PRACTICAL MANUAL BOOK

Course: Chemistry-I Lab

Course Code: CC-BT/CH-P-301

B.Sc(H) Biotechnology

Semester: III

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"The most exciting phrase to hear in science, the one that heralds new discoveries, is not 'Eureka!' but 'That's funny'….."

~ Issac Asimov

~ PREFACE ~

This manual provides the students a detailed understanding of the procedural details of various experiments they are required to perform in the course of this lab. 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 nine experiments in the Section A. The 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 three experiments provide procedural details 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. Simple laboratory techniques such as heating, cooling, stirring and filtration as well as separation and purification techniques like crystallisation and distillation shall be applied in this section.

EXPECTED LEARNING OUTCOMES

After studying this course and performing the given experiments, students 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
- 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 organic chemistry

SAFETY

- You must be careful while working in the laboratory to avoid accidents. Safe working practices must be followed while handling chemicals and apparatus.
- To protect clothing from spoiling and damage by chemicals, a laboratory coat should be worn in the laboratory.

DISPOSAL

- All disposable solutions and reagents must be disposed in the sink and washed away with water.

REPORT WRITING

- Write the principle of the experiment.
- Write about the apparatus and chemicals used in the experiment.
- Write the procedure followed in a stepwise manner.
- Present the readings in tabular form.
- Perform the calculations and state the results obtained.
- Write about the precautions taken by you to get accurate results.
- Write about the safety measures taken by you to prevent accidents.

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Section A: Physical Chemistry

Section B: Organic Chemistry

Section A: Physical Chemistry

~ INTRODUCTION ~

Section A: Physical Chemistry

PART: 1: THERMOCHEMISTRY

This is the first unit of this course. In this unit, we will study about the heat changes associated with chemical reactions and physical processes.

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 neutralization**, **enthalpy of ionisation,** etc. In this unit, we shall cover determination of enthalpy of neutralization.

SOME FUNDAMENTAL CONCEPTS

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 **surrounding** 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.

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 (dq) is said to be **positive** leading to an increase in the internal energy of the system. Also, the loss of heat from the system indicates a **negative** dq and a decrease in the internal energy of the system. Similarly, if the work (dw) 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**, dw 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 (dU) , when it absorbs dq amount of heat and a work dw is done on it, can be given as.

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

For larger changes, we can say that

$$U = q + w$$

Let us now focus our attention on another property associated with a system, called the **enthalpy (H)**. In the later sections of this unit, you will be studying about the determination of the **change in enthalpy** associated with the neutralisation reactions.

The enthalpy of a reaction

When a chemical reaction takes place in a system, generally, its temperature after the reaction T_2 is different from the temperature before the reaction T_1.

Let us consider the following general reaction:

$$\underset{T_1}{R} \longrightarrow \underset{T_2}{P}$$

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). Whereas, 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 is *+ve*).

Chemical reactions are performed under the conditions of either constant volume or constant pressure. If no work is done on or by the system, then from first law of thermodynamics, 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,

$$\underset{T_1,\, V}{R} \longrightarrow \underset{T_2,\, V}{P} \qquad q_V = \Delta U$$

$$\underset{T_1,\, P}{R} \longrightarrow \underset{T_2,\, P}{P} \qquad q_P = \Delta H$$

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 the change in internal energy can be written as follows:

$$\Delta U = q_P + (-p\, dV)$$

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. Then we have,

$$U_2 - U_1 = q_P - p\,(V_2 - V_1) = q_P - pV_2 + pV_1$$

Rearranging we have,

$$q_p = (U_2 + pV_2) - (U_1 + pV_1)$$

At this stage, we can represent $(U + pV)$ by H, the enthalpy. Thus, we can rewrite the above equation as,

$$q_p = H_2 - H_1 = \Delta H$$

Since U, p and V are state variables, H is also a state variable. Thus, by the above equation, 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** (ΔHr) 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):

$$\underset{T,\,P}{R} \longrightarrow \underset{T,\,P}{P} \qquad \Delta H_r$$

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:

$$C = \frac{dq}{dT}$$

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.

We know that heat absorbed at constant pressure is equal to change in enthalpy. Therefore we have,

$$C_p = \frac{\Delta H}{dT} \quad \text{or} \quad \Delta H = C_p dT$$

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 neutralization of hydrochloric acid with sodium hydroxide. Hydrochloric acid is a **strong acid** and sodium hydroxide is a **strong base**. This means that both hydrochloric acid and sodium hydroxide are completely dissociated in aqueous solution. Therefore, we can write,

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

and

$$NaOH\,(aq) \longrightarrow Na^+\,(aq) + OH^-\,(aq)$$

The neutralisation reaction can be represented as,

$$H^+\,(aq) + Cl^-\,(aq) + Na^+\,(aq) + OH^-\,(aq) \longrightarrow Na^+\,(aq) + Cl^-\,(aq) + H_2O$$

Or

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

$$\Delta H_{neut} = -57.3\ kJ$$

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,

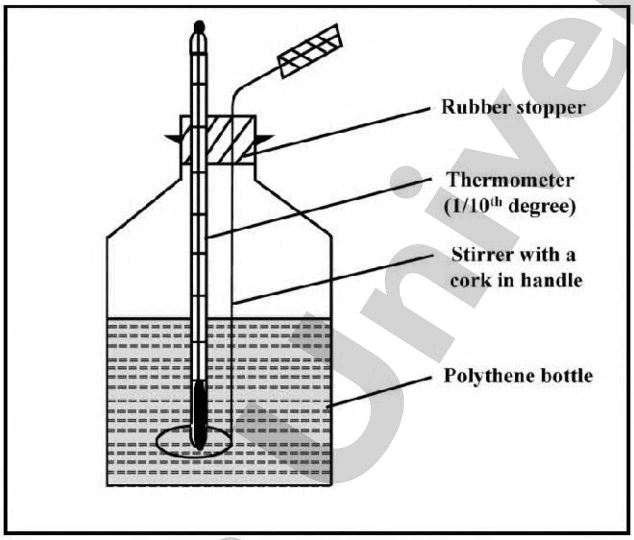
$$H^+\,(aq) + OH^-\,(aq) \longrightarrow H_2O$$

because Na^+ and $C1^-$ 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. We 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.

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 a **calorimeter** as mentioned above.



Plastic bottle Calorimeter

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.

PART: 2: pH-METRY

In this unit we would learn about the measurements of the pH of aerated drinks, fruit juices, soaps and shampoos.

pH is a measure of the concentration of hydrogen (hydronium) ions in an aqueous solution.

$$pH = - \log [H^+]$$

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 unit 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. Also, 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.

SOME FUNDAMENTAL CONCEPTS

Principle

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,

$$pH = - \log_{10} [H^+] = - \log_{10} [H_3O^+]$$

The basic logic of the scale was that by taking logarithm, the numbers expressed as negative powers of 10, representing concentration of hydrogen ions became 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.

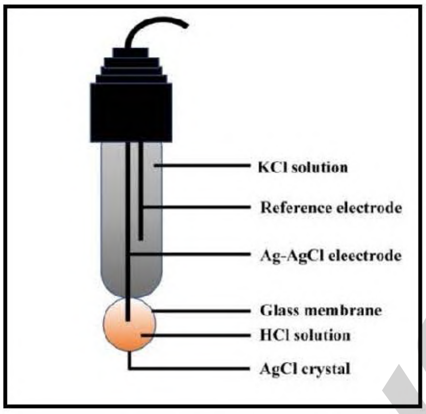
Thus, to know the pH of a given solution we need to measure the concentration of hydrogen ions in it. Now the question comes is how do we measure the concentration of hydrogen ions in an aqueous solution. One simple answer could be to titrate the solution with a standard solution of a base / acid. However, 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.

One 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. Hence we needed a better method.

Almost accurate and 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.

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) (a calomel electrode can also be used in place of Ag - AgCl electrode) dipped in it.



A glass electrode

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,

$$Ag|\ AgCl\ |\ Cl^{-},\ |\ H+\ (0.1M)\ |glass\ membrane|\ H^{+}\ (Unknown)$$

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

$$E = E^{0}_{glass} - \frac{RT}{nF}\ln[H^{+}]$$

Substituting the values of R, T, F and n; at 298 K the above equation becomes,

$$E = E^{0}_{glass} - 0.0592\,pH$$

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

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

or

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

The cell potential of this combination is given as,

$$E_{cell} = E_{calomel} - E_{glass}$$

$$E_{cell} = E_{calomel} - (E^{0}_{glass} - 0.0592\,pH)$$

The emf of standard calomel electrode is = 0.241 V

Therefore, the above equation becomes,

$$E_{cell} = 0.241 - (E^0_{glass} - 0.0592\,pH)$$

On simplification, we get,

$$pH = \frac{E_{cell} - 0.241 + E^0_{glass}}{0.0592}$$

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. 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.

A typical laboratory pH meter assembly (Source: IndiaMART website)

There are two possibilities to create the cell. 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.

E^0_{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 have,

$$4.0 = \frac{E_{cell} - 0.241 + E^0_{glass}}{0.0592}$$

Simplifying, we get,

$$E^0_{glass} = 0.4598 - E_{cell}$$

Substituting the measured value of E_{cell}, we can get the value of E^0_{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^0_{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 establish a relationship between the pH values of known (buffer solution) and unknown solutions and the corresponding E_{cell} values.

$$E_{cell}(buffer) = 0.241 - [E^0_{glass} - 0.0592\, pH(buffer)]$$

$$E_{cell}(sample) = 0.241 - [E^0_{glass} - 0.0592\, pH(sample)]$$

Therefore,

$$E_{cell}(buffer) - E_{cell}(sample) = 0.0592[\, pH(buffer) - pH(sample)]$$

You may note that by this way we do not need to calculate E^0_{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.

EXPERIMENT NO.: CC-BT/CH-P-301/PC-01

1.0 NAME OF EXPERIMENT: Thermochemistry (01)

2.0 OBJECTIVE: Determination of the Heat capacity of a calorimeter

3.0 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

Enthalpy change for (cold water + calorimeter) = Enthalpy change for hot water

We know that 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:

$$[C_P\,(\text{cold water}) + C_P\,(\text{calorimeter})]\,[T_m - T_c] = C_P\,(\text{hot water})\,[T_h - T_m] \ldots\ldots(1)$$

It is assumed that the temperature change ($dT = T_m - T_c$) is the same both for the calorimeter and the cold water.

The heat capacity of a substance is equal to the product of its mass and specific heat.

Heat capacity of a substance = mass (m) × specific heat (s)

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.***

Putting the expression of heat capacity for cold and hot water in equation (1) we have,

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

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.

Therefore, the above equation becomes,

$$[ms + C_P(calorimeter)]\,[T_m - T_c] = ms\,[T_h - T_m]$$

$$ms + C_P(calorimeter) = ms\frac{T_h - T_m}{T_m - T_c}$$

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

$$C_P(calorimeter) = ms[\frac{(T_h - T_m)}{(T_m - T_c)} - 1]$$

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

Value of m

We know that mass of a substance = volume × density. The density of water is 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,

$$Volume\ in\ dm^3\ units = Volume\ in\ cm^3\ units\ x\ 10^{-3}$$

Since the volumes of cold water and hot water are equal, we can say that

$$Volume\ of\ cold\ water = Volume\ of\ hot\ water = V\ cm^3 = V\ x\ 10^{-3}\ dm^3$$

Hence, mass of cold water (m) = mass of hot water (m) = Volume x density
$= V\ x\ 10^{-3}\ dm^3\ x\ d_w\ kg\ dm^{-3}$

$$Mass\ (m) = V\ x\ d_w\ x\ 10^{-3}\ kg$$

The SI unit of specific heat is J K^{-1} kg^{-1}. The specific heat of water in SI units is 4.185 x 10^3 J K^{-1} kg^{-1}, i.e.,

$$Specific\ heat\ of\ water\ (s) = 4.185\ x\ 10^3\ J\ K^{-1}\ kg^{-1}$$

$$C_P(Calorimeter) = V \times d_w \times 10^{-3} kg \times 4.185 \times 10^3 JK^{-1}kg^{-1}[\frac{T_h - T_m}{T_m - T_c} - 1]$$

$$C_P(Calorimeter) = 4.185 \times V \times d_w \times [\frac{T_h - T_m}{T_m - T_c} - 1]JK^{-1}$$

Having measured the volume in cm^3 units, you substitute it as such in the above equation without attempting any unit conversion. By substituting the values of T_h,T_m and T_c ,you will get the value of Cp in J K^{-1} units.

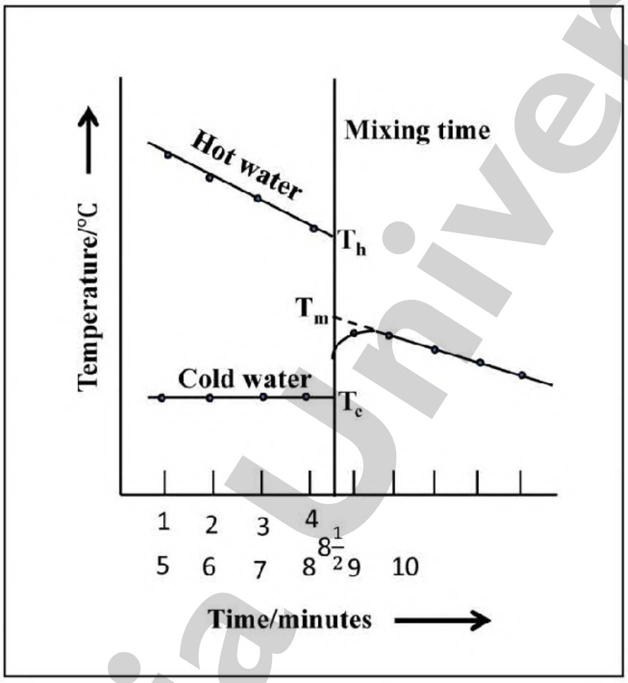
4.0 APPARATUS AND CHEMICALS:

- A wide-mouthed polythene bottle (to serve as calorimeter)
- A rubber cork having two holes
- Thermometer (1/10th degree)
- Stirrer fitted with a cork on the handle
- 100 ml measuring cylinder
- Stop watch
- Beakers (250 mL)
- Distilled water

5.0 PROCEDURE:

- Take a wide mouthed polythene bottle, fitted with a cork 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 the polythene bottle.
- Note down the temperature of water after every half a minute for about 4 minutes.
- Take 100 cm^3 of distilled 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.
- Put the 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 8½ 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 below.



Temperature - time curve

6.0 RESULTS:

Table 1: Recording of room temperature

Temp. before experiment (^{0}C)	Temp. after experiment (^{0}C)	Mean Temperature (^{0}C)

Table 2: Temperature – time data for cold, hot water and the mixture:

Volume of cold water, V = 100 cm^3

Volume of hot water, V = 100 cm^3

Set 1

Cold Water		Hot Water		Mixture	
Time (s)	**Temperature (°C)**	**Time (s)**	**Temperature (°C)**	**Time (s)**	**Temperature (°C)**
				Time of mixing	**(s)**

Set 2

Cold Water		Hot Water		Mixture	
Time (s)	**Temperature (°C)**	**Time (s)**	**Temperature (°C)**	**Time (s)**	**Temperature (°C)**
				Time of mixing	**(s)**

7.0 CALCULATIONS:

$$C_P(Calorimeter) = 4.185 \times V \times d_w \times [\frac{T_h - T_m}{T_m - T_c} - 1] JK^{-1}$$

Set 1

Volume of cold water = Volume of hot water = 100 cm^3

Density of water (d_w) = 1kg dm^{-3}

T_h (from graph) = ……… °C
T_c (from graph) = ……… °C
T_m (from graph) = ……… °C

C_P (Set 1) = ……… JK^{-1}

Set 2

Volume of cold water = Volume of hot water = 100 cm^3

Density of water (d_w) = 1kg dm^{-3}

T_h (from graph) = ……… °C
T_c (from graph) = ……… °C
T_m (from graph) = ……… °C

C_P (Set 2) = ……… JK^{-1}

The heat capacity of the given calorimeter is,

$$C_P = \frac{C_P(Set1) + C_P(Set2)}{2} \ JK^{-1}$$

Conclusion:

The heat capacity of the given calorimeter is _______ **JK^{-1}**

8.0 THINGS TO REMEMBER

- You must be careful while working in the laboratory to avoid accidents. Safe working practices must be followed while handling chemicals and apparatus.
- To protect clothing from spoiling and damage by chemicals, a laboratory coat should be worn in the laboratory.
- Due to radiation, some heat is lost to the environment.

EXPERIMENT NO.: CC-BT/CH-P-301/PC-02

1.0 **NAME OF EXPERIMENT:** Thermochemistry (02)

2.0 **OBJECTIVE:** Determination of the Enthalpy of Neutralization of Hydrochloric Acid with Sodium Hydroxide Solution

3.0 PRINCIPLE:

The **enthalpy of neutralization** (ΔH_{neut}) of an acid can be defined as the enthalpy change associated with the complete neutralization of its dilute aqueous solution containing H^+ ions by a dilute aqueous solution of a base containing equivalent amount of OH^- ions.

In this experiment, let us consider the example of neutralization of hydrochloric acid with sodium hydroxide.

We know 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

$$HCI\,(aq) \longrightarrow H^+\,(aq) + Cl^-\,(aq)$$

and

$$NaOH\,(aq) \longrightarrow Na^+\,(aq) + OH^-\,(aq)$$

The neutralization 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 neutralization 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 $C1^-$ remain unchanged in the reaction.

In other words, the enthalpy of neutralization 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. We must then also expect that the enthalpy of neutralization of the strong acids with strong bases to be of a constant value irrespective of the strong acid or the strong base used.

The heat evolved during neutralization will raise the temperature of the solution and that of the beaker (calorimeter). In other words, the enthalpy change for the neutralization 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 of the following equation:

ΔH = - [(Heat gained by the calorimeter + Heat gained by the solution)]

ΔH = - [(Heat capacity of the calorimeter x rise in temperature of the calorimeter) + (Mass of base x specific heat of base x rise in temperature of base) + (Mass of acid x specific heat of acid x rise in temperature of acid)]

ΔH = - [{C_p(calorimeter) x (T_m – T_a)} + {V_{base} x specific heat of base x (T_m – T_b)} + {V_{acid} x specific heat of acid x (T_m – T_a)}]

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 JK^{-1} kg^{-1}. For a dilute solution of an acid and a base, the specific heats can be assumed to be equal to the specific heat of water. Hence,

Specific heat of acid = Specific heat of base = Specific heat of water = s

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 = 0.05 mole

Therefore we have,

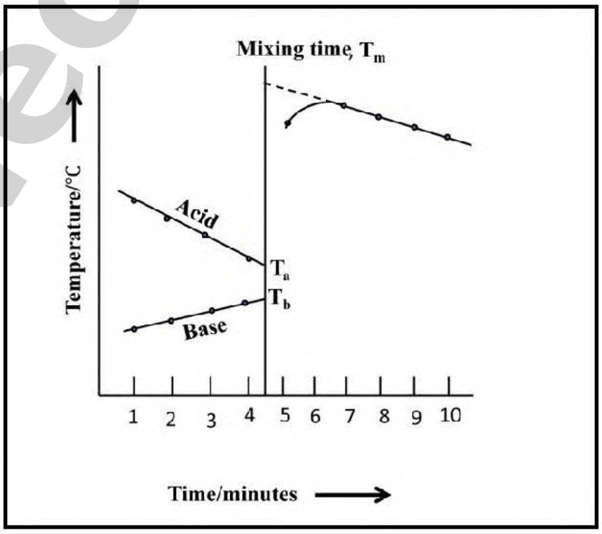
$$\Delta H = -[C_P(calorimeter)(T_m - T_a) + V_{base}s(T_m - T_b) + V_{acid}s(T_m - T_{a)}]$$

4.0 APPARATUS AND CHEMICALS:

- A wide-mouthed polythene bottle (to serve as calorimeter)
- A rubber cork having two holes
- Thermometer (1/10th degree)
- Stirrer fitted with a cork on the handle
- Stop watch
- 250 mL Beakers
- 100 mL measuring cylinder.
- 0.5 (M) NaOH solution
- 0.5 (M) HCl solution

5.0 PROCEDURE:

- Measure 100 cm^3 of 0.5 (M) HCl in a beaker for which heat capacity has already been determined in Experiment 1.
- 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 0.5 (M) 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.
- Plot temperature – time curve for the neutralization of HCl with NaOH data. You will get a plot as given below.
- 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.



Temperature - time curve for neutralization

6.0 RESULTS:

Table 1: Recording of room temperature

Temperature before experiment (ºC)	Temperature after experiment (ºC)	Mean Temperature (ºC)

Table 2: Temperature – time data for acid, base and for mixture

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

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

Set 1

HCl Solution		NaOH Solution		Mixture	
Time (s)	Temperature (ºC)	Time (s)	Temperature (ºC)	Time (s)	Temperature (ºC)
				Time of mixing	(s)

Set 2

HCl Solution		NaOH Solution		Mixture	
Time (s)	Temperature (ºC)	Time (s)	Temperature (ºC)	Time (s)	Temperature (ºC)
				Time of mixing	(s)

7.0 CALCULATIONS:

We have,

$$\Delta H = -[C_P(calorimeter)(T_m - T_a) + V_{base}s(T_m - T_b) + V_{acid}s(T_m - T_a)]$$

Set 1

Volume of acid (V_{acid}) = Volume of base (V_{base}) = 100 cm^3

Cp(calorimeter) = …………JK^{-1}

Specific heat (s) = 4.185 J K^{-1} kg^{-1})

T_m (from graph) = ……… °C
T_a (from graph) = ……… °C
T_b (from graph) = ……… °C

ΔH (Set 1) = ……… J

Set 2

Volume of acid (V_{acid}) = Volume of base (V_{base}) = 100 cm^3

Cp(calorimeter) = …………JK^{-1}

Specific heat (s) = 4.185 J K^{-1} kg^{-1})

T_m (from graph) = ……… °C
T_a (from graph) = ……… °C
T_b (from graph) = ……… °C

ΔH (Set 2) = ……… J

Therefore we have,

$$\Delta H = \frac{\Delta H(Set1) + \Delta H(Set2)}{2} \text{ J}$$

ΔH so obtained in the above equation is the enthalpy change for the neutralisation of 100 cm^3 of 0.5 M HCl with 100 cm^3 of 0.5 M NaOH. From this ΔH, you can now calculate the $\Delta H_{\mathbf{neut}}$ 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 cm^3 of 0.5 M HCl is neutralised using 100 cm^3 of 0.5 M NaOH, then, the amount (no. of moles) of HCl present in the 200 cm^3 solution (100 cm^3 acid + 100 cm^3 base) will be equal to 0.05 mole.

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

$$\Delta H_{neut} = \frac{\Delta H}{0.05} Jmol^{-1}$$

Conclusion:

Enthalpy change in the neutralization of hydrochloric acid solution with sodium hydroxide solution _______ J mol^{-1}.

8.0 THINGS TO REMEMBER

- Due to radiation, some heat is lost to the environment.
- The solution density is supposed to be 1g / ml.
- Hydrochloric acid and sodium hydroxide ionization is assumed to be 100 %.
- The solution's specific heat is taken as 4.189 J/g°C
- The mixture of HCl and NaOH should be stirred well.
- Water equivalent calorimeter or beaker should be calculated accurately.

EXPERIMENT NO.: CC-BT/CH-P-301/PC-03

1.0 NAME OF EXPERIMENT: Thermochemistry (03)

2.0 OBJECTIVE: Determination of enthalpy of ionisation of acetic acid

3.0 PRINCIPLE:

Acetic acid is a **weak acid** and is **not completely** dissociated in dilute aqueous solutions into H^+ and CH_3COO^- ions.

$$CH_3COOH\ (aq) \rightleftharpoons CH_3COO^-\ (aq) + H^+\ (aq)$$

When acetic acid is neutralised with a base (NaOH), some of the heat evolved during the neutralization is used in the process of dissociating the acetic acid to allow the completion of neutralization. Therefore, you can expect that the enthalpy change associated with the neutralization of acetic acid (a weak acid) with a strong base to the lower than that of the enthalpy of neutralization of a strong acid with a strong base (i.e., -57.3 kJ mol^{-1}). Similarly, the value of enthalpy of neutralization of a weak base with a strong acid will also be lower than that of the enthalpy of neutralization of a strong base with a strong acid. The difference in the enthalpy of neutralization of a strong acid (HCl) with a strong base (NaOH) and enthalpy of neutralization 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.,

$$\Delta H_{ionis} + \Delta H_{neutr} = \Delta H_{obs}$$

$$\Delta H_{ionis} = \Delta H_{obs} - \Delta H_{neutr}$$

$$\Delta H_{ionis} = \Delta H_{obs} - (-\ 57.3\ KJ\ mol^{-1})$$

$$\Delta H_{ionis} = \Delta H_{obs} + 57.3\ KJ\ mol^{-1}$$

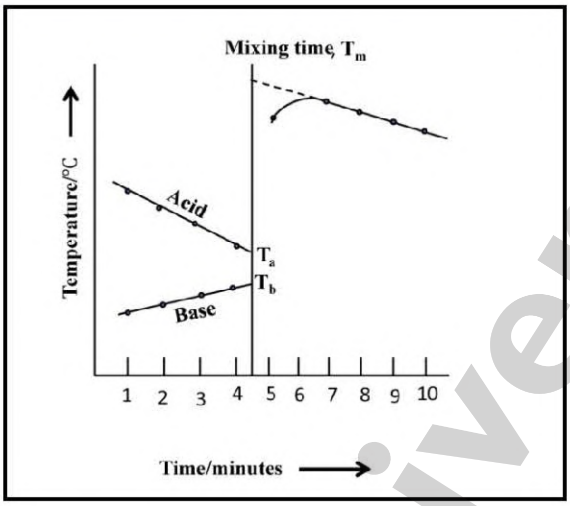
Since the ΔH_{obs} has a negative sign and is smaller in value than 57.3 kJ mol^{-1}, ΔH_{ionis} is positive. Thus ionisation is endothermic.

4.0 APPARATUS AND CHEMICALS:

- A wide-mouthed polythene bottle (to serve as calorimeter)
- A rubber cork having two holes
- Thermometer (1/10th degree)
- Stirrer fitted with a cork on the handle
- Stop watch
- 250 mL Beakers
- 100 mL measuring cylinder.
- 0.5 (M) NaOH solution
- 0.5 (M) acetic acid solution

5.0 PROCEDURE:

- Measure 100 cm^3 of 0.5 (M) acetic acid in a beaker for which heat capacity has already been determined in Experiment 1.
- 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 0.5 (M) 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.
- Plot temperature – time curve for the neutralization of acetic acid with NaOH data. You will get a plot as given below.
- 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.



Temperature - time curve for neutralization

6.0 RESULTS:

Table 1: Recording of room temperature

Temperature before experiment (°C)	Temperature after experiment (°C)	Mean Temperature (°C)

Table 2: Temperature – time data for acid, base and for mixture

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

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

Set 1

Acetic acid Solution		NaOH Solution		Mixture	
Time (s)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)	Temperature (°C)
				Time of mixing	(s)

Set 2

Acetic acid Solution		NaOH Solution		Mixture	
Time (s)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)	Temperature (°C)
				Time of mixing	(s)

7.0 CALCULATIONS:

We have,

$$\Delta H = -[C_P(calorimeter)(T_m - T_a) + V_{base}s(T_m - T_b) + V_{acid}s(T_m - T_{a)}]$$

Set 1

Volume of acid (V_{acid}) = Volume of base (V_{base}) = 100 cm^3

Cp(calorimeter) = ………..JK^{-1}

Specific heat (s) = 4.185 J K^{-1} kg^{-1})

T_m (from graph) = ……… °C
T_a (from graph) = ……… °C
T_b (from graph) = ……… °C

ΔH (Set 1) = ……… J

Set 2

Volume of acid (V_{acid}) = Volume of base (V_{base}) = 100 cm^3

Cp(calorimeter) = ………..JK^{-1}

Specific heat (s) = 4.185 J K^{-1} kg^{-1})

T_m (from graph) = ……… °C
T_a (from graph) = ……… °C
T_b (from graph) = ……… °C

ΔH (Set 2) = ……… J

Therefore we have,

$$\Delta H = \frac{\Delta H\,(Set1) + \Delta H\,(Set2)}{2}\ \text{J}$$

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.

$$\Delta H_{neut} = \frac{\Delta H}{0.05}\,Jmol^{-1}$$

$$\Delta H_{neut} = \frac{\Delta H}{0.05} \times 10^{-3}\,kJmol^{-1}$$

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

$$\Delta H_{ionis} = \Delta H_{neutr}\ (strong\ acid\ with\ strong\ base) - \Delta H_{neutr}\ (acetic\ acid\ with\ NaOH)$$

$$\Delta H_{ionis} = (57.3\ kJ\ mol^{-1}) + (value\ of\ \Delta H_{neutr}\ as\ obtained\ above)$$

$$\Delta H_{neutr} = \ldots\ldots\ldots.\ kJmol^{-1}$$

Conclusion:

The enthalpy of neutralisation of acetic acid with NaOH is ....kJ mol^{-1} and the enthalpy of ionisation of acetic acid is ……… kJ mol^{-1}.

8.0 THINGS TO REMEMBER

- Due to radiation, some heat is lost to the environment.
- The solution density is supposed to be 1g / ml.
- Sodium hydroxide ionization is assumed to be 100 %.
- The solution's specific heat is taken as 4.189 J/g^{o}C
- The mixture of acetic acid and NaOH should be stirred well.
- Water equivalent calorimeter or beaker should be calculated accurately.

EXPERIMENT NO.: CC-BT/CH-P-301/PC-04

1.0 NAME OF EXPERIMENT: Thermochemistry (04)

2.0 OBJECTIVE: Determination of the integral enthalpy of solution of ammonium chloride/potassium nitrate

3.0 PRINCIPLE:

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 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:

$$NH_4Cl + 100\,H_2O \longrightarrow NH_4Cl.100\,H_2O \qquad \Delta H_1$$

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.

$$NH_4Cl + 200\,H_2O \longrightarrow NH_4Cl.200\,H_2O \qquad \Delta H_2$$

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:

$$NH_4Cl.100\,H_2O + 100\,H_2O \longrightarrow NH_4Cl.200\,H_2O \qquad \Delta H_2 - \Delta H_1 = \Delta H$$

The enthalpy change in the above reaction 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.

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)]

$$q_P = [C_P(C) + C_P(P)][T_2 - T_1]$$

where Cp (P) and Cp (C) are the heat capacities of the products and the calorimeter, respectively. The latter can be determined as discussed in Experiment 1. 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 Cp (P) is equal to the heat capacity of the water taken, i.e.

$$Cp\,(P) = \text{Mass of water } (m_w) \times \text{specific heat of water } (s) = m_w s = m_w \times 4.185 \ JK^{-1}$$

$$q_P = [C_P(C) + m_w s][T_2 - T_1] \ldots\ldots..(1)$$

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

$$\Delta H_{solution} = \frac{q_P}{n} \ldots\ldots\ldots(2)$$

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

$$n = \frac{massofsolute(g)}{molarmassofsolute(gmol^{-1})} = \frac{m_2}{M} = \ldots\ldots..mol \ldots\ldots\ldots.(3)$$

From equations (1), (2) and (3),

$$\Delta H_{solution} = \frac{q_P}{n} = [m_w s + C_P(C)][T_2 - T_1]\frac{M}{m_2} \ldots\ldots..(4)$$

Note that s = 4.185 $JK^{-1}kg^{-1}$ and molar mass of NH_4Cl = 53.5 g = 0.0535 kg

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 moles of water is required for 1 mole of NH_4Cl.

100 × 0.018 kg of water is required for 0.0535 kg of NH_4Cl

Mass of 200 cm^3 of water = 200 g = 0.200 kg

Therefore, 0.200 kg of water requires 0.0059445 kg of NH_4Cl

4.0 APPARATUS AND CHEMICALS:

- A wide-mouthed polythene bottle (to serve as calorimeter)
- A rubber cork having two holes
- Thermometer (1/10th degree)
- Stirrer fitted with a cork on the handle
- Stop watch
- 250 mL Beakers
- 100 mL measuring cylinder.
- Funnel
- Water
- Solid Ammonium chloride

5.0 PROCEDURE:

- 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 solutes : solvent mole ratio for 0.200 kg or 200 cm^3 water.
- 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 1. 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.

- 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.
- Repeat the experiment for reproducible results.
- 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. 1 and consequently the enthalpy of solution for the dissolution of one mole of solute using Eq. 4.

6.0 RESULTS:

Table 1: Recording of room temperature

Temperature before experiment (°C)	Temperature after experiment (°C)	Mean Temperature (°C)

Table 2: Temperature-time data for pure water and for solution

Set 1

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 = ………kg

Water		Solution	
Time (s)	**Temperature (°C)**	**Time (s)**	**Temperature (°C)**
		Time of mixing	(s)

Set 2

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 = ………kg

Water		**Solution**	
Time (s)	**Temperature (°C)**	**Time (s)**	**Temperature (°C)**
		Time of mixing	**(s)**

7.0 CALCULATIONS:

Set 1

$$\Delta H_{solution} = \frac{q_P}{n} = [m_w s + C_P(C)][T_2 - T_1]\frac{M}{m_2}$$

$\Delta H_{solution}$ (Set 1) = ……… $Jmol^{-1}$

Set 2

$$\Delta H_{solution} = \frac{q_P}{n} = [m_w s + C_P(C)][T_2 - T_1]\frac{M}{m_2}$$

$\Delta H_{solution}$ (Set 1) = ……… $Jmol^{-1}$

Therefore we have,

$$\Delta H_{solution} = \frac{\Delta H_{sol}(Set1) + \Delta H_{sol}(Set2)}{2}\ J$$

Conclusion:

The integral enthalpy of solution of ammonium chloride is……… $Jmol^{-1}$.

8.0 THINGS TO REMEMBER

- Due to radiation, some heat is lost to the environment.
- The solution's specific heat is taken as 4.189 J/g°C
- The mixture of ammonim chloride and water should be stirred well.
- Water equivalent calorimeter or beaker should be calculated accurately.

EXPERIMENT NO.: CC-BT/CH-P-301/PC-05

1.0 NAME OF EXPERIMENT: Thermochemistry (05)

2.0 OBJECTIVE: Determination of enthalpy of hydration of anhydrous copper sulphate

3.0 PRINCIPLE:

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.

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,

$$CuSO_4\,(s) \quad + \quad 5H_2O\,(l) \longrightarrow CuSO_4.5H_2O(s)$$

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:

$$CuSO_4\,(s) \quad + \quad 400H_2O\,(l) \longrightarrow CuSO_4.400H_2O \quad \Delta H_1$$

$$CuSO_4.5H_2O(s) \quad + \quad 400H_2O\,(l) \longrightarrow CuSO_4.405H_2O \quad \Delta H_2$$

We know 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 above is almost equal to the following equation i.e. $\Delta H_2 = \Delta H_3$:

$$CuSO_4.5H_2O(s) + 395H_2O\,(l) \longrightarrow CuSO_4.400H_2O \quad \Delta H_3$$

Now, you need to recall Hess's law of constant heat summation. 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 the following equations. This gives the expression for hydration of anhydrous copper sulphate.

$$CuSO_4\,(s) + 400H_2O\,(l) \longrightarrow CuSO_4.400H_2O \quad \Delta H_1$$

$$CuSO_4.5H_2O(s) + 395H_2O\,(l) \longrightarrow CuSO_4.400H_2O \quad \Delta H_3$$

$$CuSO_4\,(s) + 5H_2O\,(l) \longrightarrow CuSO_4.5H_2O(s)$$

$$\Delta H = \Delta H_1 - \Delta H_3$$

As we argued above, $\Delta H_2 = \Delta H_3$, so by replacing ΔH_3 byΔH_2 the enthalpy of hydration of anhydrous copper sulphate can be given as

$$CuSO_4\,(s) + 5H_2O\,(l) \longrightarrow CuSO_4.5H_2O(s)$$

$$\Delta H = \Delta H_1 - \Delta H_2$$

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.

4.0 APPARATUS AND CHEMICALS:

- A wide-mouthed polythene bottle (to serve as calorimeter)
- A rubber cork having two holes
- Thermometer (1/10th degree)
- Stirrer fitted with a cork on the handle
- Stop watch
- 250 mL Beakers
- 100 mL measuring cylinder
- Weighing bottle
- Analytical balance
- Weight box
- Wash bottle
- Anhydrous copper sulphate
- Copper sulphate pentahydrate
- Water

5.0 PROCEDURE:

There are following four steps of the experiment:

- Determination of heat capacity of the calorimeter for a volume of 200 cm^3
- Determination of integral enthalpy of solution for anhydrous copper sulphate for a solute: solvent mole ratio of 1:400
- Determination of integral enthalpy of solution for copper sulphate pentahydrate for a solute: solvent mole ratio of 1:400
- Calculation of the enthalpy of hydration of anhydrous copper sulphate

Now, let us discuss these steps in details.

Determination of heat capacity of the calorimeter for a volume of 200 cm^3

- 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.
- 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
- 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

- Take a beaker of 250 cm^3 capacity; add 100 cm^3 of hot distilled water (having a temperature of about 20 ^{o}C 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.
- Open the lid of the thermos flask, quickly transfer the hot water to it and replace the lid.
- 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.
- 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.
- 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 Repeat step 1– 6 with the same beaker of 400 cm^3 capacity and record your observations; repeat steps 7and 8 with the new set of data.

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 1g of water $= \frac{159.6}{7200} g$

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

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

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:

- Weigh the required amount of anhydrous copper sulphate in a weighing bottle.
- 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.
- Take the 400 cm^3 beaker for which the heat capacity has been determined, add 200 cm^3 of distilled water to it with the help of a measuring cylinder and place the beaker inside the thermos flask
- 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.
- 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.
- Continue measuring the temperature of the mixture every half a minute for about another four minutes and record your observations.
- Plot graphs between the temperatures (y-axis) of water and the solution of anhydrous copper sulphate, as a function of time (x-axis). Use same set of axes to draw the graphs in the same figure.

- 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.

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

Mass of copper sulphate pentahydrate required for 1g of water $= \frac{249.7}{7200} g$

Mass of copper sulphate pentahydrate required for 200 g (200 cm^3 x 1 gcm^{-3}) of water $= \frac{249.7}{7200} \times 200g = 6.936g$

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.

- Weigh the required amount of copper sulphate pentahydrate in a weighing bottle and record your observations.
- 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.
- Take the 400 cm^3 beaker for which the heat capacity has been determined; add 200 cm^3 of distilled water to it with the help of a measuring cylinder and place the beaker inside the thermos flask.

- 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.
- 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.
- 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.
- 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.
- 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.

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,

$$\Delta H = \Delta H_1 - \Delta H_2$$

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.

6.0 RESULTS:

Table 1: Recording of room temperature

Temperature before experiment (°C)	Temperature after experiment (°C)	Mean Temperature (°C)

Determination of heat capacity of the calorimeter for a volume of 200 cm^3

Table 2: Time-temperature data for cold, hot and mixed water as a function of time

Volume of cold water = ………….. cm^3

Volume of hot water = ………….. cm^3

Set 1

Time (min)	**Temperature / ^{0}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 2

Time (min)	Temperature / ^{0}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

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

Table 3: Time-temperature data for water and solution of anhydrous $CuSO_4$

Time (min)	**Temperature / ^0C**	
	Cold Water	**Solution of anhydrous $CuSO_4$**
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

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

Mass of empty weighing bottle = m_1 = ….g

Mass of weighing bottle + $CuSO_4\cdot5H_2O$ = m_2 = ….g

Mass of weighing bottle after transferring $CuSO_4\cdot5H_2O$ = m_3 = ….g

Mass of $CuSO_4\cdot5H_2O$ transferred (m) = m_2 - m_3 = ….g

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

Table 4: Time-temperature data for water and solution of $CuSO_4.5H_2O$

Time (min)	**Temperature / ^0C**	
	Cold Water	**Solution of $CuSO_4.5H_2O$**
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

7.0 CALCULATIONS:

Determination of heat capacity of the calorimeter for a volume of 200 cm^3

- Use data recorded in Table 1 to plot graphs between the temperature and time for cold water, hot water, and their mixture. 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.
- 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

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

  $$C_P(calorimeter) = 4.185Vd_w[\frac{T_h - T_m}{T_m - T_c} - 1]JK^{-1}$$

  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

  Substitute the values of different terms in the above equation and calculate the value of heat capacity of the calorimeter (beaker) for a volume of 200 cm^3. Repeat the steps for the data of second set recorded. Plot the graphs for second set.

- 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.

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

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

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

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

$Cp(c)$ = heat capacity of the calorimeter

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

- Using data recorded in Table 3, plot graphs between the temperature and time for cold water and the solution of anhydrous copper sulphate. Indicate the time of mixing on the graph.
- 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
- Calculate the integral enthalpy of solution for anhydrous copper sulphate by using the following formula as given below.

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

- 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

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

- Using data recorded in Table 4 plot graphs between the temperature and time for cold water and the solution of copper sulphate pentahydrate.
- 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
- Calculate the integral enthalpy of solution for copper sulphate pentahydrate by using the following formula as given below.

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

- 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 = ... kJ mol-1

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,

$$\Delta H = \Delta H_1 - \Delta H_2$$

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 the above formula and calculate the enthalpy of hydration of anhydrous copper sulphate

Conclusion:

The enthalpy of hydration of anhydrous copper sulphate is, ΔH = ... kJ mol^{-1}

8.0 THINGS TO REMEMBER

- Due to radiation, some heat is lost to the environment.
- The solution's specific heat is taken as 4.189 J/g°C
- Water equivalent calorimeter or beaker should be calculated accurately.

EXPERIMENT NO.: CC-BT/CH-P-301/PC-06

1.0 NAME OF EXPERIMENT: Thermochemistry (06)

2.0 OBJECTIVE: Determination of dissolution enthalpy of benzoic acid by studying temperature dependence of its solubility

3.0 PRINCIPLE:

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.

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,

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

The corresponding equilibrium constant can be written as,

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

Where, [C6H5COOH (aq)] is the molar concentration of dissolved benzoic acid at the temperature of the solution. As the equilibrium 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,

$$\frac{d\ln K_{diss}}{dT} = \frac{\Delta H_{diss}}{RT^2}$$

As mentioned above, the molar solubility (S) of benzoic acidand K_{diss} are same. Thus we can rewrite the above equation as,

$$\frac{d\ln s}{dT} = \frac{\Delta H_{diss}}{RT^2}$$

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.

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

As ΔH and R are constants, we can write,

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

On integrating the above equation and applying limits we have,

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

$$\ln\frac{S_2}{S_1} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log\frac{S_2}{S_1} = \frac{\Delta H}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\Delta H = 2.303R\left[\frac{T_1 T_2}{T_2 - T_1}\right]\log\frac{S_2}{S_1}$$

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}. 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.

4.0 APPARATUS AND CHEMICALS:

- Volumetric flask, 100 cm^3
- Analytical balance
- Weighing bottle
- Weight box
- Beaker, 250 cm^3
- Burette
- Burette stand
- Pipette 10 cm^3
- Conical flask 100 cm^3
- Thermometer 110^0C ($1/10^0C$) 1
- Measuring cylinder 100 cm^3
- Funnel
- Glass Stirrer
- Spatula
- Wash bottle
- Dropper
- Porcelain tile
- Benzoic acid
- Oxalic acid
- Sodium hydroxide
- Phenolphthalein
- Distilled water

5.0 PROCEDURE:

- Take four 100 cm^3 conical flasks and label them as 10°C, 20°C, 30°C and 40°C respectively
- 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.
- 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.
- 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)
- Repeat the above step 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.
- Titrate the pipetted solutions with standardised sodium hydroxide solution using phenolphthalein as indicator. The procedure is:
  - 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 under the initial burette reading column.
  - 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.
  - 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 under the final reading column.

- 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.

The dissolution enthalpy of benzoic acid can be calculated by using the following formula.

$$\Delta H = 2.303R\left[\frac{T_1T_2}{T_2 - T_1}\right]\log\frac{S_2}{S_1}$$

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

6.0 RESULTS:

Table 1: Recording of room temperature

Temperature before experiment (°C)	Temperature after experiment (°C)	Mean Temperature (°C)

Table 2: Titration of different benzoic acid solutions with 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

Strength of Sodium hydroxide solution : _____M

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

7.0 CALCULATIONS:

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

At 40°C

Volume of NaOH used $=V_N=$…….cm^3

The molarity of NaOH $=M_N=$ …..M

Volume of benzoic acid solution taken $= V_B=$ …….cm3

The reaction involved in the titration:

$C_6H_5COOH + NaOH \longrightarrow C_6H_5COONa + H_2O$

Molarity equation: $M_BV_B = M_NV_N$

$$M_B = \frac{M_N V_N}{V_B}(M)$$

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

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

Temperature (^{0}C)	Temperature (K)	Concentration (solubility) of benzoic acid / mol dm−3
40	313	
30	303	
20	293	
10	283	

Calculation of dissolution enthalpy for benzoic acid

$$\Delta H = 2.303R\left[\frac{T_1T_2}{T_2-T_1}\right]\log\frac{S_2}{S_1}$$

Take the solubilities of benzoic acid at any two temperatures from the table above and the above equation to calculate the dissolution enthalpy of benzoic acid.

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

Temperature (T_1) (K)	**Temperature (T_2) (K)**	**Dissolution enthalpy (ΔH) (kJ mol^{-1})**
40	313	
30	303	
20	293	
10	283	

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

Conclusion:

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

EXPERIMENT NO.: CC-BT/CH-P-301/PC-07

1.0 NAME OF EXPERIMENT: pH-metry (01)

2.0 OBJECTIVE: Measurement of pH of aerated drinks, fruit juices, soaps and shampoos using pH-meter

3.0 PRINCIPLE:

In this experiment you would learn about and make measurements of the pH of aerated drinks, fruit juices, soaps and shampoos.

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.

4.0 APPARATUS AND CHEMICALS:

- Measuring cylinder 100 cm^3
- Beaker 100 cm^3 / 50 cm^3
- Glass Stirrer
- pH meter
- Combination glass electrode
- Wash bottle
- Blade / knife
- Standard buffer solutions
- Fruit juice samples
- Aerated drink sample
- Soap sample
- Shampoo sample

5.0 PROCEDURE:

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:

- **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.
- **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.
- **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.
- **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.

Measurement of pH of the given sample solution

- 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.
- 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)

6.0 RESULTS:

Table 1: Recording of room temperature

Temperature before experiment (ºC)	Temperature after experiment (ºC)	Mean Temperature (ºC)

Table 2: Measured pH values of different sample solutions prepared

Serial Number	Sample	pH value
1	Aerated drink	
2	Fruit juice	
3	Soap solution	
4	Shampoo solution	

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

Serial Number	Sample	pH value
1	Aerated drink	
2	Fruit juice	
3	Soap solution	
4	Shampoo solution	

EXPERIMENT NO.: CC-BT/CH-P-301/PC-08

1.0 NAME OF EXPERIMENT: pH-metry (01)

2.0 OBJECTIVE: Preparation & measurement of pH values of buffer solutions and their comparison with theoretical values

3.0 PRINCIPLE:

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.

$$pH = pK_a + \log\frac{[salt]}{[acid]}, pK_a = -\log K_a$$

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 buffer is,

$$pOH = pK_b + \log\frac{[salt]}{[base]}, pK_b = -\log K_b$$

$$pH = 14 - pK_b + \log\frac{[salt]}{[base]}$$

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 above equations 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.

4.0 APPARATUS AND CHEMICALS:

- Measuring cylinder 100 cm^3
- Beaker 100 cm^3 / 50 cm^3
- Glass Stirrer
- pH meter
- Combination glass electrode
- Wash bottle
- Standard buffer solutions
- Burettes
- Funnels
- Standard buffer solutions
- 0.2 M Acetic acid
- 0.2 M Sodium acetate
- 0.2 M Ammonium hydroxide
- 0.2 M Ammonium chloride

5.0 PROCEDURE:

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.

- Take a clean burette and rinse it with the given solution of 0.2 M acetic acid.
- 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.
- Similarly take another clean burette, rinse it with the solution of 0.2 M sodium acetate.
- 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.
- Take five beakers each of 50 cm^3 capacity and label them as A-1 to A- 5.

- Carefully transfer 0.2 M acetic acid and 0.2 M sodium acetate solutions from the respective burettes to beaker labelled as A-1 to A-5 as given below and mix the solutions.

Serial No.	Volume of 0.2 M acetic Acid (cm^3)	Volume of 0.2 M sodium acetate (cm^3)
A-1	16	04
A-2	12	08
A-3	10	10
A-4	08	12
A-5	04	16

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.

- Take a clean burette and rinse it with the given solution of 0.2 M ammonium hydroxide.
- 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.
- Similarly take another clean burette, rinse it with the solution of 0.2 M ammonium chloride.
- 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.
- Take five beakers each of 50 cm3 capacity and label them as B-1 to B- 5.
- Carefully transfer 0.2 M ammonium hydroxide and 0.2 M ammonium chloride solutions from the respective burettes to beaker labelled as B-1 to B-5 as given below and mix the solutions.

Serial No.	Volume of 0.2 M Ammonium hydroxide (cm^3)	Volume of 0.2 M Ammonium chloride (cm^3)
B-1	16	04
B-2	12	08
B-3	10	10
B-4	08	12
B-5	04	16

Measurement of pH of the buffer solutions

- 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.
- Gently stir the solution; note the pH value from the pH meter and record it in the Table 2.
- Wash the bulb of the glass electrode with distilled water poured with a wash bottle. Gently wipe the electrode bulb.
- Repeat the same procedure with the other buffer solutions of A- series.
- Similarly, measure the pH of buffer solutions of B-series and record your observations in Table 3.

6.0 RESULTS:

Table 1: Recording of room temperature

Temperature before experiment (^{o}C)	Temperature after experiment (^{o}C)	Mean Temperature (^{o}C)

Table 2: Measured pH values of acetic acid –sodium acetate buffer solutions

Serial No.	Volume of 0.2 M acetic Acid (cm^3)	Volume of 0.2 M sodium acetate (cm^3)	pH
A-1	16	04	
A-2	12	08	
A-3	10	10	
A-4	08	12	
A-5	04	16	

Table 3: Measured pH values of ammonium hydroxide –ammonium chloride buffer solutions

Serial No.	Volume of 0.2 M Ammonium hydroxide (cm^3)	Volume of 0.2 M Ammonium chloride (cm^3)	pH
B-1	16	04	
B-2	12	08	
B-3	10	10	
B-4	08	12	
B-5	04	16	

7.0 CALCULATIONS:

The pH values of the acidic buffer solution can be calculated by using the following equation. For acetic acid-sodium acetate buffer the equation becomes,

$$pH = pK_a + \log\frac{[sodiumacetate]}{[aceticacid]}$$

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

$$pH = 4.76 + \log\frac{[sodiumacetate]}{[aceticacid]}$$

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 labelled as A-1 would be,

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

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 Table given below. For comparison the measured pH values can be taken from Table 2.

Table 4: Expected and observed pH values of the prepared acetic acid and sodium acetate buffer solution (A–series)

Serial No.	Expected pH value	Measured pH value (from Table 2)
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.

$$pH = 14 - pK_b + \log\frac{[salt]}{[base]} \text{ where } pk_W = pH + pOH$$

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

$$pH = 14 - 4.76 + \log \frac{[ammoniumchloride]}{[ammoniumhydroxide]} = 9.24 + \log \frac{[ammoniumchloride]}{[ammoniumhydroxide]}$$

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 Table given below. For comparison the measured pH values can be taken from Table 3.

Table 5: Expected and observed pH values of the prepared ammonium hydroxide – ammonium chloride buffer solution (B–series)

Serial No.	Expected pH value	Measured pH value (from Table 3
B-1		
B-2		
B-3		
B-4		
B-5		

Conclusion:

The calculated and measured pH values of the prepared buffer solutions are:

Serial No.	Expected pH value	Measured pH value
A-1		
A-2		
A-3		
A-4		
A-5		
B-1		
B-2		
B-3		
B-4		
B-5		

Section B: Organic Chemistry

~ INTRODUCTION ~

Section B: Organic Chemistry

PART: 1: QUALITATIVE ANALYSIS OF ORGANIC SUBSTANCES

A fundamental difference exists between the qualitative analysis of inorganic materials and the identification of organic substances. Inorganic compounds are, for the most part, ionic, and since the number of different ionic species which may be encountered is relatively limited, it is possible to develop a set scheme, by adherence to which a complete analysis may be achieved. Organic compounds, on the other hand, are essentially covalent, and in consequence each one of the enormous number of known compounds is a separate entity, and no rigid scheme can be developed which is applicable to all cases. The method outlined here should therefore be taken only as a guide, since substances may be encountered which show exceptional behaviour. The student requires to have a sound knowledge of the properties of organic compounds, and must use this knowledge to the fullest extent in order to arrive at the correct interpretation of the experimental results.

SUGGESTED PROCEDURE

The method of investigation may be divided roughly into four parts:

- Preliminary investigation of the physical properties, and the physical separation of mixtures, where applicable.
- Detection of elements present.
- Detection of characteristic groupings, and the chemical separation of mixtures.
- Preparation of derivatives for complete characterization.

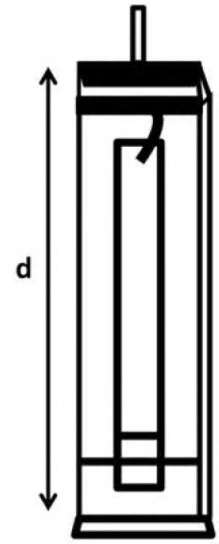
PART: 2: PAPER CHROMATOGRAPHY

Chromatography is a widely used analytical technique for separation, isolation, purification and identification of organic, inorganic and biochemical compounds from complex mixtures. Russian botanist Mikhail Tswett first employed the technique in 1906 to separate various plant pigments such as chlorophylls, carotenes and xanthophylls by passing the plant extracts through glass column packed with finely divided calcium carbonate. The separated species appeared as coloured bands on the column from which the name *Chromatography* (Greek-*khroma* meaning colour and *graphein* meaning to draw a graph or to write) originated.

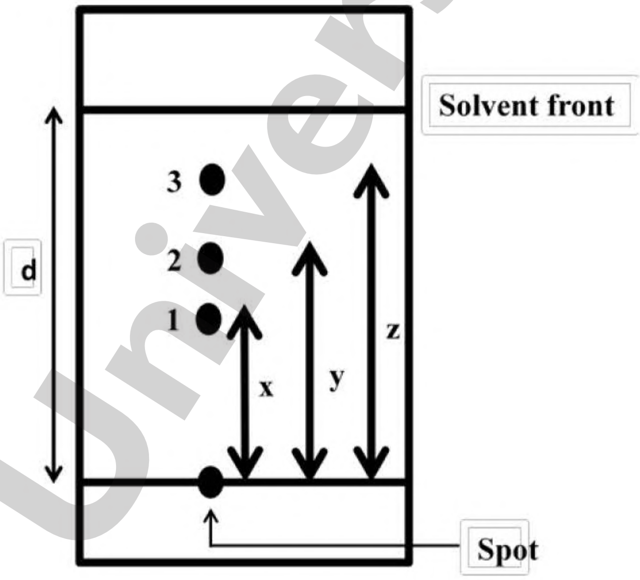
Chromatographic separation is based on the principle of differential distribution of the components of a mixture between two phases, a stationary phase and a mobile phase. The stationary phase may be either a solid or a liquid and the mobile phase may be a liquid or a gas. In *partition chromatography*, the stationary phase is a thin liquid film adsorbed on the surface of an inert support and the mobile phase is either a liquid (*liquid-liquid partition chromatography*) or a gas (*gas-liquid partition chromatography*). In either case, the separation depends largely upon the partition of the components present in the mixture between two phases. ***Paper chromatography*** is an example of partition chromatography. In *adsorption chromatography*, the stationary phase is a finely divided solid adsorbent such as alumina, silica gel etc. and the mobile phase is usually a liquid (*solid-liquid chromatography*). Here, the separation depends upon the selective adsorption of the components of the mixture on the surface of the solid.

PAPER CHROMATOGRAPHY

Paper chromatography is a form of partition chromatography in which the stationary phase is absorbed water molecules present in the filter paper (ca 22%) supported by the cellulose molecules of the paper. A paper strip made from Whatman No. 1 filter paper is spotted at one end with the solution of the test sample to be investigated by means of a capillary tube and dried in air. The paper is then supported vertically in a closed jar containing the developing solvent which is the mobile phase in such a way that the paper edge nearest to the spot origin just dips into the solvent (***ascending technique***). The solvent level is kept well below the spot (Figure below). Development of the chromatogram occurs by upward movement of the solvent by capillary action.



Paper chromatography



Paper chromatography:
Separation of three components 1, 2 and 3

The paper is then dried and sprayed with a suitable reagent to locate the position of the separated components. Identification is made on the basis of *retention factor* or *retardation factor* (R_F values) defined as,

$$R_F = \frac{distance\ \ moved\ \ by\ the\ solute}{distance\ \ moved\ \ by\ the\ solvent\ \ front}$$

As the above figures indicate the method of measurement of R_F values of each of the components of a typical chromatogram. R_F values of compounds 1, 2 and 3 are x/d, y/d and z/d respectively, where ‘d’ is the distance moved by the solvent front and x, y and z are the distances moved by the compounds 1, 2 and 3 respectively.

EXPERIMENT NO.: CC-BT/CH-P-301/OC-01

1.0 NAME OF EXPERIMENT: Detection of extra elements in organic compounds

2.0 OBJECTIVE: Detection of extra elements (N, S, halogens) in organic compounds

3.0 PRINCIPLE:

It is not usual to test for carbon and hydrogen in any organic substance. A little substance should be ignited on a crucible lid until all the carbon has burnt away. In difficult cases, cooling, moistening the black residue with ammonium nitrate solution and reigniting may assist. If a white or coloured residue remains, the presence of a metal is indicated. Its nature should be determined by applying the methods of inorganic analysis to the residue. The presence of nitrogen, sulphur and the halogens is detected by the **Lassaigne test.**

4.0 APPARATUS AND CHEMICALS:

- Sample
- Sodium metal
- Fusion test tube
- Pair of tongs
- Burner
- Distilled water
- Porcelain mortar pestle
- Fume hood
- Pure anhydrous sodium carbonate
- Filter Paper
- Funnel
- Test tubes
- Sodium nitroprusside
- Ferrous sulphate
- Dilute sulphuric acid
- Ferric chloride solution

- Silver nitrate solution
- Carbon tetrachloride
- Sodium hypochloride
- Concentrated nitric acid

5.0 PROCEDURE:

- A small piece of clean sodium, about the size of a rice grain is placed in fusion test tube, which is held in a pair of tongs.
- About 2 drops of the substance, if a liquid, or 0.1g, if a solid, is added, and the tube is gently warmed.
- Any vigorous reaction is allowed to subside, and the tube is then heated more and more strongly, until finally a red heat is attained.
- After maintaining this temperature for 1-2 minutes, the tube is plunged into 15 cm^3 of distilled water contained in a small porcelain mortar pestle. The tube is crushed and the remaining sodium dissolves in a flash.
- This process should always be carried out in the fume hood, with the front drawn down to protect the operator.
- If the substance under investigation refuses to react under these conditions, the procedure may be slightly modified. The substance is introduced into the fusion tube, and mixed with an excess (about 0.3 g) of pure anhydrous sodium carbonate. The mixture is covered with a layer of sodium carbonate, and the piece of sodium is place on top of this. The tube is now heated to the level of the sodium, until the later melts and begins to vaporize. The heating is gradually extended downwards, so that the substance is slowly volatilized over the hot sodium. Finally, the whole mass is brought to red heat. The further procedure is same as before.
- The fusion converts any nitrogen to sodium cyanide, sulphur to sodium sulphide and halogens to sodium halide; these dissolve when the tube is plunged into water. After stirring and gentle warming, the aqueous solution is filtered. The filtrate should be almost colorless. If it is coloured, the heating with sodium was not strong enough and the test must be repeated.

- The solution is divided into portions and the following tests are done.

  Sulphur

  To a portion of the alkaline solution, 1 drop of a feshly prepared aqueous solution of sodium nitroprusside is added.

  Nitrogen

  To a portion of the solution are added a few drops of a freshly prepared solution of ferrous sulphate; a dark green precipitate of ferrous hydroxide is formed. (If sulphur is present, the precipitate will be black; rather more ferrous solution should be added in this case.) The mixture is heated to boiling, with shaking, cooled and acidified with dilute sulphuric acid. If nitrogen is present, a blue or green colour (Prussian blue) appears immediately, or on the addition of a trace of ferric chloride solution. In absence of nitrogen, a pale yellow solution is obtained.

  Halogens

  The remainder of the solution is acidified with dilute sulphuric acid, and if nitrogen or sulphur has been found, it is boiled for 2 minutes, to expel HCN and H_2S. Silver nitrate solution is then added to a potion; a precipitate indicates presence of a halogen. A blank test should be carried out on the reagents used.

  To distinguish the individual halogens, a drop of carbon tetrachloride is added to a fresh portion of the solution, and very dilute sodium hypochloride is added slowly with shaking.

  Iodine gives a violet colour in the carbon tetrachloride, discharged by excess hypochlorite.

  Bromine gives a yellow colour, stable to excess reagent.

  Chlorine is detected in the presence of bromine and iodine by boiling a portion of the original solution with an equal volume of concentrated nitric acid for 5 minutes, then adding silver nitrate.

6.0 RESULTS:

Table 1: Recording of room temperature

Temp. before experiment (^0C)	Temp. after experiment (^0C)	Mean Temperature (^0C)

Table 2: Detection of extra elements

Serial Number	Element	Present / Absent
1	Sulphur	
2	Nitrogen	
3	Chlorine	
4	Bromine	
5	Iodine	

Conclusion:

The extra elements present in the given sample are………………………………..

EXPERIMENT NO.: CC-BT/CH-P-301/OC-02

1.0 NAME OF EXPERIMENT: Paper chromatography (01)

2.0 OBJECTIVE: Separation and identification of amino acids in a mixture (*DL*-alanine, *L*-lysine and *L*-leucine) by paper chromatography

3.0 APPARATUS AND CHEMICALS:

- Amino acids (*DL*-alanine, *L*-lysine, *L*-leucine)
- Acetic acid
- Measuring cylinder (25 cm^3 and 10 cm^3)
- Test tubes
- Electrical air oven (100 to 110 ^0C)
- Solvent chamber (development jar) (20 cm x 4 cm)
- 1-Butanol
- Sprayer
- Distilled water
- Fine capillary tubes
- Whatman No.1 chromatograhy paper strip (20 cm x 4 cm)
- Spraying agent (0.3% ninhydrin solution in 95% ethanol)

4.0 PROCEDURE:

Preparation of sample solutions

Prepare the solutions by dissolving 10 to 15 mg of each of pure samples of the amino acids and of the given unknown mixture in ~1 mL of distilled water in separate test tubes and label them accordingly.

Application of sample solutions

Draw with pencil a base line (~ 3 cm) above the over end of the chromatography paper strip. Put four pencil dots on the base line at equal distances apart. Using separate fine capillary tubes, put spots of the solutions of three known amino acids and that of the unknown mixture on the pencil dots (diameter of the spots should be ~2 to 3 mm) and record their respective positions. Allow the spots to dry in air for 5 minutes.

Preparation of the developing solvents

Prepare the required quantity of the developing solvent by mixing 1-butanol, acetic acid and distilled water respectively in 12 : 3 : 5 (v/v/v) proportion. Pour the solvent into the developing jar, cover the same with lid, swirl the solvent inside and allow standing for a few minutes.

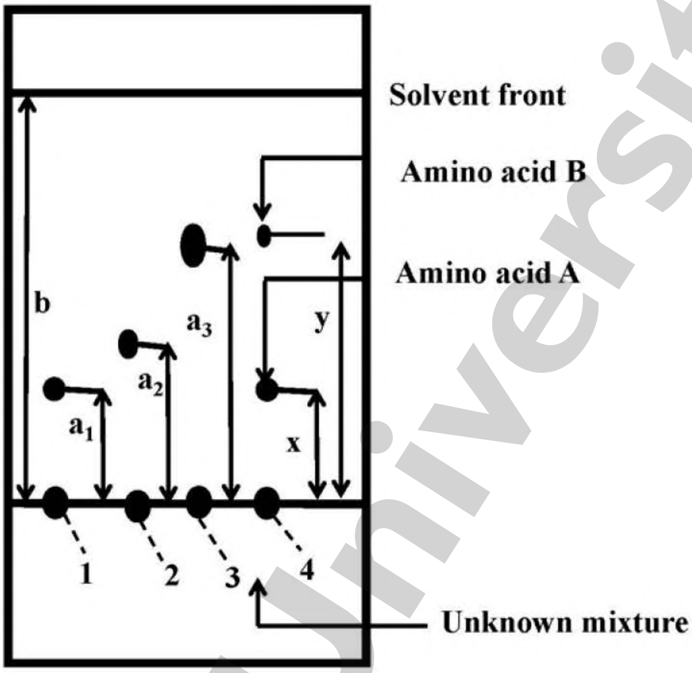
Development of the chromatogram

Open the jar and suspend the paper strip into the developing solvent to a depth of ~ 1 cm keeping the solvent level well below the base line. Care must be taken so that the paper strip does not touch the side of the vessel. Allow the solvent to ascend upto ~14 to 15 cm from the base line (it will take about 2 hours). Then remove the paper strip from the jar, mark the solvent front with pencil and dry the paper in air.

Location of the spots

Spray the ninhydrin reagent on both sides of the dried paper chromatogram and then dry the paper at 100 to 110^{0}C by suspending vertically in an electric air oven (or dry the paper with warm air blower) for ~5 minutes, when blue or purple colours are visible at the respective positions of the amino acids on the chromatogram. Encircle the developed spots with pencil marks and measure the distances moved by the amino acids and also distance moved by the solvent front from the base line.

Calculate the R_F values and identify the amino acids in the unknown mixture by comparison of their R_F values with those of the standards.



Paper chromatogram (1: L-lysine, 2: DL-alanine, 3: L-leucine, 4: unknown)

5.0 RESULTS:

Table 1: Recording of room temperature

Temp. before experiment (^{0}C)	Temp. after experiment (^{0}C)	Mean Temperature (^{0}C)

Table 2: Evaluation of R_F values

R_F (L-lysine)	R_F (DL-alanine)	R_F (L-leucine)	Unknown mixture	
			R_F (A)	R_F (B)
$\frac{a_1}{b}=$........	$\frac{a_2}{b}=$........	$\frac{a_3}{b}=$........	$\frac{x}{b}=$........	$\frac{y}{b}=$........

Conclusion:

From comparison of R_F values of the components A and B (in the unknown mixture) with those of the standards (1, 2 and 3), the amino acids A and B may be identified to be *L*-lysine and *L*-leucine respectively.

Approximate R_F values of the three amino acids are,

- *L*-lysine = 0.17
- *DL*-alanine= 0.35
- *L*-leucine = 0.62

EXPERIMENT NO.: CC-BT/CH-P-301/OC-03

1.0 NAME OF EXPERIMENT: Paper Chromatography (02)

2.0 OBJECTIVE: Separation and identification of sugars (glucose, fructose and sucrose) by paper chromatography

3.0 APPARATUS AND CHEMICALS:

- Sugars (glucose, fructose and sucrose)
- Whatman No.1 chromatograhy paper strip (20 cm x 4 cm)
- Fine capillary tubes
- Measuring cylinder (25 cm^3 and 10 cm^3)
- Acetic acid
- Spraying agent (aniline oxalate: Dissolve 0.093 g (~9 to 10 drops of aniline) in 50 mL of 95% ethanol and mix with 50 mL of 0.2 (M) aqueous oxalic acid)
- Test tubes
- Electrical air oven (100 to 110 ^{0}C)
- Solvent chamber (development jar) (20 cm x 4 cm)
- 1-Butanol
- Sprayer
- Distilled water

4.0 PROCEDURE:

Preparation of sample solutions

Prepare the solutions of glucose, fructose and sucrose by dissolving ~30 mg of each sugar in 0.25 mL of water in separate test tubes.

Application of sample solutions

Draw with pencil a base line (~ 3 cm) above the over end of the chromatography paper strip. Put four pencil dots on the base line at equal distances apart. Using separate fine capillary tubes, put spots of the solutions of three known sugars and that of the unknown mixture on the pencil dots (diameter of the spots should be ~2 to 3 mm) and record their respective positions. Allow the spots to dry in air for 5 minutes.

Preparation of the developing solvents

Prepare the required quantity of the developing solvent by mixing 1-butanol, acetic acid and distilled water respectively in 4 : 1 : 5 (v/v/v) proportion. Pour the solvent into the developing jar, cover the same with lid, swirl the solvent inside and allow standing for a few minutes.

Development of the chromatogram

Open the jar and suspend the paper strip into the developing solvent to a depth of ~ 1 cm keeping the solvent level well below the base line. Care must be taken so that the paper strip does not touch the side of the vessel. Allow the solvent to ascend upto ~14 to 15 cm from the base line (it will take about 2 hours). Then remove the paper strip from the jar, mark the solvent front with pencil and dry the paper in air.

Location of the spots

Spray the aniline oxalate reagent on both sides of the dried paper chromatogram and then dry the paper at 100 to 110^0C by suspending vertically in an electric air oven (or dry the paper with warm air blower) for ~5 minutes, when yellow spots are visible at the respective positions of the sugars on the chromatogram. Encircle the developed spots with pencil marks and measure the distances moved by the amino acids and also distance moved by the solvent front from the base line.

Calculate the R_F values and identify the sugars in the unknown mixture by comparison of their R_F values with those of the standards.

5.0 RESULTS:

Table 1: Recording of room temperature

Temp. before experiment (^{0}C)	Temp. after experiment (^{0}C)	Mean Temperature (^{0}C)

Table 2: Evaluation of R_F values

R_F (Sucrose)	R_F (Glucose)	R_F (Fructose)	Unknown mixture	
			R_F (A)	R_F (B)
$\frac{a_1}{b}$ = ……..	$\frac{a_2}{b}$ = ……..	$\frac{a_3}{b}$ = ……..	$\frac{x}{b}$ = ……..	$\frac{y}{b}$ = ……..

Conclusion:

From comparison of R_F values of the components A and B (in the unknown mixture) with those of the standards (1, 2 and 3), the sugard A and B may be identified to be ……………………. and …………… respectively.

Approximate R_F values of the three sugars are,

- Sucrose = 0.08
- Glucose = 0.17
- Fructose = 0.25

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