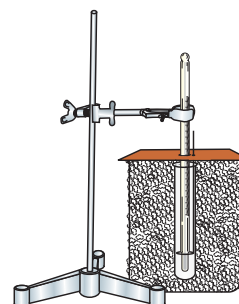


## UNIT-3

# THERMOCHEMICAL MEASUREMENT



**M**OST of the reactions are carried out at atmospheric pressure, hence heat changes noted for these reactions are enthalpy changes. Enthalpy changes are directly related to the temperature changes by the relation:

$$\begin{aligned}\Delta H &= q_p \\ &= m C_p \Delta T \\ &= \mathbf{VdC_p \Delta T} \quad \dots (1)\end{aligned}$$

where **V** = Volume of the solution.

**d** = Density of the solution

**C<sub>p</sub>** = Heat capacity

**ΔT** = Change in temperature

Measurement of heat changes are carried out in vessels called **calorimeters**. Reactions may also be carried out in beakers placed in thermos flask or in thermally insulated box or in styrofoam cup. Metallic calorimeters are not used for measuring thermochemical changes because metals may react with substances. Stainless steel or gold plated copper calorimeters may be used. During measurement of heat changes, calorimeter, thermometer and stirrer also absorb some heat; this amount of heat should also be known. It is called **calorimeter constant**. In the case of a glass vessel, (e.g. beaker) calorimeter constant for that part is found, which is actually in contact with the reaction mixture. This is so because when thermal conductivity of the material of calorimeter is low, only the area of the calorimeter in contact with the liquid absorbs maximum heat. Method of mixtures is used to determine the calorimeter constant. To determine calorimeter constant, known volume of hot water at a specified temperature is added to known volume of water contained in the calorimeter at room temperature. Since energy is conserved, the heat taken by calorimeter and cold water should be equal to heat given by hot water. Thus, we can write the following equation :

$$\begin{array}{rcccl} \Delta H_1 & + & \Delta H_2 & = & -\Delta H_3 & \dots (2) \\ \text{Enthalpy change} & & \text{Enthalpy} & & \text{Enthalpy} & \\ \text{of calorimeter,} & & \text{change of} & & \text{change of} & \\ \text{stirrer and} & & \text{cold water} & & \text{hot water} & \\ \text{thermometer} & & & & & \end{array}$$

Let  $t_c$ ,  $t_h$  and  $t_m$  be temperatures of cold water, hot water and mixture respectively. Then, in view of the definition of enthalpy change given in equation

(1) we can rewrite equation (2) as

$$m_1 C_{p_1} (t_m - t_c) + m_2 C_p (t_m - t_c) + m_3 C_p (t_m - t_h) = 0 \quad \dots (3)$$

where  $m_1$ ,  $m_2$  and  $m_3$  are masses of calorimeter, cold water and hot water respectively and  $C_{p_1}$  and  $C_p$  are heat capacities of calorimeter and water respectively. Since, thermal conductivity of glass is low, only that part of the beaker gains maximum heat which comes in contact with water therefore, we can calculate only effective  $m_1 C_{p_1}$  (i.e. calorimeter constant,  $W$ ). On rewriting equation (3) we get

$$W (t_m - t_c) + m_2 C_p (t_m - t_c) + m_3 C_p (t_m - t_h) = 0$$

$$W = \frac{m_2 C_p (t_m - t_c) + m_3 C_p (t_m - t_h)}{(t_m - t_c)} \quad \dots (4)$$

but  $mC_p = VdC_p$ , where  $V$ ,  $d$  and  $C_p$  are volume, density and heat capacity of water respectively. By definition, heat capacity of a substance is the amount of energy required to raise the temperature of 1 g of substance by 1 K (or 1°C). The amount of energy required to raise the temperature of 1 g of water by 1 K (or 1°C) is 4.184 Joules. This means that for 1 g water for rise of 1 Kelvin temperature  $VdC_p = 4.184 \text{ JK}^{-1}$ . Therefore, product of density and heat capacity can be taken as  $4.184 \text{ J.mL}^{-1}.\text{K}^{-1}$ . Thus, equation (4) can be written as :

$$W = \frac{(4.184) [V_c (t_m - t_c) + V_h (t_m - t_h)]}{(t_m - t_c)} \text{ J K}^{-1} \quad \dots (5)$$

where  $V_c$  = volume of cold water

$V_h$  = volume of hot water

Technique for measuring the enthalpy changes are given in the following experiments.

### EXPERIMENT 3.1

#### Aim

To determine the enthalpy of dissolution of copper sulphate/potassium nitrate.

#### Theory

In thermochemical measurements generally aqueous solutions are mixed therefore, water in the reaction medium and the temperature changes result due to the chemical reactions taking place in solution.



According to law of conservation of energy, the sum of enthalpy changes taking place in the calorimeter (loss and gain of energy) must be zero. Thus, we can write the following equation-

$$\begin{array}{ccccccc}
 (\Delta H_1) & & (\Delta H_2) & & (\Delta H_3) & & (\Delta H_4) \\
 \text{Heat gained by} & + & \text{Enthalpy} & + & \text{Enthalpy change} & + & \text{Enthalpy} \\
 \text{calorimeter,} & & \text{change of} & & \text{of added solution/} & & \text{change of} \\
 \text{thermometer} & & \text{solution/water} & & \text{water in} & & \text{reaction} \\
 \text{and stirrer} & & \text{in calorimeter} & & \text{calorimeter} & & \\
 & & & & & & = 0 \quad \dots (6)
 \end{array}$$

In these reactions we take the product of density and heat capacity of solutions,  $dC_p$ , to be  $4.184 \text{ J}\cdot\text{mL}^{-1}\cdot\text{K}^{-1}$ , nearly the same as that of pure water.\*

Solution formation often accompanies heat changes. Enthalpy of solution is the amount of heat liberated or absorbed when one mole of a solute (solid/liquid) is dissolved in such a large quantity of solvent (usually water) that further dilution does not make any heat changes.

### Material Required

	• Beakers (250 mL)	: Three		• Copper sulphate/ potassium nitrate : 2g
	• Beaker (500 mL)	: One		
	• Thermometer (110°C)	: One		
	• Glass rod	: One		
	• Cotton wool	: As per need		
	• Small wooden block	: One		
	• Small piece of cardboard	: One		
	• Stirrer	: One		

### Procedure

#### A. Determination of Calorimeter constant of calorimeter (Beaker)

- (i) Take 100 mL of water in a 250 mL beaker marked 'A'.
- (ii) Place this beaker on a wooden block kept in a larger beaker of capacity 500 mL (Fig. 3.1).
- (iii) Pack the empty space between the large and the small beaker with cotton wool. Cover the beaker with a cardboard. Insert thermometer and stirrer in the beaker through it.

\* *Density of the solutions is 4 to 6% higher than that of pure water and heat capacity is about 4 to 8% less than pure water so the product of density and heat capacity ( $dC_p$ ) is nearly the same as the product of pure water.*

















