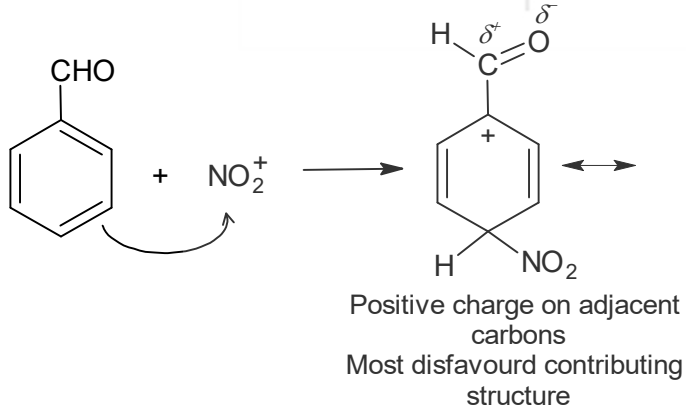
From the above you can see that nearly all substituent groups fall in two categories, activating and *ortho/para* directing or deactivating and *meta* directing. The halogens are in a class by themselves being deactivating but *ortho/para* directing. This is because their inductive effect is $-I$, however, due to mesomeric effect or resonance they direct the incoming substituent to *ortho/para* positions.

Ortho and *para* directing orientation of substituent group for electrophilic aromatic substitution can be explained on the basis of the relative stability of carbocation intermediates formed by attack of electrophile on substituted

benzene. Groups such as —OH, —NH_2,—Br *ortho* or *para* to the site of electrophilic attack can help to stabilise the carbocation intermediate more by delocalisation of the positive charge through resonance involving unshared electron pairs. Such stabilisation is not possible for carbocation intermediate formed on *meta* attack.



On the other hand in case of deactivating substituent group, following carbocation structure formed on ortho/para attack of electrophile is most disfavoured contributing structure.



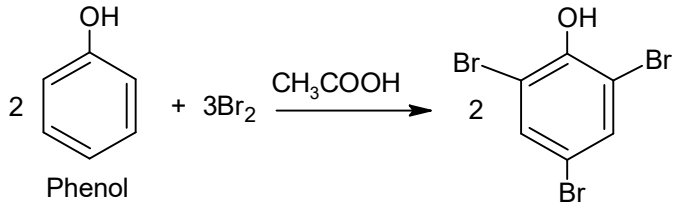
None of the contributing structures for meta attack places positive charge on adjacent atoms. As a result resonance stabilisation of the cation intermediate for meta attack is more than that of para/ortho attack.

On the basis of these effects, it is possible to predict fairly accurately the course of any aromatic substitution.

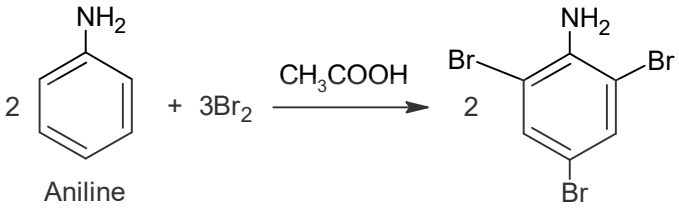
Bromination of Phenol or Aniline:

Phenol and aniline undergoes electrophilic substitution quite readily. Sometimes both hydroxyl and amino groups can be too powerful activating groups and it is

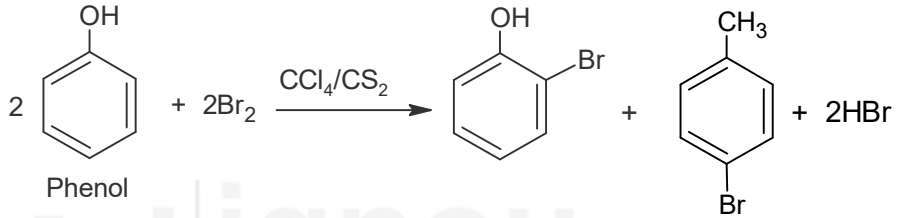
difficult to control the reaction to one substitution. For example, on shaking phenol/aniline with bromine solution in polar solvent such as glacial acetic acid at room temperature, 2,4,6-tribromophenol/2,4,6-tribromoaniline is formed:

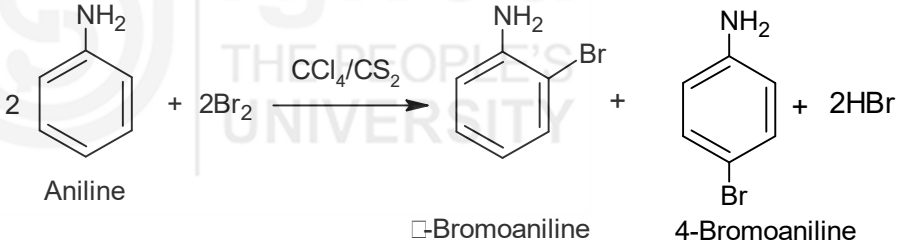


Phenol in polar solvent such as water is available mainly in the form of phenoxide ion (PhO^-) which is more reactive than Phenol.

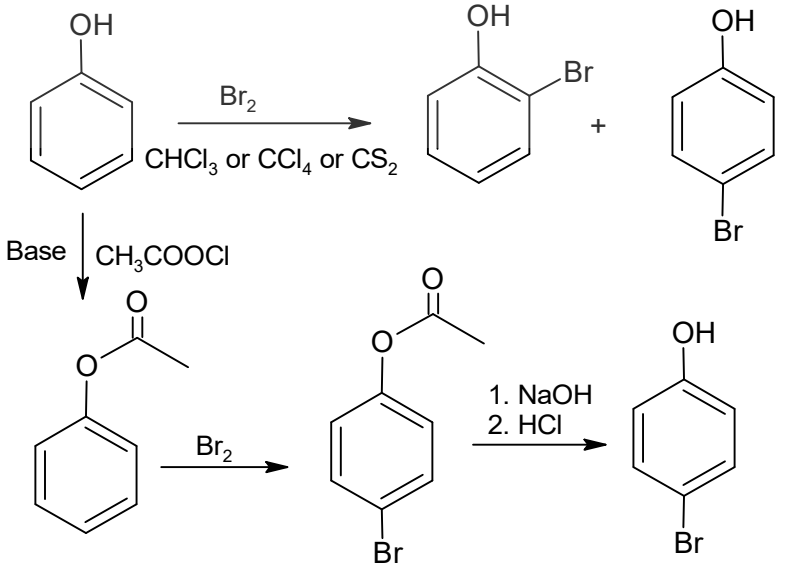


The activating power of —OH/—NH_2 groups can be decreased by carried out reaction in less polar solvent such as $CHCl_3$, CCl_4 or CS_2 etc..

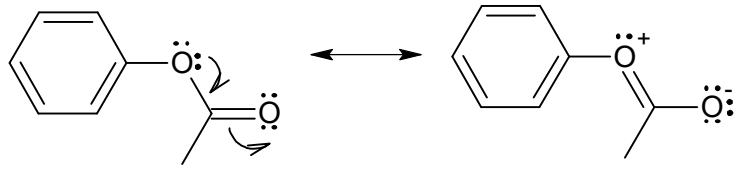




Other way is by converting the phenol to ester that can be removed by hydrolysis once electrophilic substitution carried out. Since the ester is weak activating group and also bulky, it will discourage ortho attack and para product will be the major product.

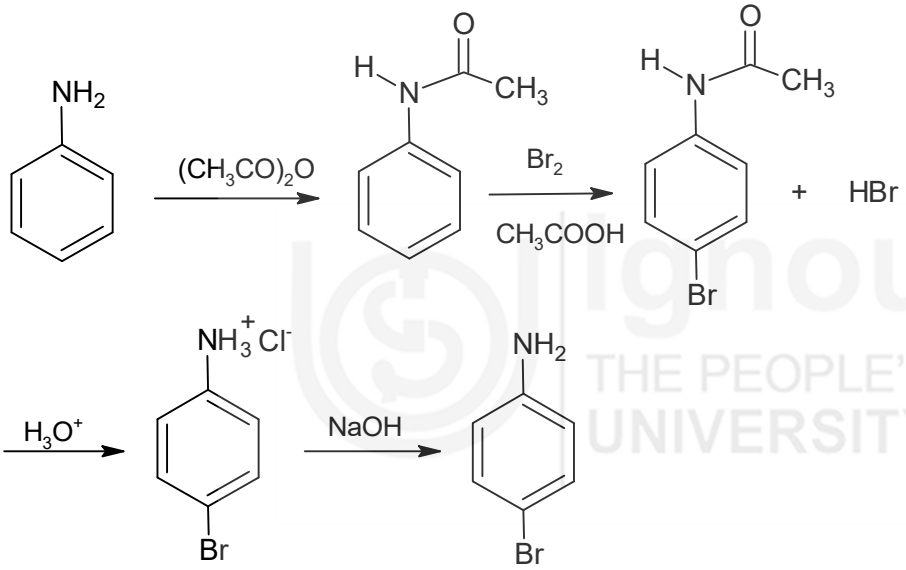


Following resonating structures explain less reactivity of phenyl acetate (acetoxybenzene):



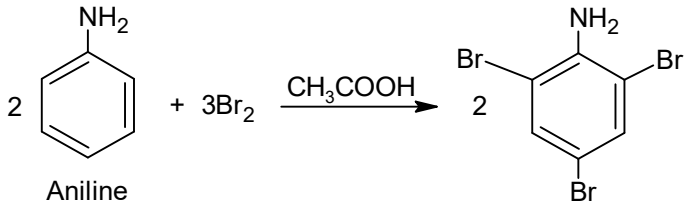
Due to these resonating structures, oxygen electrons are less available to ring

Similarly, the amino group is a strongly activating ortho, para-directing group which upon bromination of aniline would give the 2,4,6-tribromo derivative. When monobromination is desired the amino group is converted to the less activating acetamido (—$NHCOCH_3$) group by acetylation. This bulky group further servesto inhibit formation of the ortho-isomer, which is therefore only a minor by-product in the bromination of acetanilide. Once bromination is carried out, deacetylation of *p*-bromoacetanilide is achieved by mild hydrolysis.



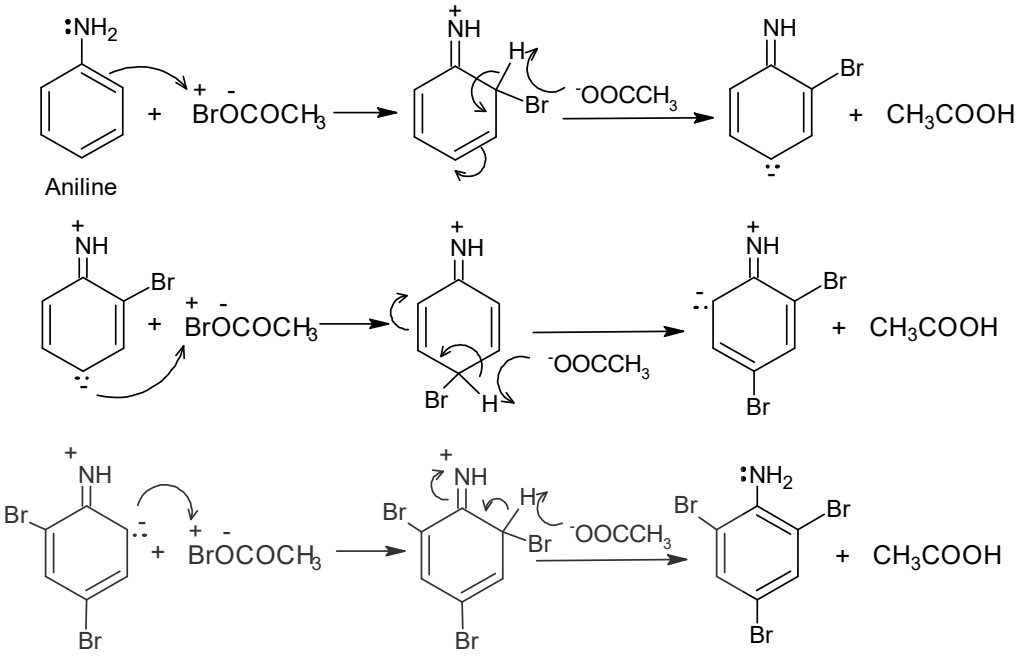
In this experiment, we are describing the preparation of 2,4,6-tribromoaniline from aniline. Since, —NH_2 group is a strongly activating group, you would expect aniline to undergo further substitution easily. That indeed happens; reaction, in fact, is exothermic, and with multiple substitutions we get the tribromo product. Further, as the —NH_2 group is ortho/para directing the substituents take the two ortho and a para positions.

Reaction



Mechanism

$$3Br_2 + 3CH_3COOH \rightleftharpoons 3CH_3COO\overset{-}{B}r^{+} + 3HBr$$



10.3.1 Requirements

Chemicals

Bromine

Aniline

Ethyl alcohol

Acetic acid

Apparatus

Conical flask (100 cm^3)	1
Measuring Cylinder (25 cm^3)	1
Glass rod	1
Glass funnel	1

Filter paper

Filtration assembly

Melting point apparatus

Precautions

Bromine is very corrosive and causes serious burns. Its vapors are extremely toxic and irritating to eyes, mucous membrane, and respiratory tract.

Aniline, phenols and their brominated products are irritants. Avoid any contact with skin, eyes and clothing.

10.3.2 Procedure

Dissolve 2.3g (2.25 cm^3, 0.025 mol) of aniline in 10 cm^3 of acetic acid in a 100 cm^3 Erlenmeyer flask. To this add dropwise a solution of 4.0 cm^3 (13.3 g, 0.083 mol) of bromine dissolved in 10 cm^3 of glacial acetic acid. The reaction is exothermic, so the reaction mixture would need cooling during the addition of bromine. After the addition is compete, add 50 cm^3 of water filter the yellow solid on suction, wash it with cold water and dry in in air on a filter paper. Weigh the product and determine the yield. Recrystallise a part of product with ethyl alcohol. Finally determine the melting point of recrystallised product. Note the yield and the melting point.

Side Reactions

None.

Other Methods of Preparation

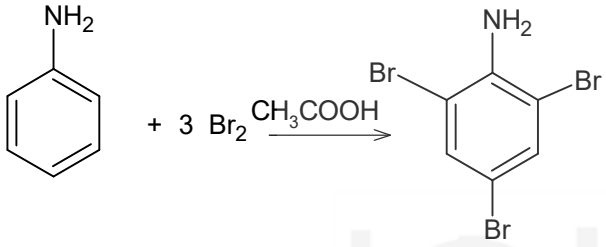
None.

10.4 EXPERIMENT REPORT – 10: PREPARATION OF 2,4,6-TRIBROMO-ANILINE

Introduction

In the experiment, 2,4,6-tribromo aniline is prepared by bromination of aniline with bromine in acetic acid.

Reaction



2,4,6-tribromoaniline

Table of Reactants and Products

Sl. No.	Compound	Mol. Mass	Weight Used	Moles Used	Molar Ratio	Other Data

Yield

Theoretical yield of 2,4,6-tribromoaniline:_____g

Actual yield of 2,4,6-tribromoaniline:_____g

% yield of 2,4,6-tribromoanilibne:_____g

Observed Properties of the Product

Melting point of crystallised product --------- °C.

10.5 Terminal Questions

1. Explain with the help of equation the function of acetic acid in bromination of aniline.

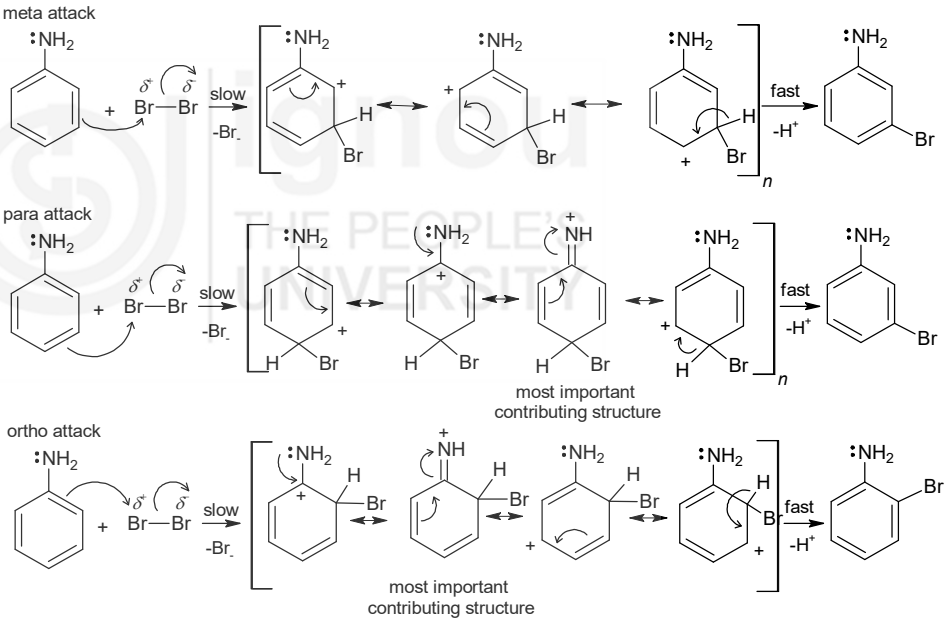
2. Draw all resonating structure for carbocation intermediate for ortho, para and meta attack of bromine on aniline.

3. Explain why monosubstituted product dominate in non polar solvents in bromination phenol/bromine.

10.6 ANSWERS

1. Polar solvents like acetic acid and water are used to polarise the Bromine molecules. In water and acetic acid, bromine is ionised up to greater extent to form large number of bromonium ions.Thus polar solvents increase the electrophilicity of attacking electophiles. Reaction of bromine acetic acid can be represented as:

$$3Br_2 + 3CH_3COOH \rightleftharpoons 3CH_3COO\overset{-}{B}r^{+} + 3HBr$$

2. 

3. In non polar solvent, bromine is only polarized to lesser extent and hence relatively less number of bromonium ions are available for electrophilic addition.

EXPERIMENT 11

BENZOYLATION OF PHENOLS

Structure

11.1 Introduction

Expected Learning Outcomes

11.2 Esterification

11.3 Requirement

11.4 Procedure

11.5 Experiment Report – 11: Preparation of 2-Naphthyl Benzoate

11.6 Alternate Experiment: Benzoylation of Aniline

11.7 Terminal Questions

11.8 Answers

11.1 INTRODUCTION

Both alcohols and phenols form ester with carboxylic acids, acyl halides and acid anhydrides. In these reactions the oxygen-hydrogen bond in the alcohol is broken. This conversion of alcohols and phenols to esters is known as esterification. In this experiment you will learn about the mechanism of esterification of phenols and procedural detail for the preparation of 2-naphthyl benzoateusing 2-naphthol and benzoyl chloride.

Expected Learning Outcomes

After reading the procedural details and performing this experiment you should be able to:

- ❖ explain the mechanism of the esterification reactions;
- ❖ prepare 2-naphthyl benzoate using 2-naphthol and benzoyl chloride;
- ❖ calculate yield of final product; and
- ❖ determine the melting point of crystallised product.

11.2 ESTERIFICATION

Esters of alcohols can be prepared by a number of methods such as,

- Direct esterification,

$$RCOOH + R'OH \longrightarrow RCOOR' + HCl$$

- Use of acyl chlorides and acid anhydrides,

$$RCOCl + R'OH \longrightarrow RCOOR' + HCl$$

$$(RCO)_2O + R'OH \longrightarrow RCOOR' + RCOOH$$

- Benzoylation,

$$C_6H_5OH + C_6H_5COCl \longrightarrow C_6H_5OCOC_6H_5 + HCl$$

$$C_6H_5NH_2 + C_6H_5COCl \longrightarrow C_6H_5NHCOC_6H_5 + HCl$$

- Alcoholysis of nitrile,

$$RC{\equiv}N + R'OH \longrightarrow RCOOR' + NH_4^+$$

- Methyl esters can be conveniently made using diazomethane,

$$RCOOH + CH_2N_2 \longrightarrow RCOOCH_3 + N_2$$

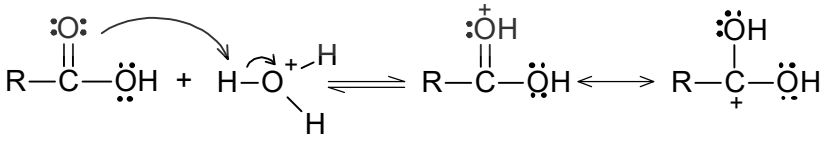
We are describing below the three important ones.

(i) Direct esterification: The interaction between a carboxylic acid and an alcohol a reversible process. It proceeds very slowly and equilibrium is, attained after refluxing for several days. If, however, either sulphuric acid or dry hydrogen chloride, to the extent of about 3 percent of the weight of alcohol, is added to the reaction mixture, the equilibrium is reached within a few hours. Direct esterification reaction seldom goes to completion. When equimolecular quantities of the acid and alcohol are employed, only about two-thirds of the theoretically possible yield of the ester is obtained. In order to displace the equilibriumto the right, i.e., in favour of the ester one of the reactants, generally the less expensive one, is taken in excess.

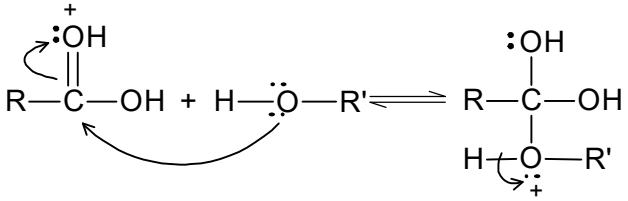
$$RCOOH + R'OH \longrightarrow RCOOR' + H_2O$$

The acid catalysed esterification reaction may proceed via an acyl-oxygen fission as shown below in the mechanism:

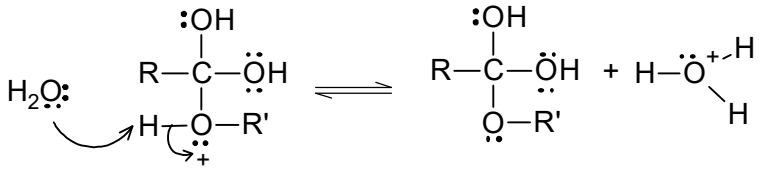
Step1: Addition of Proton. The reaction begins with protonation of carbonyl group of carboxylic acid, this increases the electrophilicity of its carbon centre



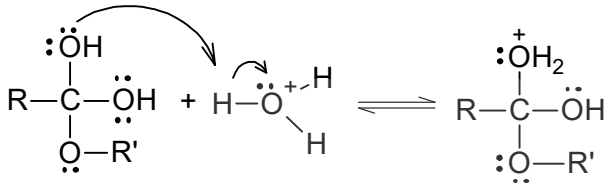
Step 2: Bond formation between a nucleophile and an electrophile. The alcohol adds to the activated carbonyl carbon atom.



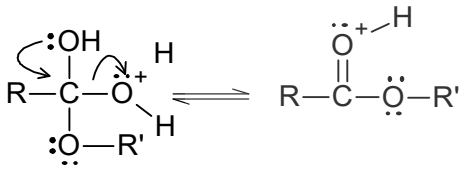
Step 3: Deprotonation: Intermediate formed in Step 2 gets deprotonated.



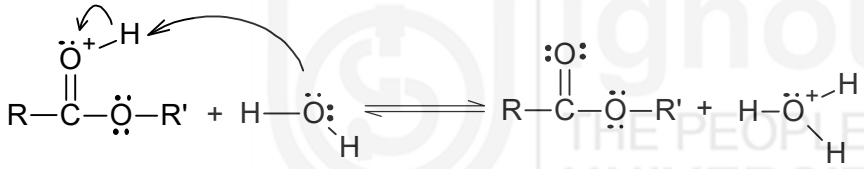
Step 4: Addition of Proton. –OH group on protonation converts to better leaving group $-OH_2^+$



Step 5: Removal of protonated hydroxyl group to form stable ion. Water molecule departs as a leaving group.



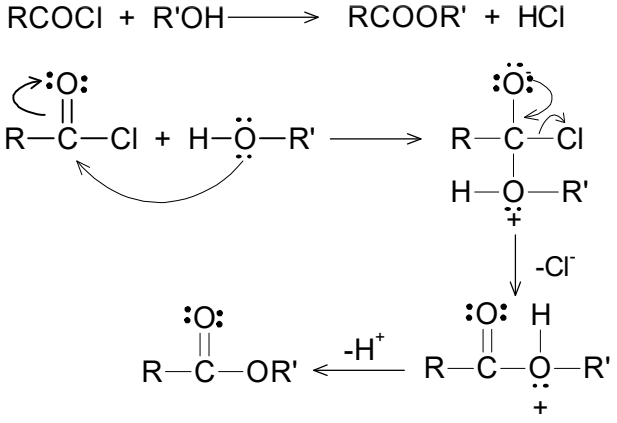
Step 6: Deprotonation. A final deprotonation gives ester.



Acid catalysed esterification gets greatly facilitated if the reaction is carried out in the presence of benzene or preferably toluene. In this case, water produced in the reaction gets distilled off as an azeotrope.

However, unlike alcohols, phenol reacts so slowly with carboxylic acids that why we normally carry out its esterification with acyl/aryl chlorides (acid chlorides) or acid anhydrides instead.

(ii) **Using acyl chlorides and acid anhydrides method:** Acyl chlorides react readily with alcohols to give esters in good yield. Generally a base a tertiary amine like dimethyl aniline or pyridine, as added to neutralize HCl formed.



In acyl chlorides, the electronegative chlorine atom attached to the carbonyl group makes the carbonyl carbon more electron-deficient, thereby increasing its reactivity towards nucleophiles.

Acylation with acid anhydrides can be carried out in the presence of a suitable catalyst, such as sulphuric acid or zinc chloride or a basic catalyst like pyridine. The second acyl group, facilitates the attack of nucleophiles on the carbonyl carbon, thus, making acid anhydrides more reactive.

Similarly, phenols also react with acyl chlorides or anhydrides in presence of base such as pyridine or NaOH to form esters. These reactions can be done under milder conditions than those used for alcohols due to the greater acidity of phenols. As you know, phenols can be converted to phenoxide ions with sodium hydroxide rather than very strong bases or metallic sodium. It is important to note that phenoxide which formed in basic reaction conditions is a better nucleophile than phenol because of the negative charge on oxygen which increases the nucleophilicity and thus basic conditions facilitate the ester formation.

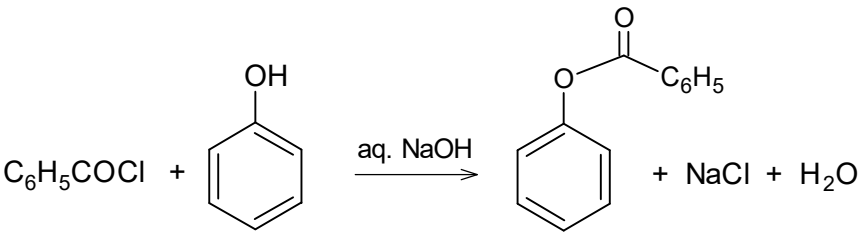
(iii) Benzo□lation: This is one of the best methods for the preparation of esters and and involves the introduction of an aromatic acyl or benzoyl group in organic molecules containing one or more active hydrogen atoms. This method is frequently used for the preparation of benzoyl derivatives of alcohols, phenols primary,and secondary amines.

$$C_6H_5OH + C_6H_5COCl \longrightarrow C_6H_5OCOC_6H_5 + HCl$$

$$C_6H_5NH_2 + C_6H_5COCl \longrightarrow C_6H_5NHCOC_6H_5 + HCl$$

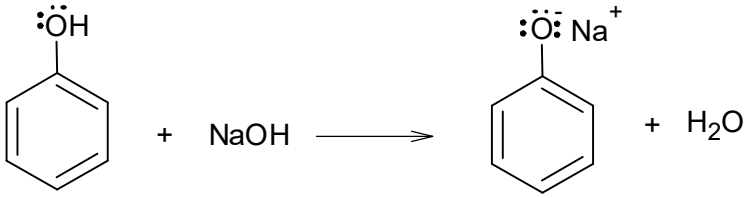
There are two reasons for favouring this method over acylation process. Firstly, acyl chloride and acid anhydride are easily hydrolysed in aqueous conditions. Hence acylation is often done in non aqueous medium whereas benzyol chloride being insolable in water reacts with it very slowly and so we can easily carry out benzoylation in aqueous medium. Secondly benzoyl derivative are insoluble in water, therefore they can be separated from the reaction mixture very effortlessly. On the other hand acetyl derivative are generally soluble in water.

When esterification using benzoyl chloride is carried out in in the presence of dilute aqueous alkali, the reaction is called **Schotten-Baumann reaction**. The aqueous alkali not only neutralizing HCl formed during reaction (HCl promotes side reaction) but as discussed earlier it also increases nucleophilicity of phenols because of the negative charge on oxygen. Using same reaction conditions primary and secondary amines can also be converted to amides. Reaction of phenol with benzoyl chloride in presence of aqueous sodium hydroxide can be written as:

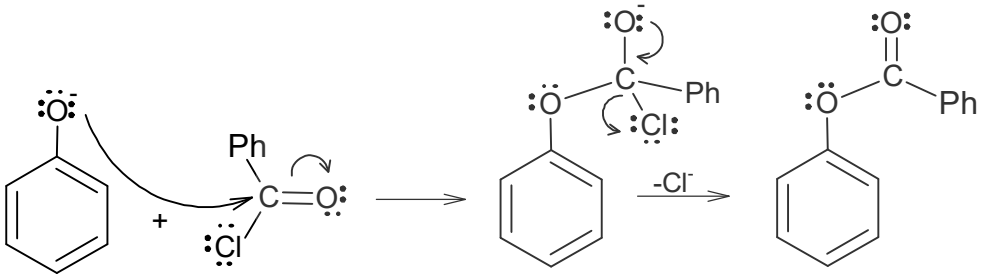


Mechanism of above can be proposed as:

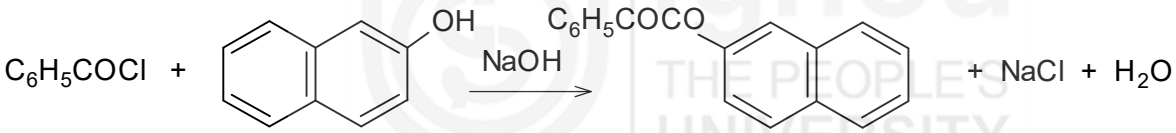
Step 1: Fornation of phenoxide ion



Step 2: Phenoxide ion (as nucleophile) attacks on carbonyl carbon of benzoyl chloride and replaces chloride ion (Addition elimination)



In this experiment you are going to carry out benzoylaytion of 2-Naphthol (*β*-naphthol). In this preparation, 2-naphthol reacts with benzoyl chloride in the presence of dilute sodium hydroxide.The reaction for this preparation may be represented as:



11.3 REQUIREMENTS

Chemicals	Apparatus	
2-Napthol	Conical flask (110 cm^3) with stopper	2
Sodium Hydroxide	Measuring Cylinder (10 cm^3)	1
Benzoyl chloride	Ordinary glasses funnel	1
Ethyl alcohol	Glass red	1
	Filtration assembly	
	Filter paper	
	Melting point apparatus	
	Capillary tubes	

11.4 PROCEDURE

Dissolve 3.6 g (0.025 mol) of 2-naphthol in 20 cm^3 of 5 per cent sodium hydroxide in cold in a 100 cm^3 conical flask. Add a little more water if needed to dissolve 2-naphthol completely. Add 3.5 g (2.9 cm^3, 0.025 mol) of benzoyl

Precautions

Benzoyl chloride is a very lachrymatory substance. It should be preferably handled in a fume hood. Avoid inhaling or contact with skin.

chloride. Stopper the flask tightly and shake vigorously until the smell of benzoyl chloride has disappeared. This may take 10-15 minutes. Filter off the solid on suction, wash with a little cold water. Recrystallise the crude ester from about 30 cm^3 of ethyl alcohol. Filter off the crystals and dry them in air. Note the yield and the melting point of pure 2-naphthyl benzoate.

Side reactions: If any benzoyl chloride gets hydrolysed to benzoic acid with sodium hydroxide, it remains in solution as a sodium benzoate

$$C_6H_5{-}COCl + NaOH \longrightarrow C_6H_5{-}COONa + NaCl + H_2O$$

Other methods of preparation: 2-Napthyl benzoate can be prepared by any of the other methods mentioned in the introduction.

11.5 EXPERIMENT REPORT – 11: PREPARATION OF 2-NAPHTHYL BENZOATE

Introduction

2-Naphthyl benzoate is prepared by the Schotten-Baumann method by reacting 2-naphthol with benzoyl chloride in the presence of cold dilute aqueous sodium hydroxide.

Reaction

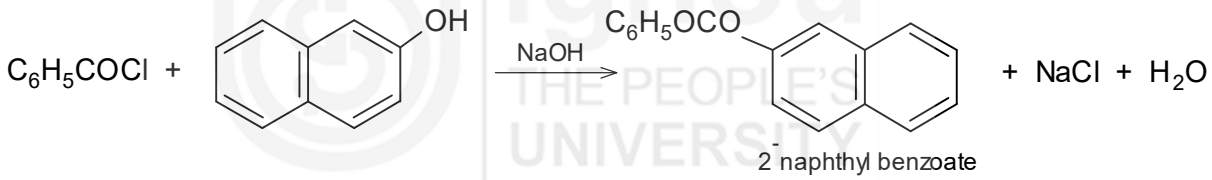


Table of Reactants and Products

Sl. No.	Compound	Mol. Wt.	Weight Used	Moles Used	Molar Ratio	Other Data

Yield

Theoretical yield of 2-Naphthyl benzoate:_____g

Actual yield of 2-Naphthyl benzoate:_____g

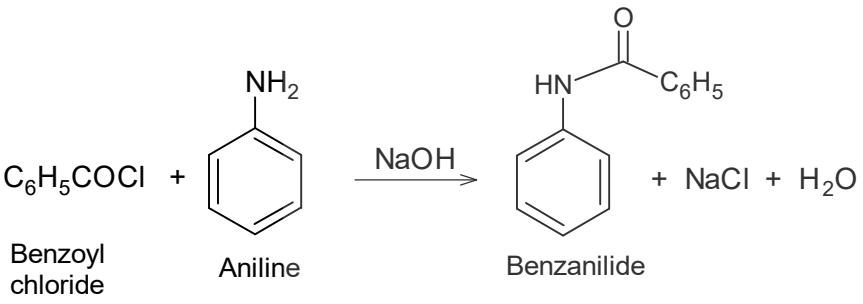
% yield of 2-Naphthyl benzoate:_____

Observed properties of the product

Melting point of crystallised product ----------^{0}C.

11.6 ALTERNATE EXPERIMENT: BENZOYLATION OF ANILINE

Similar to benzoylation of phenols, benzoylation of aniline also carried out by taking the aniline (2 cm^3/2.08 g) in of sodium hydroxide solution (30 cm^3 of 10% aqueous NaOH) in 100 cm^3 conical flask. Then by the addition of a little excess of benzoyl chloride (3 cm^3/3.5 g), the mixture is vigorously shaken in a stoppered conical flask for 15 to 20 minutes. Work up the product following the similar procedure discussed above. Benzanilide (*N*-Phenylbenzamide) is separated from reaction mixture and crystallised from cold alcohol. The reaction of this preparation may be represented as:



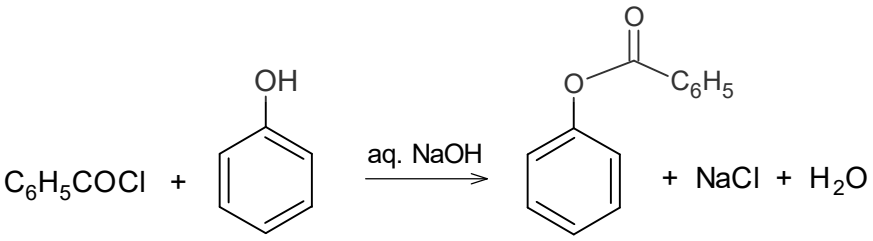
11.7 TERMINAL QUESTIONS

1. Write an equation for the reaction of benzoyl chloride with phenol in presence of aqueous NaOH.
2. Write equations to show how phenylbenzoate may be prepared starting with benzoic acid.
3. Discus the role of sodium hydroxide in benzolation reaction of phenol.
4. Write the mechanism for benzoylation reaction of aniline

11.8 ANSWERS

Terminal Questions

1. Chemical equation for this reaction can be written as:



2. This can be represented as:

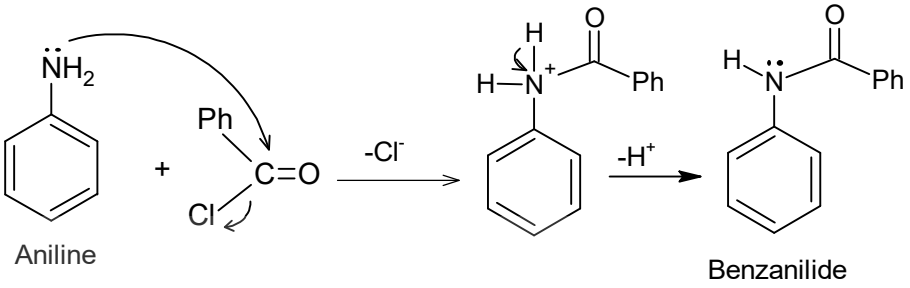
$$C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl$$

$$C_6H_5COCl + C_6H_5OH \xrightarrow{Base} C_6H_5OCOC_6H_5 + H_2O$$

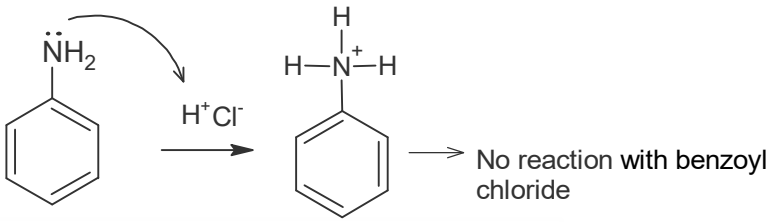
3. i) The aqueous NaOH is neutralized HCl formed during reaction (HCl promotes side reaction)

   ii) It also increases nucleophilicity of phenols by converting it to phenoxide ion.

4. Mechanism of benzoylation of aniline can be written as:



Here addition of base helps in neutralising of HCl formed during the reaction, otherwise HCl decreases nucleophilicity of aniline by its protonation.



EXPERIMENT 12

PREPARATION OF OXIME AND PHENYLHYDRAZONE

Structure

12.1 Introduction

Expected Learning Outcomes

12.2 Reactivity of Carbonyl Group

Mechanism of Imine Formation: Preparation of Oxime and Hydrazone

12.3 Experiment 12(a): To Prepare Benzophenone Oxime

Requirements

Procedure

12.4 Experiment 12(b): To Prepare 2, 4-Dinitro-phenylhydrazone

Requirements

Procedure

12.5 Experiment Report

12.6 Answers

12.1 INTRODUCTION

You have performed two experiments concerning the preparation of organic compounds after studying the basic concepts of preparative organic chemistry. The experiments were based on the aromatic compounds more specifically the phenols or the amines having OH or NH_2 as the functional groups. You must be familiar with another higher order functional group called the carbonyl group ($R_2C=O$) that you have studied as part of your theory course. You very well know that these are very important class of organic compounds present in some or the other form in the products of everyday use, for example, plastics, perfumes, cosmetics, dyes, etc. You also know that carbonyl compound are of two types viz. aldehydes (R-CHO) and ketones ($R_2C= O$). In the experiments given here you will prepare the derivatives of ketones that are aromatic in nature.

In the first experiment you will prepare an oxime starting with benzophenone as the ketone. The second experiment is the preparation of derivative of another ketone i.e. acetophenone. A detail of the mechanisms involved in the reaction are also discussed in detail. The products obtained have to be recrystallised,

and tested for their purity by the procedures you have learnt and performed in the previous experiments. In the first section we would recapitulate some of the aspects of the carbonyl functional group especially the reactivity of these compounds.

Expected Learning Outcomes

After studying and performing the experiments you should be able to:

- explain the mechanism of preparation of oxime from benzophenone;
- prepare the oxime derivative of benzophenone as per the procedure;
- recrystallise the prepared oxime using an appropriate solvent;
- check the purity of the recrystallised oxime by determining its melting point;
- explain the mechanism of preparation of phenylhydrazone from acetophenone;
- prepare the phenylhydrazone derivative of acetophenone as per the procedure;
- recrystallise the prepared phenylhydrazone using an appropriate solvent;
- check the purity of the recrystallised phenylhydrazone by determining its melting point; and
- report the yield, the recrystallising solvent and the melting points of the derivatives prepared.

12.2 REACTIVITY OF CARBONYL GROUP

You are well aware that carbonyl compounds are of two types; **aldehydes** with one R and one H attached to the carbonyl i.e. C=O group and **ketones** which contain two R groups attached to the carbonyl function. The carbonyl functional group is considered to be the most important functional group as it is involved in multiple types of reactions. Let us recall a few facts about the reactivity of carbonyl functional group. This will help you in understanding the mechanisms discussed later.

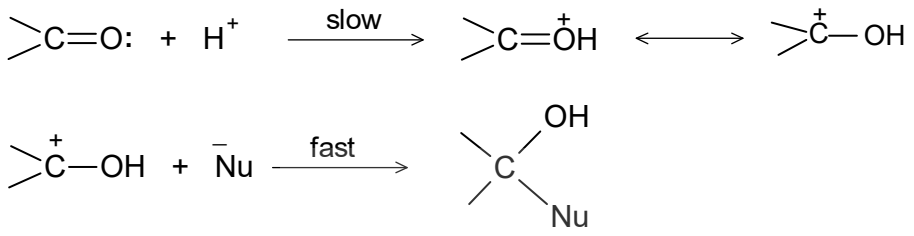
The chemistry of the carbonyl group lies in the fact that the carbonyl carbon is sp^2 hydridised with an unhydridised *p* orbital responsible for the double bond formation by an overlap with the *p* orbital of oxygen. The double bond of carbonyl group is very polar with a tendency of oxygen pulling the electrons towards it leaving carbon with a positive charge as shown below.

Structure of C=O

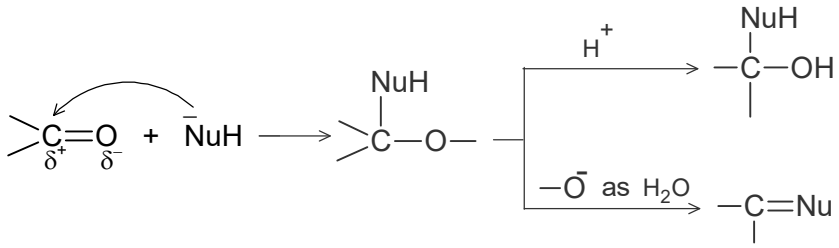
The carbon acts as an electrophile and a nucleophilic centre while oxygen acts as a nucleophile. It is reflected in the reactions shown by these compounds.

Carbonyl compounds generally undergo nucleophilic addition reactions. The attack by a reagent can be either at C or O by the nucleophilic or the electrophilic part respectively. The reaction product in both the cases would remain the same. If we consider a general reaction, the two ways of attack can be depicted as given below.

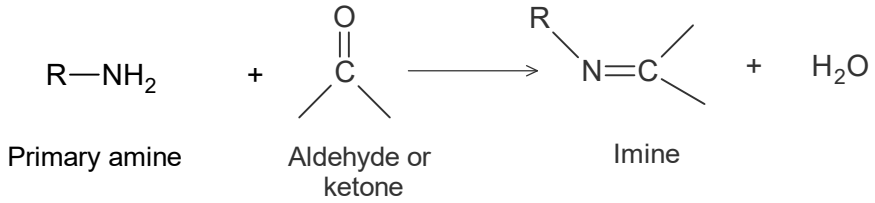
Attack by the electrophilic part: This takes place in the presence of an acid.



Attack by the nucleophilic part: This takes place in the presence of a base.



However, with amines and ammonium compounds carbonyl compounds undergo condensation reaction and give **imine** derivatives. An imine is a nitrogen analog of an aldehyde or ketone in which the C=O group is replaced by a C=NR group, where R = alkyl, aryl or H. It is also called the **Schiff's base**. Imines are important intermediates in many metabolic pathways. These are prepared by the reaction of aldehydes or ketones with primary amines as per the following reaction.

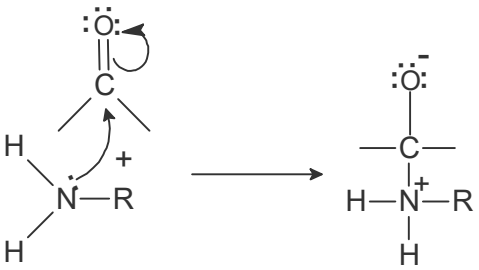


The two derivatives, which will be prepared by you, are based on this condensation reaction. These derivatives are **oximes** and **hydrazones**. In the above reaction, when the amine is a hydroxyl amine, we get the formation of an imine product called the **oxime**. The product of condensation of a hydrazine and an aldehyde or ketone is called a **hydrazone**. Oximes carry a lot of significance in the protection, purification, and characterisation of carbonyl compounds. These are used as important intermediate compounds in the synthesis of nitriles and amides via Beckmann rearrangement. The formation of hydrazone is done to identify a carbonyl compound thus the reaction has an important use in qualitative analysis. As the mechanism of formation of oximes and the hydrazones remains the same except for the starting amine, let us understand the mechanism of these reactions in general.

12.2.1 Mechanism of Imine Formation: Preparation of Oxime and Hydrazone

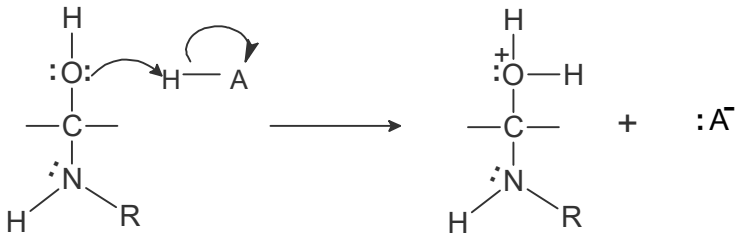
Imine is formed in a reversible acid catalysed process that begins with the nucleophilic addition of the primary amine to the carbonyl group, followed by transfer of a proton from nitrogen to oxygen to yield a neutral amino alcohol, or carbinolamine. Protonation of carbinolamine, removal of water and finally deprotonation leads to the formation of the final product imine. The stepwise mechanism is given as follows:

1) Nucleophilic attack: The amine N attacks the carbonyl carbon.

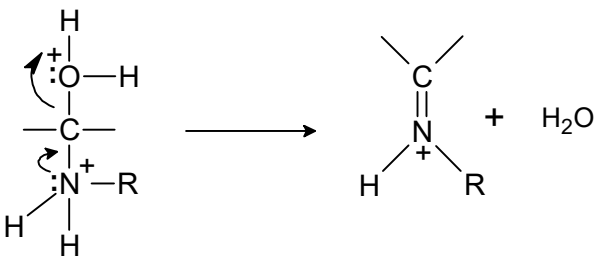


2) Proton transfer: The proton gets transferred from quarternary ammonium group to the anion to form carbinolamine.

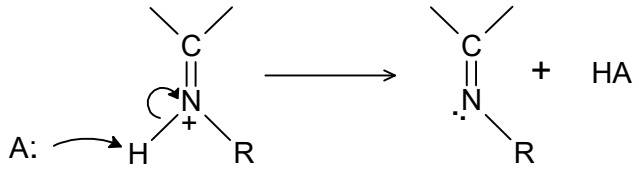
3) Protonation of OH: Protonation of carbinolamine oxygen by an acid catalysed reaction converts –OH into better leaving group ($-OH_2^+$).



4) Removal of water: The hydronium ion leaves as water leaving behind an iminium ion.

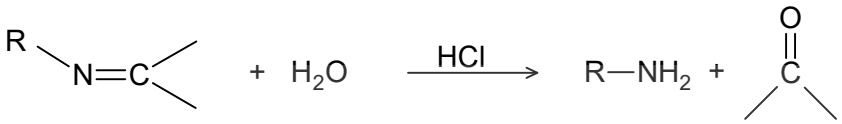


5) Deprotonation: Loss of a proton from iminium nitrogen gives the final product i.e. the oxime/hydrazone and regenerates the acid catalyst.



Reversibility of imine forming reactions

Formation of imines is a reversible reaction in which imine can be hydrolysed back to the corresponding primary amines under acidic conditions.



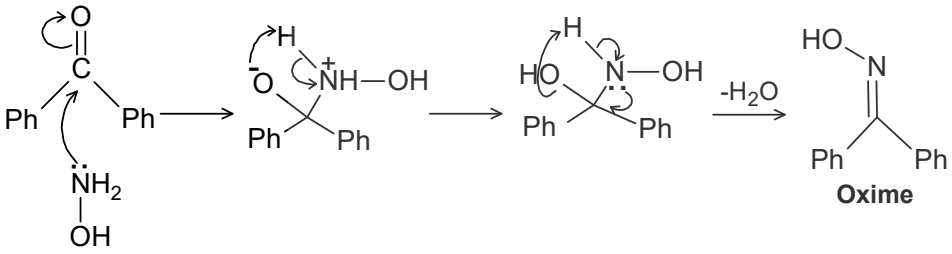
In the experiments you will follow the principles of preparations as explained in Experiment 10. In the first experiment with carbonyl compounds you will prepare the oxime.

12.3 EXPERIMENT 12 (a): TO PREPARE BENZOPHENONE OXIME

In this experiment you will first prepare benzophenone oxime starting with benzophenone and hydroxyl amine, recrystallise it and then check its purity by melting point determination. Before you start the experiment let us look into the mechanism involved in this reaction.

Mechanism of Formation of Benzophenone Oxime

The imine that is formed with hydroxyl amine is called the oxime. With benzophenone the mechanism of the reaction can be a written as below.



12.3.1 Requirements

Apparatus	Chemicals
Round bottom flask	Benzophenone
Vacuum desiccator	Hydroxylamine hydrochloride
Beaker	Rectified spirit
Condenser with rubber tubings	Sodium hydroxide
Conical flask	Conc. HCl
Measuring Cylinder	Distilled water
Ordinary glass funnel	

Glass rod

Filtration assembly with filter paper

Melting point apparatus

Capillary tubes

12.3.2 Procedure

The procedure for the preparation of benzophenone oxime is given below. Follow the steps with the help of your counsellor.

1. Take 4 g (0.022 mol) bezophenone and 2.4 g (0.035 mol) hydroxylamine hydrochloride in a round bottom flask (RB).
2. Add 15 cm^3 ethanol and 3 cm^3 water into the RB with stirring so that the earlier added chemicals are dissolved in this mixture.
3. Dissolve 4.8 g sodium hydroxide in 5 cm^3 water and add in small portions to the above flask. *In case the reaction becomes hot, it has to be cooled under the tap water.*
4. After the addition of sodium hydroxide is complete fit a condenser to the round bottom flask and reflux the contents for 20 minutes.
5. Cool the reaction mixture with 40 cm^3 water. You may observe some unreacted benzophenone in the flask. This can be filtered off.
6. The filtrate is cooled and poured into dilute hydrochloric acid prepared by mixing 12 cm^3 conc. HCl in 75 cm^3 water. You will get a precipitate of the oxime.
7. Filter the solid and wash with cold water.
8. Separate and dry the solid. Recrystallise it with methanol. Take the weight of the final product.
9. Check the melting point of the recrystallised compound for purity.
10. Write the result/report.

Before proceeding further you can try to answer the following questions.

SAQ 1

Write a detailed mechanism for the following general reaction for the preparation of carbonyl compound derivatives.

$$R_2C = O + NH_2G \longrightarrow R_2C = N - G + H_2O$$

SAQ 2

Write the product in the following reaction.

$$CH_3CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2CH_3 + HONH_2 \xrightarrow{H^+}$$

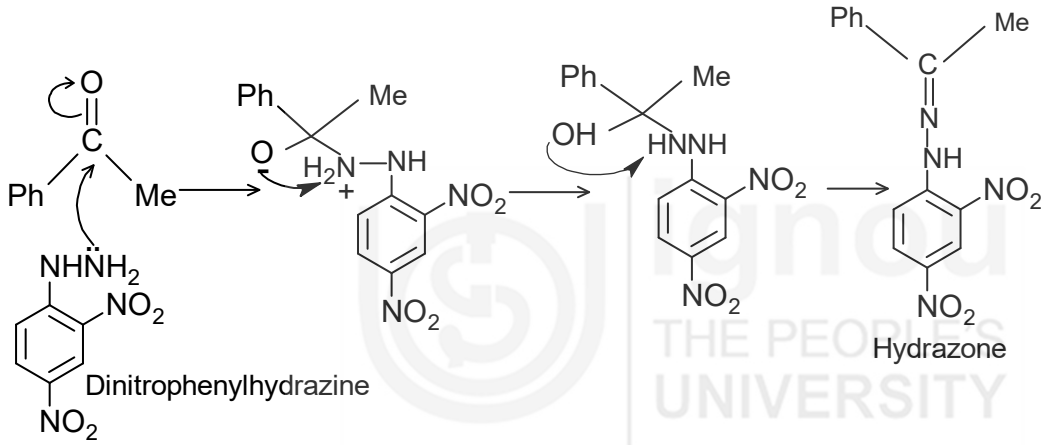
Based on the concepts of preparation of organic compounds you would perform another experiment with a different ketone. The details are given in the next section.

12.4 Experiment 12(b): To Prepare 2,4-Dinitro-phenylhydrazone

In this experiment you will first prepare 2,4-dinitrophenylhydrazone starting with acetophenone and 2,4-dinitrophenylhydrazine, recrystallise it and then check its purity by melting point determination. Before you start the experiment let us look into the mechanism involved in this reaction.

Mechanism of Formation of 2,4-Dinitrophenylhydrazone

The imine that is formed with hydrazine is called the hydrazone and 2,4-dinitrophenylhydrazone in this case . With 2,4-dinitrophenylhydrazine, the mechanism can be a written as follows.



12.4.1 Requirements

Apparatus	**Chemicals**
Boiling tube	Acetophenone
Measuring Cylinder	2,4-Dinitrophenylhydrazine
Ordinary glass funnel	Distilled water
Glass rod	Glacial acetic acid
Filtration assembly	
Filter paper	
Melting point apparatus	
Capillary tubes	

12.4.2 Procedure

The procedure for the preparation of 2,4-dinitrophenylhydrazone is given below. As in the previous experiment, follow the steps with the help of your counsellor.

1. Take a boiling tube and place a solution of acetophenone (4.12 g, 34.3 m mol) in glacial acetic acid (20 cm^3) into it.

2. Take a solution of 2,4-dinitrophenylhydrazine (5.49 g, 50.8 m mol) in glacial acetic (10 cm^3) and water (10 cm^3) in another test tube.
3. Add the above solution into the boiling tube prepared in step 1.
4. Cool the mixture in ice and shake the tube for 5 minutes. You will get colourless precipitate of hydrazone.
5. Filter the product through a fluted filter paper using gravity filtration and wash with dil. acetic acid white filtering.
6. Dry the colourless crystals in an oven, weigh these and recrystallise with ethanol.
7. Determine the melting point of the recrystallised product for purity.
8. Write the result/report.

Before proceeding further you can try to answer the following questions.

SAQ 3

Write the mechanism of acid catalysed reaction of hydrazine hydrate with acetaldehyde.

SAQ 4

Write the product in the following reaction.

12.5 Experiment Report

In Unit 2 of this block you learnt how to write the experiment report of an experiment involving the preparation of an organic compound. You will have to write the report of both the experiments explained above in the following manner. The reports should be verified by your counselor.

Experiment Report 1: Preparation of Benzophenone Oxime

Introduction: When benzophenone is reacted with hydroxyl amine hydrochloride in presence of a base and an imine called oxime is formed. The reaction of oxime formation can be written as follows.

Reaction:

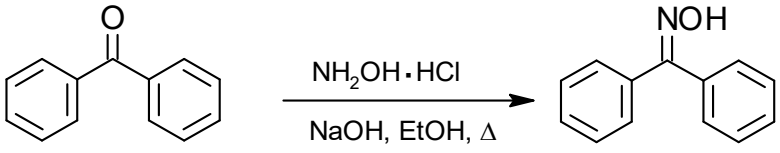


Table of Reactants and Products

Sl. No.	Compound	Mol. Wt.	Weight Used	Moles Used	Molar Ratio	Other Data

Yield = ---------- g.

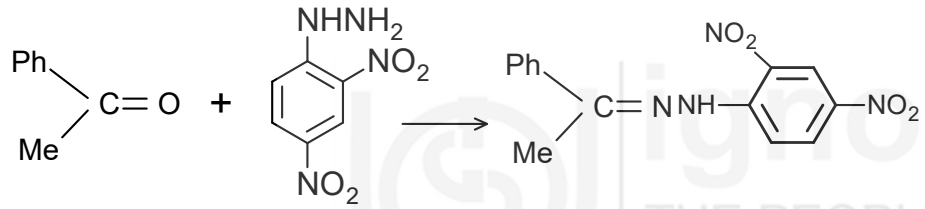
Observed properties of the product

Melting point of the recrystallised product = ---------- ^{o}C.

Experiment Report 2: Preparation of 2,4 - Dinitrophenylhydrazone

Introduction: When acetophenone is reacted with 2,4-dinitrophenyhydrazine in presence of a base 2,4-dinitrophenylhydrazone is formed. The reaction of hydrazone formation can be written as follows.

Reaction:



Acetophenone **2, 4 - Dinitrophenylhydrazine** **Dinitrophenylhydrazone**

Table of Reactants and Products

Sl. No.	Compound	Mol. Wt.	Weight Used	Moles Used	Molar Ratio	Other Data

Yield = ---------- g.

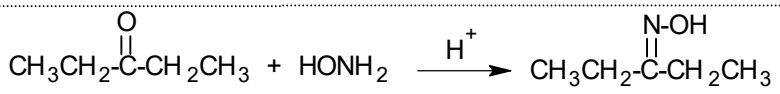
Observed properties of the product

Melting point of the recrystallised product ----------.

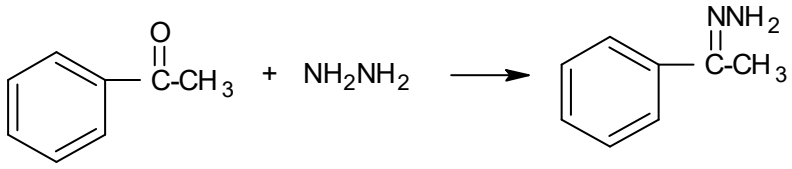
12.6 ANSWERS

Self-Assessment Questions

1. Please refer to subsection 12.2.1.

2. 

3. Please refer to section 12.4.

4. 

FURTHER READINGS

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