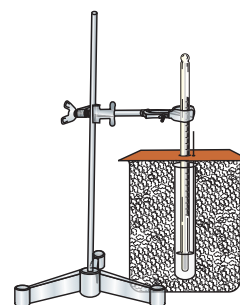# THERMOCHEMICAL MEASUREMENT

MOST 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:

$$\Delta H = q_p$$
$$= mC_p \Delta T$$
$$= VdC_p \Delta T \qquad \qquad \text{... (1)}$$

where V = Volume of the solution.

   d = Density of the solution

   C_p = 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 :

ΔH_1	+	ΔH_2	=	$-\Delta H_3$	... (2)
Enthalpy change		Enthalpy		Enthalpy	
of calorimeter,		change of		change of	
stirrer and		cold water		hot water	
thermometer					

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

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

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

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

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

but $mC_p = V d C_p$, 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 Kelven temperature $V d C_p = 4.184 \, JK^{-1}$. Therefore, product of density and heat capacity can be taken as $4.184 \, J.mL^{-1}.K^{-1}$. Thus, equation (4) can be written as :

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

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-

$$
\underset{\substack{\text{Heat gained by}\\ \text{calorimeter,}\\ \text{thermometer}\\ \text{and stirrer}}}{(\Delta H_1)} + \underset{\substack{\text{Enthalpy}\\ \text{change of}\\ \text{solution/water}\\ \text{in calorimeter}}}{(\Delta H_2)} + \underset{\substack{\text{Enthalpy change}\\ \text{of added solution/}\\ \text{water in}\\ \text{calorimeter}}}{(\Delta H_3)} + \underset{\substack{\text{Enthalpy}\\ \text{change of}\\ \text{reaction}}}{(\Delta H_4)} = 0 \quad .. (6)
$$

In these reactions we take the product of density and heat capacity of solutions, dC_p, to be 4.184 J.mL^{-1}.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
- 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

- Copper sulphate/ potassium nitrate   :   2g

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.
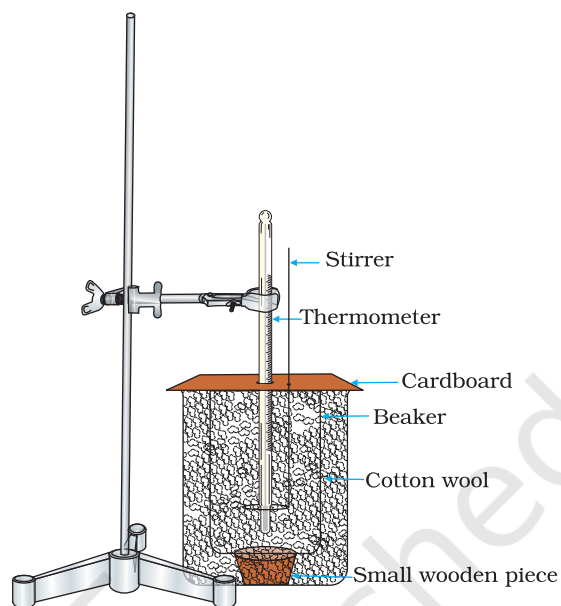
Fig. 3.1 : *Determination of calorimeter constant*

(iv) Record the temperature of water. Let this temperature be t_c°C.

(v) In another beaker of 250 mL capacity marked 'B' take 100 mL of hot water (50-60°C).

(vi) Note the exact temperature of hot water. Let this temperature be t_h°C.

(vii) Lift the card board and pour the hot water contained in beaker B into beaker A. Stir the mixed water and note the temperature. Let this temperature be t_m°C.

(viii) Calculate the calorimeter constant of the beaker by using the expression (5) given above.

(Remember the three temperatures are in the order $t_h > t_m > t_c$).

B. Determination of Enthalpy of Dissolution

(i) Take 100 mL of distilled water in the beaker of which calorimeter constant has been determined and place it on a wooden block kept in a larger beaker of capacity 500 mL (Fig. 3.1).

(ii) Pack the empty space between the larger and the smaller beaker with cotton wool and cover with a cardboard.

(iii) Record the temperature of water already taken in the small beaker. Let this be t'_1°C.

(iv) Add weighed amount, say W_1 g of well powdered copper sulphate in water and stir the solution with a stirrer till the entire amount of copper sulphate dissolves.

(v) Note down the temperature attained by the solution after the addition of copper sulphate. Let this be $t_2'°C$. Calculate the enthalpy of dissolution of copper sulphate as follows:

Total mass of the solution = Mass of Solvent + Mass of Solute

$$= (100 + W_1) \text{ g}$$

(Assuming density of water to be equal to 1 gL^{-1} at the experimental temperature)

Change in temperature $= (t_2' - t_1')°C$

Enthalpy change of the calorimeter (beaker) $= W (t_2' - t_1')$

where, W = Calorimeter constant

Enthalpy change of solution $= [(100 + W_1) (t_2' - t_1')] 4.184$ J

for $(t_2' - t_1')$ °C rise in temperature

Note : To find out enthalpy change for the dissolution of potassium nitrate, use potassium nitrate in place of copper sulphate in this experiment.

Total enthalpy change
of the Calorimeter $= [W (t_2' - t_1') + (100 + W_1) (t_2' - t_1')] \times 4.184$ J
(beaker) and solution

$$\text{Heat liberated on dissolution of 1 g copper sulphate} = \frac{[W (t_2' - t_1') + (100 + W_1) (t_2' - t_1')] \times 4.184 \text{ J}}{W_1}$$

Since 1 mol of copper sulphate weighs 249.5 g. Therefore,

$$\Delta_{Sol}H \text{ of } CuSO_4.5H_2O = 249.5 \times \frac{[W(t_2' - t_1') + (100 + W_1)(t_2' - t_1')] 4.184}{W_1} \text{ J mol}^{-1}$$

Result

Enthalpy change in the dissolution of copper sulphate/potassium nitrate is _____ Jmol^{-1}.

Precautions

(a) To record the temperature of water, use a thermometer with 0.1°C graduation.

(b) In the determination of calorimeter constant record the temperature of hot water just before mixing.

(c) Avoid using very large amounts of copper sulphate/potassium nitrate.

(d) Stir the solution well to dissolve the solid and record the temperature. Avoid too much stirring, it may produce heat due to friction.

(e) Weigh copper sulphate carefully as it is hygroscopic in nature.

(f) Use cotton wool to create insulation between the two beakers.

Discussion Questions

(i) What is meant by the term, calorimeter constant?

(ii) Why is $\Delta_{Sol}H$ for some substances negative while for others it is positive?

(iii) How does $\Delta_{Sol}H$ vary with temperature?

(iv) Will the enthalpy change for dissolution of same amount of anhydrous copper sulphate and hydrated copper sulphate in the same amount of water be the same or different? Explain.

(v) How will the solubility of copper sulphate and potassium nitrate be affected on increasing the temperature? Explain.

EXPERIMENT 3.2

Aim

To determine the enthalpy of neutralisation of a strong acid (HCl) with a strong base (NaOH).

Theory

A neutralisation reaction involves the combination of H^+(aq) ions furnished by an acid and OH^-(aq) ions furnished by a base, evidently leading to the formation of H_2O (l). Since the reaction envisages bond formation, therefore, this reaction is always exothermic. Enthalpy of neutralisation is defined as the amount of heat liberated when 1mol of H^+ ions furnished by acid combine with 1 mole of OH^- ions furnished by base to form water. Thus:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O \text{ (l)}, \quad \Delta_{neut}H \text{ is negative}$$
$$\text{(Acid)} \quad \text{(Base)}$$
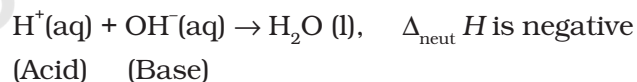
where $\Delta_{neut}H$ is known as enthalpy of neutralisation.

If both the acid and the base are strong then for the formation of 1 mol H_2O (l), always a fixed amount of heat, viz, 57 kJ mol^{-1} is liberated. If any one of the acid or the base is weak or if both of these are weak, then some of the heat liberated is used for the ionisation of the acid or base or both of them (as the case may be) and the amount of heat liberated is less than 57 kJ mol^{-1}.

Material Required

- Beakers (250 mL)   : Three
- Beaker (500 mL)   : One
- Thermometer (110°C) : One
- Glass rod   : One
- Cotton wool   : As per need
- Small wooden block : One
- Piece of cardboard   : One
- Stirrer   : One
- Calorimeter   : One

- 1 M HCl   : 100 mL
- 1 M NaOH   : 100 mL

Procedure

A. Determination of calorimeter constant

This may be determined by following the procedure, as detailed in experiment 3.1.

B. Determination of Enthalpy of Neutralisation

(i) Take 100 mL of 1.0 M HCl solution in the calorimeter (beaker) and cover it with cardboard. In another beaker of 250 mL capacity take 100 mL of 1.0 M NaOH solution.

(ii) Note down the temperature of both the solutions, which is likely to be the same. Let it be t_1°C.

(iii) Pour 100 mL 1 M NaOH solution into the calorimeter containing 100 mL of 1.0 M HCl solution.

(v) Mix the solutions by stirring and note the final temperature of the mixture. Let it be t_2°C.

Calculate the enthalpy of neutralisation as follows:

(i) Note the rise in temperature of the mixture, which in this case is $(t_2 - t_1)$ °C.

(ii) Calculate the total amount of heat produced during the neutralisation process, using the following expression

Heat evolved = $(100 + 100 + W) (t_2 - t_1) \times 4.18$ J

(where W, is the calorimeter constant)

(iii) Finally calculate the heat evolved when 1000 mL of 1M HCl is allowed to neutralise 1000 mL of 1M NaOH. This quantity would be ten times the quantity obtained in step (ii).

(iv) Express the quantity of heat evolved in kJ mol^{-1}.

Result

Enthalpy change in the neutralisation of hydrochloric acid solution with sodium hydroxide solution _____ kJmol^{-1}.

Precautions

(a) Record the temperature carefully with the help of a thermometer graduated up to 0.1°C.

(b) Measure the volume of hydrochloric acid and sodium hydroxide solution to be taken for the experiment carefully.

(c) Proper insulation should be made between the two beakers.

(d) Avoid unnecessary and excessive stirring to prevent heating due to friction.

Discussion Questions

(i) Why do we calculate the heat evolved for the neutralisation of 1000 mL of a (1 M) acid by 1000 mL of a (1 M) monoacidic base?

(ii) In comparison to heat evolved in neutralisation reaction between a strong acid and a strong base. Why is lesser quantity of heat evolved when any one of the acid or the base is weak and still less when both are weak?

(iii) Why does the reaction: H_2O (l) $\quad$ H^+(aq) + OH^-(aq) proceed in the forward direction with rise in temperature of the system?
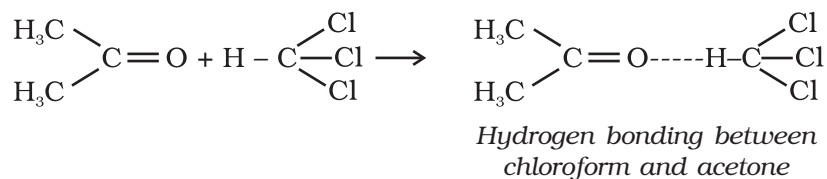
EXPERIMENT 3.3

Aim

To determine the enthalpy change for the interaction between acetone and chloroform (hydrogen bond formation).

Theory

On mixing, liquid pairs show departure from ideal behaviour. Acetone and chloroform form non-ideal liquid pair system, which shows a negative deviation from Raoult's law. This negative deviation from Raoult's law implies that the two components are strongly held together in liquid state on mixing due to hydrogen bonding. On the other hand in the pure state, only weak Van der waal's forces hold molecules of chloroform as well as acetone. The hydrogen bonding between the molecules of acetone and chloroform is depicted as follows:

$$\begin{array}{c} H_3C \\ \diagdown \\ C=O + H-C-Cl \longrightarrow \\ \diagup \\ H_3C \end{array} \quad \begin{array}{c} Cl \\ | \\ Cl \\ | \\ Cl \end{array} \quad \begin{array}{c} H_3C \\ \diagdown \\ C=O-----H-C-Cl \\ \diagup \\ H_3C \end{array} \quad \begin{array}{c} Cl \\ | \\ Cl \\ | \\ Cl \end{array}$$

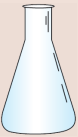*Hydrogen bonding between chloroform and acetone*

In this process enthalpy change takes place due to hydrogen bond formation. The enthalpy change is an extensive thermodynamic property, therefore, the heat evolved from the system depends upon the amount of the liquid components mixed. It is for this reason that the heat change is reported for specified amount. Therefore, enthalpy change during mixing of 1 mol chloroform with 1 mol acetone is reported.

$$
\underset{\substack{\text{Heat gained by}\\\text{calorimeter,}\\\text{thermometer}\\\text{and stirrer}}}{(\Delta H_1)} + \underset{\substack{\text{Enthalpy}\\\text{change of}\\\text{chloroform}}}{(\Delta H_2)} + \underset{\substack{\text{Enthalpy}\\\text{change for}\\\text{acetone}}}{(\Delta H_3)} + \underset{\substack{\text{Enthalpy}\\\text{change of}\\\text{interaction}}}{(\Delta H_4)} = 0
$$

$$
\therefore \quad \Delta H_4 = -(\Delta H_1 + \Delta H_2 + \Delta H_3)
$$

Material Required

- Beaker (250 mL)   : One
- Boiling tube   : One
- Thermometer (110°C): One
- Cotton wool   : As per need
- Glass rod   : One
- Measuring
  cylinder (250mL)   : One
- Piece of cardboard   : As per need
- Stirrer   : One

- Chloroform   :   20 mL
- Acetone   :   10 mL

Procedure

A. Determination of calorimeter constant

This may be determined in a manner detailed in previous experiments; except that here instead of a beaker, boiling tube may be taken and 8 mL of cold and 7.5 mL of hot water can be used instead of 100 mL.
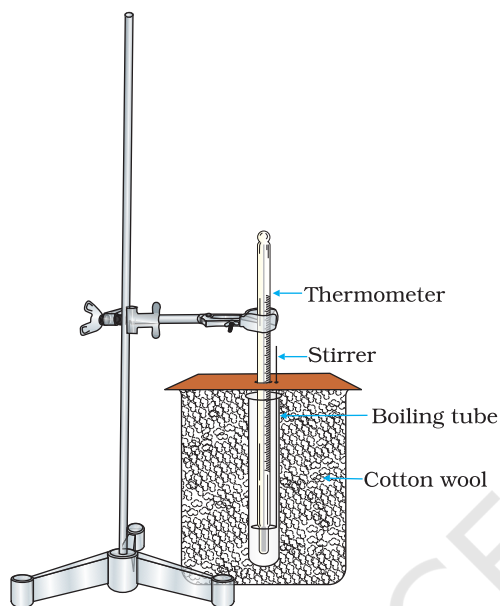
Chloroform

Acetone

B. Determination of Enthalpy Change on Mixing Chloroform and Acetone*

(i) Transfer the volume of chloroform equivalent to 0.1 mol (≈ 8.14 mL) after measuring from a measuring cylinder into the insulated boiling tube as shown in Fig. 3.2. Let the mass of chloroform taken be m_1 grams.

(ii) Record the temperature of chloroform. Let it be t_1°C.

(iii) Transfer the volume of acetone equivalent to 0.1 mol of acetone (≈ 7.34 mL) in a clean measuring cylinder. Let its mass be m_2 grams.

(iv) Record the temperature of acetone. Let it be t_2°C.

(v) Pour acetone from the measuring cylinder into the chloroform contained in the insulated boiling tube.

(vi) Stir gently the mixture of chloroform and acetone carefully with the help of a stirrer.

(vii) Record the temperature of the mixture of chloroform and acetone. Let it be t_3°C.

Fig. 3.2 : *Determination of enthalpy of interaction of chloroform and acetone*

- Thermometer
- Stirrer
- Boiling tube
- Cotton wool

---

*Volume of one mole of $CHCl_3$ **=** $\dfrac{Molar\ mass\ of\ CHCl_3}{Density\ of\ CHCl_3}$

Volume of 0.1 mole **=** $\dfrac{1}{10}$ th of the above volume

(Similarly you can calculate the volume of 0.1 mole of acetone).

Density of chloroform= 1.47 g /mL

Molar mass of chloroform = 119.5 g

1.47 g = 1 mL volume

119.5 g = $\dfrac{119.5}{1.47}$ mL

1 mole = 81.4 mL

0.1 mole = 8.14 mL

Density of acetone = 0.79 g /mL

Molar mass of acetone = 58.0

0.79 g = 1 mL

58 g = $\dfrac{58}{0.79}$ mL

1 mole = 73.4 mL

0.1 mole = 7.34 mL

Total volume of acetone and chloroform = 8.14 +7.34 = 15.48 mL

Calculate the enthalpy of interaction as follows :

(i) Let the room temperature be t°C, then heat gained by calorimeter (boiling tube) is $W \times (t_3 - t)$, where W is the calorimeter constant, i.e. boiling tube in this experiment.

(ii) Note the value of specific heat of chloroform from literature. Let it be q_1.

Then heat gained by chloroform = $m_1 \times q_1 \times (t_3 - t_1)$.

(iii) Note the value of the specific heat for acetone from literature. Let it be q_2. Thus heat gained by acetone = $m_2 \times q_2 \times (t_3 - t_2)$.

(iv) Total heat gained by all the three components, i.e. boiling tube, chloroform and acetone = $-\{W \times (t_3 - t_1) + m_1 \times q_1 \times (t_3 - t_1) + m_2 \times q_2 \times (t_3 - t_2)\}$. This in fact is the enthalpy change of interaction, on mixing 0.1 mol chloroform with 0.1 mol acetone.

The negative sign simply implies that the mixing of chloroform and acetone is an exothermic process.

Note : *Here, care should be taken that the total volume of acetone and chloroform is equal to the volume of water for which water equivalent of the calorimeter has been calculated.*

Precautions

(a) Measure chloroform and acetone carefully.
(b) Record the temperature very carefully with a thermometer graduated up to 0.1°C.

Discussion Questions

(i) Chloroform and acetone do not form an ideal liquid pair, whereas acetone and benzene do form. Why?

(ii) Why does liquid pair of ethanol and water show positive deviation from Raoult's law?

(iii) Give two examples of each of the liquid pairs for which $\Delta_{Mixing} H$ is negative and positive respectively.

(vi) How is the vapour pressure of the liquids related to interaction pattern between the molecules of the components of a liquid mixture?

(v) How can you correlate the heat evolved from the system with the strength of the hydrogen bond?