UNIT 1

THERMOCHEMISTRY AND DETERMIANTION OF ENTHALPY OF NEUTRALISATION

Structure

1.1 INTRODUCTION

This is the first unit of this course. In this unit, you will study about the heat changes associated with chemical reactions and physical processes. You are aware that the chemical reactions are accompanied by **either the absorption or the evolution of heat**. The study of heat absorbed or evolved in a chemical reaction is called **thermochemistry**. There are many kinds of enthalpies which are named according to the type of transformation or reaction they are associated with. The examples of some such enthalpies include **enthalpy of combustion, enthalpy of fusion, enthalpy of formation, enthalpy of**

hydration, enthalpy of neutralisation, enthalpy of ionisation, etc. In this unit, we will be dealing with the determination of enthalpy of neutralisation.

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

Expected Learning Outcomes

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

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

1.2 SOME FUNDAMENTAL CONCEPTS

Let us first understand some of the concepts and terms which are often used in thermochemical studies.

Systems and Surroundings

A **system** is any part of the universe which is under study and is separated from the rest of the universe by a **boundary**. The rest of the universe is considered as the bold for that system. Further, a system can be **homogeneous, heterogeneous, open, closed** or **isolated** as explained below:

A system is said to be **homogeneous** or having a **single phase**, if the physical properties and chemical composition are identical throughout the system. On the other hand, a **heterogeneous system** has two or more phases which are separated by boundaries.

An **open system** is a system which allows the exchange of **both** matter and energy with its surroundings. A **closed system** only allows the exchange of energy with the surroundings and not that of matter. An **isolated system** is the one which exchanges **neither** energy **nor** matter with its surroundings.

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

A reaction in a closed flask is an example of a c**losed system** because the exchange of matter is **not** allowed with the surroundings. In this system, **only** energy transactions with the surroundings are allowed.

A reaction inside a closed thermos flask is an example of an **isolated system. B**oth matter and energy transactions with the surroundings are **not** allowed.

State and State Variables

A system is said to be in a **definite state** when each of its properties such as pressure, volume, temperature, composition, density etc. have definite values. These properties are also called **state** or **thermodynamic variables**. It is important here to note that a state variable is independent of the way the state has been reached.

Extensive and Intensive Variables

A property is said to be **extensive** if it is dependent on the amount of the substance, e.g., volume, mass etc. On the other hand, properties such as temperature and pressure which do not depend on the amount of a substance are called **intensive** variables.

Having understood the above terms, let us also study the First Law of Thermodynamics because the experiments which you will be performing in this unit and next unit are based on it.

1.3 THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics deals with the **conservation of energy**. It states *that the energy can neither be created nor be destroyed but it can be changed from one form to another*. Thus, if a system is left undisturbed, its energy will not change.

The internal energy, U, of a system is the total energy of the atoms and molecules which constitute the system. It is a state variable and is an extensive property. Since it is a state variable, the change in internal energy (ΔU) *depends only on the initial and final states* and **not** on the way **how** the system has changed from one state to another.

The internal energy of a system can be changed by two agencies, *viz.*, heat (q) and work (w). By convention, when heat is absorbed by the system, the heat change $(\mathrm{d}q)$ is said to be **positive** leading to an increase in the internal energy of the system. Also, the loss of heat from the system indicates a **negative** $\mathrm{d}q$ and a decrease the in internal energy of the system.

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

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

For larger changes, we can say that

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

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

1.4 THE ENTHALPY OF A REACTION

When a chemical reaction takes place in a system, generally, its temperature after the reaction (T_2) is different from the temperature before the reaction (T_1). Let us consider the following general reaction:

$$\underset{T_1}{\mathrm{R}} \xrightarrow{\qquad} \underset{T_2}{\mathrm{P}} \qquad \ldots(1.3)$$

To restore the system to its initial temperature (T_1), heat must flow either *to* or *from* the surroundings. If the system is hotter after the reaction than before $(T_2 > T_1)$, heat must flow to the surroundings to restore the system to its initial temperature (T_1). In this case, the reaction is called **exothermic** and by convention, the flow of heat is negative (q is –ve). If the system is colder after the reaction $(T_2 < T_1)$, heat must flow from the surroundings to restore the system to its initial state of temperature. This reaction is **endothermic** and flow of heat is positive $(q = +ve)$.

The chemical reactions are performed under the conditions of constant volume or constant pressure. If no work is done on or by the system, then from Eq. 1.2 heat transfer at constant volume is equal to the change of internal energy, ΔU. Similarly, heat transfer at constant pressure is identified as the change of enthalpy, ΔH. Thus, we can write,

$$\underset{T_1, V}{\mathrm{R}} \xrightarrow{\qquad} \underset{T_2, V}{\mathrm{P}} \qquad q_v = \Delta U \qquad \ldots(1.4)$$

$$\underset{T_1, p}{\mathrm{R}} \xrightarrow{\qquad} \underset{T_2, p}{\mathrm{P}} \qquad q_p = \Delta H \qquad \ldots(1.5)$$

In the general laboratory conditions, the chemical reactions are carried out at constant pressure. When q_p is the heat absorbed by the system and $p\,\mathrm{d}V$ is the work done by it, then according to Eq. 1.2 the change in internal energy can be written as follows:

$$\Delta U = q_p + (-p\mathrm{d}V) \qquad \ldots(1.6)$$

where q_p is the heat absorbed at constant pressure and $-\,p\,\mathrm{d}V$ is the amount of work done.

Let U_2 be the **final** internal energy and U_1, the **initial** internal energy; also let V_2 be the final volume and V_1, the **initial** volume. The, Eq. 1.6 can be written as,

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

$$= q_p - pV_2 + pV_1$$

rearranging, we get,

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

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

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

Since U, p and V are state variables, H is also a state variable. Thus, by Eq. 1.8, we are able to express heat absorbed (which is **not** a state variable) as a difference of enthalpy which is a state variable. Thus, the heat change (q_p) can be taken as the change in enthalpy (ΔH) provided the only work done is pressure volume work.

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

The heat of a reaction or more precisely, **the enthalpy of a reaction** (ΔH_r) is the enthalpy change in the transformation of reactants at a certain temperature (T) and pressure (p) to products at the same initial temperature (T) and pressure (p):

$$\underset{T,p}{\mathrm{R}} \longrightarrow \underset{T,p}{\mathrm{P}} \qquad \Delta H_r \qquad \ldots(1.9)$$

When heat is supplied to a system, its temperature rises. If dq is the amount of heat absorbed by the system and dT *is* the increase in temperature, then the quantity of heat required to raise the temperature by 1^0C is called the **heat capacity**. The symbol for heat capacity is C and it can be expressed by the following relation:

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

When the volume of the system is **constant**, heat capacity is denoted by C_V. On the other hand, when the pressure of the system is kept constant, heat capacity is represented as C_p.

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

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

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

1.5 THE ENTHALPY OF NEUTRALISATION

The **enthalpy of neutralization** (ΔH_{neut}) of an acid can be defined as the enthalpy change associated with the complete neutralisation of its dilute aqueous solution containing one mole of H^+ ions by a dilute aqueous solution of a base containing one mole of ^-OH ions. Let us consider the example of neutralisaiton of hydrochloric acid with sodium hydroxide. You are aware that hydrochloric acid is a **strong acid** and sodium hydroxide is a **strong base**. This means that both hydrochloric acid and sodium hydroxide are completely dissociated in aqueous solution. Therefore, we can write

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

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

The neutralisation reaction can be represented as

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

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

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

Thus, the neutralisation of a strong acid with a strong base can be considered as the combination or reaction of $H^+(aq)$ ions with $OH^-(aq)$ ions and can be represented as

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

because Na^+ and Cl^- remain unchanged in the reaction.

In other words, *the enthalpy of neutralisation of strong acids and strong bases is the enthalpy of formation of 1 mole of water from one mole each of* H^+ *and* OH^- *ions*.

You must then also expect that the enthalpy of neutralisation of the strong acids with strong bases to be of a constant value irrespective of the strong acid or the strong base used.

Let us now focus our attention on the actual determination of the enthalpy of neutralisation.

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

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

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

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

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

The following two methods are generally adopted for determining the heat capacity of the calorimeter: (1) Dilution method, (2) Heat exchange method. Here, we will discuss the second method in detail because you will be actually using this method for experimental determination of heat capacity of the calorimeter. So, let us begin with the details of this experiment.

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

1.6.1 Principle

Heat Exchange Method

In this method, a definite volume, V, of the cold water is taken in the calorimeter. To this, the same volume of hot water is mixed. The temperatures of the cold water (T_c), hot water (T_h) and the mixture (T_m) are noted. In this case, the heat will be lost by hot water which will be gained by both the cold water and the calorimeter. Thus,

Heat gained by (cold water + calorimeter) = Heat lost by hot water i.e.,

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

From Eq. 1.11, the heat or the enthalpy change is equal to $C_p.\mathrm{d}T$. Substituting this formula for the individual components into the above equation, we get the following expression:

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

The left hand side of Eq. 1.12 is obtained from Eq. 1.11 using the fact that the temperature change ($\mathrm{d}T = T_m - T_c$) is the same both for the calorimeter and the cold water. In order to use Eq. 1.12, for the determination of heat capacity of the calorimeter, we shall see yet another definition for the term heat capacity. The heat capacity of a substance is equal to the product of its mass and specific heat.

Heat capacity of a substance = mass × specific heat

We use this relationship only to denote C_p (cold water) and C_p (hot water) but not for C_p (calorimeter). It is our aim to find out C_p (calorimeter) by performing this experiment ! Using this relation, the above equation can be modified as:

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

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*.**

We assume that,

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

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

Hence, Eq. 1.13 becomes,

$$[ms + C_p(\text{calorimeter})][T_\mathrm{m} - T_\mathrm{c}] = ms(T_\mathrm{h} - T_\mathrm{m}) \quad \ldots(1.14)$$

$$\therefore \quad ms + C_p(\text{calorimeter}) = ms\frac{(T_\mathrm{h} - T_\mathrm{m})}{(T_\mathrm{m} - T_\mathrm{c})}$$

$$C_p(\text{calorimeter}) = ms\frac{(T_\text{h} - T_\text{m})}{(T_\text{m} - T_\text{c})} - ms$$

$$= ms\left[\frac{(T_\text{h} - T_\text{m})}{(T_\text{m} - T_\text{c})} - 1\right] \qquad \text{…(1.15)}$$

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.

You can understand the unit conversion for density of water as follows:

$$1 \text{ g cm}^3 = 1\ (10^{-3}\text{ kg})\ (10^{-1}\text{ dm})^{-3}$$
$$= 1 \times 10^{-3}\text{ kg} \times 10^3\text{ dm}^{-3}$$
$$= 1\text{ kg dm}^{-3}$$

In other words, the magnitude of density is same in both the units expressed above.

$1\text{ cm} = 10^{-1}\text{ dm}$

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

$= 10^{-3}\text{ dm}^3$

Note that,

$$\text{Volume in dm}^3 \text{ units} = \frac{\text{Volume in cm}^3 \text{ units}}{10^3}$$

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

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

Hence, mass of cold water (*m*)

$$= \text{mass of hot water } (m)$$
$$= \text{Volume} \times \text{density}$$
$$= \frac{V}{10^3}\text{ dm}^3 \times d_w\text{ kg dm}^{-3}$$

i.e.

$$m = \frac{V}{10^3} d_w\text{ kg} \qquad \text{…(1.16)}$$

Note that now you have got mass in terms of volume you are measuring experimentally. You simply substitute the **magnitude of volume you measure** in the place of V above. Mass so obtained is in kg units.

Value of *s*

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

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

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

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

$$C_p(\text{calorimeter}) = 4.185\,V\,d_w\left[\frac{T_\text{h} - T_\text{m}}{T_\text{m} - T_\text{c}} - 1\right]\text{J K}^{-1} \qquad \text{…(1.18)}$$

Having measured the volume in cm^3 units, you substitute it as such in Eq. 1.18 without attempting any unit conversion. By substituting the values of T_h, T_m and T_c, you will get the value of C_p in J K^{-1} units.

1.6.2 Requirements

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

1.6.3 Procedure

Take a thermos flask with a lid having two holes. Through one of these holes insert the thermometer and through the other insert the stirrer. Take 100 cm^3 of distilled water into a 250/400 cm^3 beaker. Keep this beaker in the thermos flask. Note down the temperature of water after every half a minute for about 4 minutes. Take 100 cm^3 of water in another beaker and increase its temperature by 20 degrees more than the room temperature. Remove the burner and note down the temperature at an interval of half a minute for another 4 minutes. Then quickly pour this hot water into the calorimeter, stir the contents and note **down the temperature after every half minute for about 4 minutes.**

Plot the temperature-time curves for the cold water, hot water and the mixture on a graph paper. You will get curves similar to those shown in Fig. 1.1. Calculate the temperature of the cold water (T_c), hot water (T_h) and the mixture (T_m) at the time of mixing from the graph. Then find out the heat capacity of the calorimeter by substituting the above values in Eq. 1.18.

Repeat the experiment to get reproducible results.

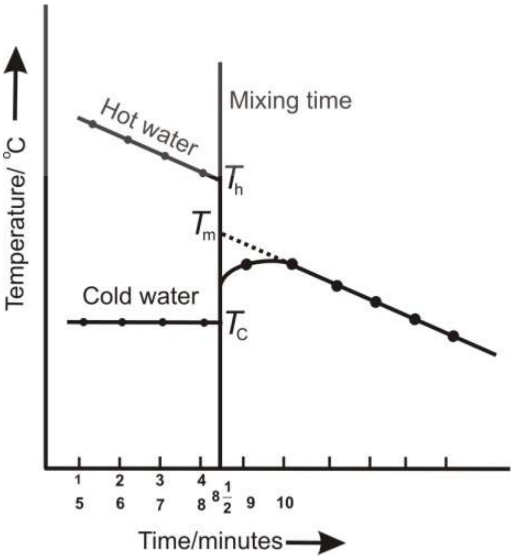

Fig. 1.1 Temperature-time curve.

How to plot temperature-time curve

Take a graph paper. Draw with a pencil, X and Y axes. Represent temperature on Y axis and Time on X axis. Put points corresponding to temperature recorded for the cold water with respect to time. Suppose you have recorded the temperature for cold water for 4 minutes. Then do similarly for the hot water (i.e., plot the temperature recorded for hot water for another 4 minutes). At the time when hot water is mixed with cold water (i.e., at $8\frac{1}{2}$ minutes), draw a line as mixing line. Start plotting the temperature of the mixture from next reading of time (i.e., at 9 minutes).

Extrapolate the three lines and get T_c, T_h and T_m as shown in Fig. 1.1.

1.6.4 Observations

SET I

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

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

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

Time/s	Temperature/°C		Time/s	Temperature/°C Mixture
	Cold Water	Hot Water		
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
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……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
				Time of mixing = ……………S

SET II: Similar observations as reported above.

Time/s	Temperature/°C		Time/s	Temperature/°C (Mixture)
	Cold Water	Hot Water		
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
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……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
				Time of mixing = ……………S

You can do the calculations as shown below:

1.6.5 Calculations

Plot a graph of temperature versus time for cold water, hot water and for the mixture on a single graph paper. Find the temperature of cold water (T_c), hot water (T_h) and for the mixture (T_m) from the curves. Put these values in

Eq. 1.21 and calculate the heat capacity of the calorimeter, C_p . Similarly, calculate C_p with the help of the data of the second set of observations. Then take the average value if the results are not very far from each other; otherwise repeat the experiment.

Report your result as follows.

1.6.6 Result

The heat capacity of the given calorimeter is = ...J K^{-1}.

SAQ 1

Explain how the unit of heat capacity is J K^{-1}.

Having determined the heat capacity (or the water equivalent) of the calorimeter, you can now proceed to the determination of enthalpy of neutralisation of solution.

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

1.7.1 Requirements

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

Solutions Provided

0.50 mol dm^{-3} NaOH

0.50 mol dm^{-3} HCl

1.7.2 Procedure

Measure 100 cm^3 of HCl in a beaker for which heat capacity has already been determined in Experiment 1a. Place it in a thermos flask. Insert the stirrer and the thermometer through the two holes and cover the thermos flask with the lid. Stir the contents with the stirrer and note down the temperature of the acid after every half a minute for 5 minutes. Take 100 cm^3 of NaOH in another beaker (preferably in a flask) and note down its temperature after every half a minute for five minutes. Pour the NaOH solution in the acid already placed in the thermos flask and note down the exact time of mixing. Close the lid and keep on stirring the solution and note down temperature after every half minute for another 5 minutes. Repeat the experiment for second set of readings.

You can record your observations as given below:

1.7.3 Observations

Neutralisation of HCl with NaOH:

SET I

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

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

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

Time/s	Temperature/°C		Time/s	Temperature/°C Mixture
	HCl	NaOH		
……………	……………	……………	……………	……………
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……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
				Time of mixing = ……………S

SET II: Take observations in a similar way and record them in the same manner as given above for Set I.

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

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

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

Time/s	Temperature/°C		Time/s	Temperature/°C Mixture
	HCl	NaOH		
……………	……………	……………	……………	……………
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……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
				Time of mixing = ……………s

1.7.4 Calculations

(1) Plot temperature – time curve for the neutralisation of HCl with NaOH data. You will get a plot as given in Fig. 1.2. From the graph, calculate T_b and T_a (the temperature of the reactants: base and acid, respectively) and T_m, the temperature of the products.

(2) The heat evolved during neutralisation will raise the temperature of the solution and that of the beaker (calorimeter). In other words, the enthalpy change for the neutralisation of the given amount of the acid with the given amount of the base is equal in magnitude but opposite in sign to the heat gained by the calorimeter and its contents. That is why there is a negative sign in the right hand side of Eq. 1.19 as given below:

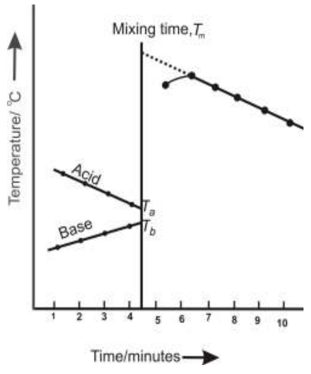


Fig. 1.2: Temperature-time curve for neutralisation.

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

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

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

Using Eq. 1.21,

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

Calculate ΔH from Eq. 1.22 by substituting the values of $T_\mathrm{m}, T_\mathrm{a}$ and T_b as obtained by the plot of temperature versus time curve and those of heat capacity of calorimeter [C_p(c) form Experiment 1a] and specific heat ($s = 4.185\ \mathrm{J\,K^{-1}\,kg^{-1}}$). ΔH so obtained in the above equation is the enthalpy change for the neutralisation of $100\,\mathrm{cm}^3$ of 0.5 M HCl with $100\,\mathrm{cm}^3$ of 0.5 M NaOH. From this ΔH, you can now calculate the ΔH_neut as follows.

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

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

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

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

$$= \ldots\ldots.\mathrm{J\ mol^{-1}}$$

Now report your result as given below:

1.7.5 Result

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

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 $\mathrm{JK^{-1}\ kg^{-1}}$. 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. Let us denote the specific heat of water as *s*. Hence, specific heat of acid

= specific heat of base

= specific heat of water
= *s* … (1.21)

0.5 M HCl means 0.5 mole of HCl present in 1 dm^3 of the solution. Thus, amount (no. of moles) of HCl present in 100 cm^3 of HCl (or 200 cm^3 of the solution)

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

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

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

Thus, to get the amount (number of moles) present in 100 cm^3 of 0.5 HCl or 200 cm^3 of the solution from the molarity (or amount in no. of moles of substance present in 1 dm^3), we have to divide the molarity by 10 as done above.

1.8 ANSWERS

Self Assessment Question

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

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

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

EXPERIMENT 2

DETERMIANTION OF ENTHALPY OF IONISATION OF A WEAK ACID

Structure

2.1 INTRODUCTION

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

Expected Learning Outcomes

After performing this experimet, you should be able to:

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

2.2 PRINCIPLE

The enthalpy of neutralisation of acetic acid can be determined by the similar method as done above for the hydrochloric acid. The acetic acid, in contrast to the hydrochloric acid, is a **weak acid** and is **not completely** dissociated in dilute aqueous solutions into H^+ and CH_3COO^- ions.

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

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

The difference in the enthalpy of neutralisation of a strong acid (HCl) with a strong base (NaOH) and enthalpy of neutralisation of weak acid (CH_3COOH) with strong base (NaOH) will give the enthalpy of ionisation of the weak acid (CH_3COOH).

Since the ionisation proceeds simultaneously with neutralisation, the enthalpy change observed is the sum of enthalpy of ionisation and enthalpy of neutralisation, i.e.,

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

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

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

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

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

2.3 REQUIREMENTS

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

Solutions Provided

0.50 mol dm^{-3} CH_3COOH

0.50 mol dm^{-3} NaOH

2.4 PROCEDURE

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

Record your observations in the following manner.

2.5 OBSERVATIONS

Neutralisation of CH_3COOH with NaOH

SET I

Volume of CH_3COOH in the calorimeter, $V_{acid} = 100\,cm^3$

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

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

Time/s	Temperature/°C		Time/s	Temperature/°C Mixture
	CH_3COOH	NaOH		
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
				Time of mixing = ……………S

SET II

Repeat same observations as done above for Set I.

Volume of CH_3COOH in the calorimeter, $V_{acid} = 100\,cm^3$

Volume of NaOH, $V_{\text{base}} = 100\,\text{cm}^3$

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

Time/s	**Temperature/°C**		**Time/s**	**Temperature/°C Mixture**
	CH_3COOH	**NaOH**		
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
Time of mixing = ……………S				

2.6 CALCULATIONS

From the observations that you have recorded, plot a graph of temperature versus time for the acid, the base and the mixture. You will get a similar plot as you got in the previous experiment. From this plot, note down the temperature of the acid (T_n), the base (T_b) and the mixture (T_m). Now, substitute the values of T_a, T_b and T_m in Eq. 1.22 and get the value of enthalpy change (ΔH) or heat evolved during the neutralisation of 100 cm^3 of 0.5 M CH_3COOH with 100 cm^3 of 0.5 M NaOH. Then divide the above value of enthalpy change with the number of moles of acetic acid present in the amount of solution taken for neutralisation.

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

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

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

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

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

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

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

2.7 RESULT

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

SAQ 1

Calculate the mass of acetic acid present in 75.0 cm^3 of 0.150 molar solution.

2.8 ANSWERS

Self Assessment Questions

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

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

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

   $= 0.01125$ mol

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

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

EXPERIMENT 3

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

Structure

3.1 INTRODUCTION

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

Let us first understand what do we mean by enthalpy of solution. The dissolution of a solute in a solvent is often accompanied by either evolution or absorption of heat. The amount of heat evolved or absorbed depends on the *nature of the solute* and *the solvent* and also on the *composition of the solution*. Thus, *the enthalpy change accompanying the complete dissolution of one mole of solute in a definite amount of the solvent to give a solution of a specified concentration* is known as the **integral enthalpy (or heat) of solution.** For example, the dissolution of one mole of ammonium chloride in 100 moles of water is represented by the following reaction with ΔH_1 as the enthalpy of solution:

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

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

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

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

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

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

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

Expected Learning Outcomes

After performing this, you should be able to:

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

3.2 PRINCIPLE

In the laboratory, the integral enthalpy of solution is determined by observing the initial temperature, T_1 of a known volume of water (if water is used as the solvent) and the final temperature, T_2 of the contents when a known mass of the solute is completely dissolved in it. The enthalpy of solution of ammonium chloride can be calculated by taking into account the heat capacity of the calorimeter in the following manner.

Heat change = [(Heat capacity of the calorimeter + Heat capacity of the products) × (temperature change)]

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

where C_p(P) and C_p(C) are the heat capacities of the products and the calorimeter, respectively. The latter can be determined as discussed in Experiment 1(a). The heat capacity of the products can be calculated presuming the solution to be quite dilute. In other words, considering the heat capacity component of the solute as negligible, we can assume that C_p(P) is equal to the heat capacity of the water taken, i.e.,

$$C_p(\mathrm{P}) = \text{Mass of water } (m_\mathrm{w}) \times \text{specific heat of water } (s) \qquad \ldots(3.5)$$

$$= m_\mathrm{w} s = m_\mathrm{w} \times 4.185 \text{ J K}^{-1} \qquad \ldots(3.6)$$

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

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

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

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

Using Eqs. 3.4 to 3.8, we can say,

1 mol of NH_4Cl

= 14 + 4+ 35.5 = 53.5 g

∴ Molar mass of NH_4Cl

= 0.0535 kg

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

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

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

The calculation of the mass of ammonium chloride required for preparing a solution with a specific solute-solvent mole ratio of 1:100 in 200 cm^3 of water can be done as follows:

100 mol of water is required for 1 mol of NH_4Cl

100 × 0.018 kg (18 g) of water is required for 0.0535 kg (53.5 g) of NH_4Cl

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

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

$= 5.9445$ g of NH_4Cl

3.3 REQUIREMENTS

Apparatus			**Chemicals**
Thermos flask	—	1	Solid Ammonium Chloride
Glass stirrer	—	1	Water
Thermometer 110°C (1/10 °C)	—	1	
Stop watch or stop clock	—	1	
Beaker 250/400 cm^3	—	1	
Measuring cylinder 100 cm^3	—	1	
Weighing bottle	—	1	
Funnel	—	1	

3.4 PROCEDURE

1. Weigh the appropriate mass of ammonium chloride on a glazed paper or in a weighing bottle, i.e., 0.0059445 kg (5.9445 g) for 1:100 solute-solvent mole ratio for 0.200 kg or 200 cm^3 water.

2. Take 200 cm^3 of distilled water (solvent) in a beaker. Use the beaker (calorimeter) for which the heat capacity has already been determined in the Experiment 1a. Place it in a thermos flask. Insert the thermometer and the stirrer into the holes of the lid. Note down the temperature of water for about 4 minutes at an interval of half-a minute.

3. Add ammonium chloride (solute) to the water. Stir the solution well with the help of the stirrer already placed in the beaker. Note down the time of mixing and the temperature readings after every half a minute for another 4 minutes.

4. Repeat the experiment for reproducible results.

5. Plot temperature–time curve on a graph paper and find out the initial and final temperature from it. Then calculate the enthalpy of solution for this mass of solute using Eq. 3.4 and consequently the enthalpy of solution for the dissolution of one mole of solute using Eq. 3.9.

You can record your observations as shown below:

3.5 OBSERVATIONS

SET I

Mass of empty weighing bottle = $m_1 = \dots\dots$g

Mass of weighing bottle +NH_4Cl = $m_2 = \dots\dots$g

Mass of weighing bottle after transferring of salt = $m_3 = \dots\dots$g

Mass of salt transferred (m) = $m_2 - m_3 = \dots\dots$g

Volume of water in calorimeter = $V = \dots\dots$ cm^3

Mass of water = $m_w = \dots$ g $= \frac{\dots\dots}{1000}$ kg

Temperature-time data for pure water and for solution:

Time/s	Temperature/°C of water		Time/s	Temperature/°C of solution
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
				Time of mixing = ……………s

SET II: Similarly present the data for the second set also.

Mass of empty weighing bottle $= m_1$ =……g

Mass of weighing bottle +NH_4Cl $= m_2$ =……g

Mass of weighing bottle after transferring of salt $= m_3$ =……g

Mass of salt transferred $= m_2 - m_3$ =……g

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

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

Temperature-time data for pure water and for solution:

Time/s	Temperature/°C of water		Time/s	Temperature/°C of solution
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………
……………	……………	……………	……………	……………

Time of mixing = ……………s

3.6 CALCULATIONS

Plot the graph of temperature-time curve on a graph paper and find out the value of T_1, the constant temperature of water and T_2, the temperature of the solution at the time of mixing. Calculate the enthalpy change for dissolving the specific mass of ammonium chloride in the above mentioned salt-water ratio.

The same procedure is adopted to calculate the value of ΔH for the second set. Calculate the average value of enthalpy of solution from the two sets of values.

3.7 RESULT

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

EXPERIMENT 4

DETERMINATION OF ENTHALPY OF HYDRATION OF ANHYDROUS COPPER SULPHATE

Structure

4.1 INTRODUCTION

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

Expected Learning Outcomes

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

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

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

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

4.2 PRINCIPLE

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

4.3 REQUIREMENTS

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

4.4 PROCEDURE

There are following four steps of the experiment:

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

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

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

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

Let us learn about the procedure for these.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Mass of copper sulphate pentahydrate required for 400 moles

($400 \text{ mol} \times 18 \text{ g mol}^{-1} = 7200 \text{ g}$) of water = 249.7 g

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

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

Mass of copper sulphate pentahydrate required for 200 g

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

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

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

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

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

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

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

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

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

4.5 OBSERVATIONS

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

Volume of cold water = ____ cm^3

Volume of hot water = ____ cm^3

Set – I

Observation Table 1

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

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

Time of mixing: ……min.

Set – II

Observation Table 2

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

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

Time of mixing: …… min.

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

Mass of empty weighing bottle = m_1 = ….g

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

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

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

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

Observation Table 3

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

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

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

Time of mixing: …… min.

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

Mass of empty weighing bottle = m_1 = ….g

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

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

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

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

Observation Table 4
Time-temperature data for water and solution of $CuSO_4{\cdot}5H_2O$

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

Time of mixing: …… min.

4.6 CALCULATIONS

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

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

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

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

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

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

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

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

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

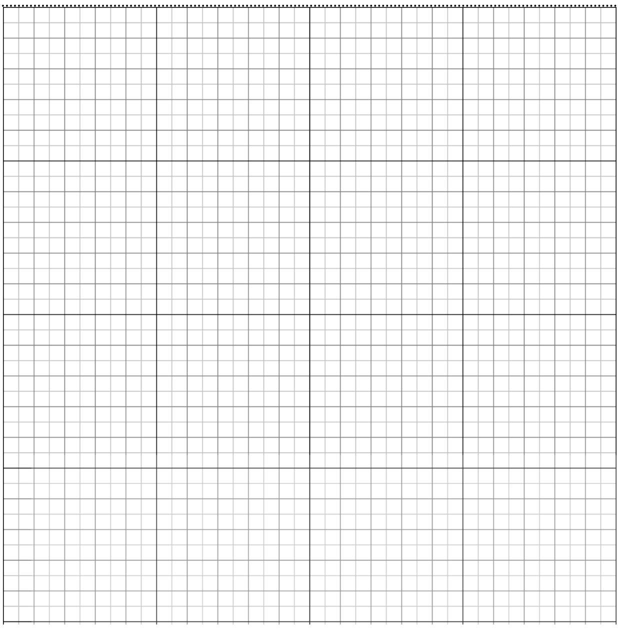
Where, T_c, T_h and T_m are the temperatures of cold water, hot water and their mixture respectively at the time of mixing.

V= total volume of water

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

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

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



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

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

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

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

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

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

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

where,

T_1= temperature of the water at the time of mixing

T_2= temperature of the solution at the time of mixing

m_1 = the mass of solvent taken

m_2 = the mass of solute taken

M = molar mass of the solute

C_p(c) = heat capacity of the calorimeter

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

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

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

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

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

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

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

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

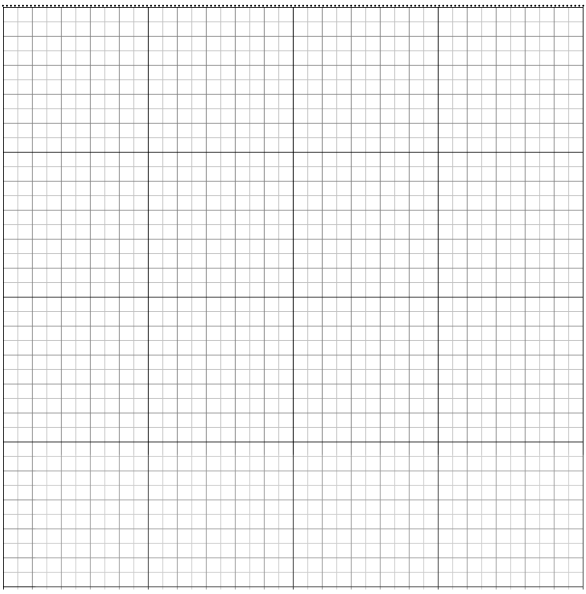
The integral enthalpy of solution for anhydrous copper sulphate for a solute: solvent mole ratio of 1:400 is found to be, $\Delta H_1 = \dots\dots$ kJ mol^{-1}

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

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

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

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



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

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

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

The integral enthalpy of solution for anhydrous copper sulphate pentahydrate for a solute: solvent mole ratio of 1:400 is found to be, $\Delta H_2 = ...$ kJ mol^{-1}

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

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

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

Where, ΔH_1 and ΔH_2respectively are the integral enthalpies of solution for anhydrous copper sulphate and copper sulphate pentahydrate for a solute: solvent mole ratio of 1:400. Substitute the values of ΔH_1 and ΔH_2 (as determined in steps B and C) in the above formula and calculate the enthalpy of hydration of anhydrous copper sulphate

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

4.7 RESULT

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