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# UNIT 6 THERMOCHEMISTRY

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## 6.1 INTRODUCTION

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In Units 4 and 5 of this block, you studied about the measurement of surface tension and viscosity. In this unit and in the next unit, i.e., Unit 7, you will study about the heat changes associated with chemical reactions. Chemical reactions are accompanied by either the absorption or the evolution of heat. The study of heat absorbed or evolved in a chemical reaction is called **thermochemistry**. In this unit, we will be dealing with the determination of heat of solution.

We will be first explaining some fundamental concepts of thermodynamics because this kind of study may be new to you. After that we shall discuss the actual determination of heat of solution.

### Objectives

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

- state the first law of thermodynamics,
- define the enthalpy of a reaction,
- explain the integral and differential enthalpies of solution,
- explain how to determine the heat capacity of a calorimeter, and
- describe the determination of integral heat of solution of a given solute.

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

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

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

A **phase** is defined as a region of uniformity in a system.

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## 6.2 SOME FUNDAMENTAL CONCEPTS

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

### Systems and Surroundings

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

A system is said to be **homogeneous** or having a **single phase**, if the physical properties and chemical composition are identical throughout the system.

On the other hand, a **heterogeneous system** has two or more phases which are separated by boundaries.

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

### State and State Variables

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

### Extensive and Intensive Variables

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

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

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## 6.3 THE FIRST LAW OF THERMODYNAMICS

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

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

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

Similarly, if the work ( $dw$ ) is done **on the system**, it is said to be **positive** because it **increases** the internal energy of the system. 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.

$$dU = dq + dw \text{ (for infinitesimal changes)} \quad \dots (6.1)$$

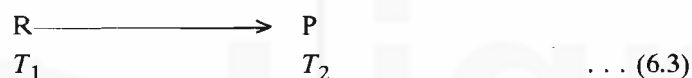
For larger changes, we can say,

$$U = q + w \quad \dots (6.2)$$

Let us now focus our attention on another property associated with a system, called the **enthalpy**. In the later sections of this unit, you will be studying about the determination of the **change in enthalpy** associated with the dissolution of a solute into a solvent to give a solution.

## 6.4 THE ENTHALPY OF A REACTION

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



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 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. 6.2 heat transfer at constant volume is equal to the change of internal energy,  $\Delta U$ . Similarly, heat transfer at constant pressure is identified as the change of enthalpy,  $\Delta H$ . Thus, we can write,

$$\begin{array}{ccc} \text{R} & \longrightarrow & \text{P} \\ T_1, V & & T_2, V \end{array} \quad q_v = \Delta U \quad \dots (6.4)$$

$$\begin{array}{ccc} \text{R} & \longrightarrow & \text{P} \\ T_1, p & & T_2, p \end{array} \quad q_p = \Delta H \quad \dots (6.5)$$

In the general laboratory conditions, the chemical reactions are carried out at constant pressure. When  $q_p$  is the heat absorbed by the system and  $p dv$  is the work done by it, then according to Eq. 6.2 the change in internal energy can be written as follows :

$$\Delta U = q_p + (-pdV) \quad \dots (6.6)$$

where  $q_p$  is the heat absorbed at constant pressure and  $-pdV$  is the amount of work done.

Let  $U_2$  be the **final** internal energy and  $U_1$ , the **initial** internal energy; also let  $V_2$  be the final volume and  $V_1$ , the **initial** volume. Then Eq. 6.6 can be written as,

$$\begin{aligned} U_2 - U_1 &= q_p - p(V_2 - V_1) \\ &= q_p - pV_2 + pV_1 \end{aligned}$$

Rearranging, we get,

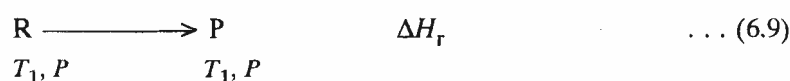
$$q_p = (U_2 + PV_2) - (U_1 + PV_1) \quad \dots (6.7)$$

At this stage, we can represent  $U + PV$  by  $H$ , the enthalpy. We can rewrite Eq. 6.7 as,

$$q_p = H_2 - H_1 = \Delta H \quad \dots (6.8)$$

Since  $U$ ,  $P$  and  $V$  are state variables,  $H$  is also a state variable. Thus, by Eq. 6.8, we are able to express heat absorbed (which is **not** a state variable) as a difference of enthalpy which is a state variable. Thus, the heat change ( $q_p$ ) can be taken as the change in enthalpy ( $\Delta H$ ) provided the only work done is pressure volume work.

The heat of a reaction or more precisely, **the enthalpy of a reaction** ( $\Delta H_r$ ) is the enthalpy change in the transformation of reactants at a certain temperature ( $T_1$ ) and pressure ( $p$ ) to products at the same initial temperature ( $T_1$ ) and pressure ( $p$ ):



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  $1^\circ\text{C}$  is called the **heat capacity**. The symbol for heat capacity is  $C$  and it can be expressed by the following relation :

$$C = \frac{dq}{dT} \quad \dots (6.10)$$

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

From Eq. 6.8, you know that heat absorbed at constant pressure is equal to change in enthalpy. Then, substituting  $dq$  in Eq. 6.10 by  $\Delta H$ , we get,

$$C_p = \frac{\Delta H}{dT} \quad \text{or} \quad \Delta H = C_p dT \quad \dots (6.11)$$

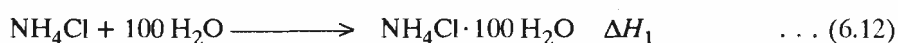
Having understood the above concepts, you can now proceed to the next section which explains the determination of enthalpy of solution.

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## 6.5 DETERMINATION OF THE ENTHALPY OF SOLUTION

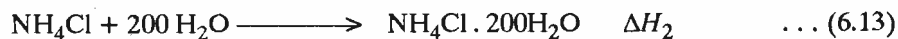
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Let us first understand what do we mean by enthalpy of solution. The dissolution of a solute in a solvent is often accompanied by either evolution or absorption of heat. The amount of heat evolved or absorbed depends on the nature of the solute and 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  $\Delta H_1$  as the enthalpy of solution:

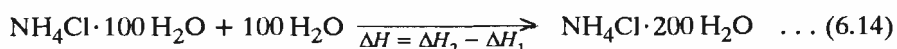


Work could be of various varieties: mechanical, volume-expansion, compression, surface increase, electrical, gravitational etc

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,  $\Delta H_2$ .



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:



The enthalpy change in the above reaction (Eq. 6.14) 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, called 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**.

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 solution 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 for experimental determination.

## 6.5.1 EXPERIMENT 3 : DETERMINATION OF THE HEAT CAPACITY OF A CALORIMETER

### Heat Exchange Method

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

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

i.e.,

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

From Eq. 6.11, the heat or the enthalpy change is equal to  $C_p \cdot dT$ . Substituting this formula for the individual components into the above equation, we get the following expression:

$$\left[ C_p (\text{cold water}) + C_p (\text{calorimeter}) \right] \left[ T_m - T_c \right] = C_p (\text{hot water}) \left[ T_h - T_m \right] \quad \dots (6.15)$$

The left hand side of Eq. 6.15 is obtained from Eq. 6.11 using the fact that the temperature change ( $dT = T_m - T_c$ ) is the same both for the calorimeter and the cold water. In order to use Eq. 6.15, for the determination of heat capacity of the calorimeter we shall see yet another definition for the term heat capacity. The heat capacity of a substance is equal to the product of its mass and specific heat.

Heat capacity of a substance = mass  $\times$  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:

$$\left[ m \times s (\text{cold water}) + C_p (\text{calorimeter}) \right] \left[ T_m - T_c \right] = \left[ m \times s (\text{hot water}) \right] \left[ T_h - T_m \right] \quad \dots (6.16)$$

We assume that,

$$s (\text{cold water}) = s (\text{hot water}) = s (\text{say})$$

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

Hence, Eq. 6.16 becomes,

$$\left[ ms + C_p (\text{calorimeter}) \right] \left[ T_m - T_c \right] = ms (T_h - T_m) \quad \dots (6.17)$$

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

$$\begin{aligned} C_p (\text{calorimeter}) &= ms \frac{(T_h - T_m)}{(T_m - T_c)} - ms \\ &= ms \left[ \frac{(T_h - T_m)}{(T_m - T_c)} - 1 \right] \quad \dots (6.18) \end{aligned}$$

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

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

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

**Value of  $m$** 

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

Note that,

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

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

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

Hence, mass of cold water ( $m$ )

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

$$\text{i.e., } m = \frac{V}{10^3} d_w \text{ kg} \quad \dots (6.19)$$

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

$$s = 4.185 \times 10^3 \text{ J K}^{-1} \text{ kg}^{-1} \quad \dots (6.20)$$

Substituting Eqs. 6.19 and 6.20 in Eq. 6.18, we get,

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

$$C_p (\text{calorimeter}) = 4.185V d_w \left[ \frac{T_h - T_m}{T_m - T_c} - 1 \right] \text{ J K}^{-1} \quad \dots (6.21)$$

Having measured the volume in  $\text{cm}^3$  units, you substitute it as such in Eq. 6.21 without attempting any unit conversion. By substituting the values of  $T_h$ ,  $T_m$  and  $T_c$ , you will get the value of  $C_p$  in  $\text{J K}^{-1}$  units.

**Requirements****Apparatus**

Thermos flask	—	1
Glass Stirrer	—	1
Thermometer $-110^\circ\text{C}$ ( $1/10^\circ\text{C}$ )	—	1
Stop watch or stop clock	—	1
Beaker $250/400 \text{ cm}^3$	—	2
Measuring cylinder $100 \text{ cm}^3$	—	1

**Chemicals**

Only water is needed

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

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

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

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

$$\begin{aligned} (1 \text{ cm})^3 &= (10^{-1} \text{ dm})^3 \\ &= 10^{-3} \text{ dm}^3 \end{aligned}$$

Note that the value of density  $d_w$  is to be used as given in the table in Appendix of this Block.

Magnitude wise the density is same both in  $\text{g cm}^{-3}$  and  $\text{kg dm}^{-3}$  units.

**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  $100 \text{ cm}^3$  of distilled water into a  $250/400 \text{ cm}^3$  beaker. Keep this beaker in the thermos flask. Note down







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

$$q_p = [C_p(P) + C_p(c)](T_2 - T_1) \quad \dots (6.22)$$

Where  $C_p(P)$  and  $C_p(c)$  are the heat capacities of the products and the calorimeter, respectively. The latter can be determined as discussed in Experiment 3. The heat capacity of the products can be calculated presuming the solution to be quite dilute. In other words, considering the heat capacity component of the solute as negligible, we can assume that  $C_p(P)$  is equal to the heat capacity of the water taken, i.e.,

$$C_p(P) = \text{Mass of water } (m_w) \times \text{specific heat of water } (s) \quad \dots (6.23)$$

$$= m_w s \quad \dots (6.23)$$

$$= m_w \times 4.185 \text{ J K}^{-1} \quad \dots (6.24)$$

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

$$\Delta H_{\text{sol}} = q_p/n \quad \dots (6.25)$$

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

$$n = \frac{\text{mass of solute/g}}{\text{molar mass of solute/g mol}^{-1}} = \frac{m_2}{M} \dots \text{mol} \quad \dots (6.26)$$

Using Eqs. 6.22 to 6.26, we can say,

$$\Delta H_{\text{sol}} = \frac{q_p}{n} = [m_1 s + C_p(c)](T_2 - T_1) \frac{M}{m_2} \quad \dots (6.27)$$

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

Therefore, this  $\Delta H$  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  $200 \text{ cm}^3$  of water can be done as follows:

$$\begin{aligned} 1 \text{ mol of NH}_4\text{Cl} \\ = 14 + 4 + 35.5 = 53.5 \text{ g} \end{aligned}$$

$$\therefore \text{molar mass of NH}_4\text{Cl} = 0.0535 \text{ kg}$$

100 mol of water is required for 1 mol of  $\text{NH}_4\text{Cl}$

$100 \times 0.018 \text{ kg}$  (18 g) of water is required for 0.0535 kg (53.5 g) of  $\text{NH}_4\text{Cl}$

Mass of  $200 \text{ cm}^3$  of water =  $200 \text{ g} = 0.200 \text{ kg}$

$$\begin{aligned} 0.200 \text{ kg of water requires } \frac{0.0535 \times 0.200}{1.8} &= 0.0059445 \text{ kg of NH}_4\text{Cl} \\ &= 5.9445 \text{ g of NH}_4\text{Cl} \end{aligned}$$

### Requirements

#### Apparatus

Thermos flask	—	1
Glass Stirrer	—	1
Thermometer $110 \text{ }^\circ\text{C}$ (1/10 $^\circ\text{C}$ )	—	1
Stop watch or stop clock	—	1
Beaker $250/400 \text{ cm}^3$	—	1
Measuring cylinder $100 \text{ cm}^3$	—	1
Weighing bottle	—	1
Funnel	—	1

#### Chemicals

solid Ammonium Chloride  
Water

### Procedure

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



