

## ENTHALPY CHANGES

### 1. Introduction:

Chemical substances have some *heat energy* content in them known as enthalpy (usually denoted by  $H$ ).

Before a reaction takes place, reactants have some heat energy in them, known as enthalpy of reactants – denoted by  $H_{\text{reactants}}$ . After the reaction has taken place, the products too have some heat energy in them, known as enthalpy of products – denoted by  $H_{\text{products}}$ .

For a chemical reaction, the enthalpy of products is never equal to the enthalpy of reactants. It therefore means that when a reaction takes place, an enthalpy change (denoted by  $\Delta H$ ) occurs.

By definition, the enthalpy change of a reaction is given by:

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

For a given reaction, if:

- (i)  $H_{\text{products}}$  is less than  $H_{\text{reactants}}$ , it implies  $\Delta H$  is negative.

This situation arises when a reaction occurs with loss of heat to the surroundings, thereby increasing temperature of the immediate surroundings (the reaction mixture itself).

Such a reaction, which occurs with loss of heat to the surroundings is called an exothermic reaction.

- (ii)  $H_{\text{products}}$  is greater than  $H_{\text{reactants}}$ , it implies  $\Delta H$  is positive.

This situation arises when a reaction occurs with absorption of heat from the surroundings, thereby decreasing temperature of the immediate surroundings (the reaction mixture itself).

Such a reaction, which occurs with absorption of heat from the surroundings is called an endothermic reaction.

## 2. Factors Affecting Enthalpy Change of a Reaction

The factors affecting the enthalpy change of a reaction include the following:

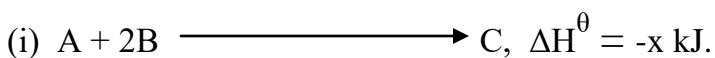
- (i) Temperature
- (ii) Pressure
- (iii) Physical state of both reactants and products
- (iv) Nature of allotrope involved in reaction (*e.g for carbon, whether it is graphite or diamond*)

## 3. Standard Enthalpy Change ( Standard Heat) of a Reaction

If a reaction takes place at a temperature of 298K and a pressure of 1atm, then the accompanying enthalpy change is Standard Enthalpy Change (usually denoted by  $\Delta H^\theta$  or  $\Delta H^\circ$  ).

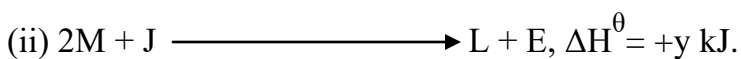
The enthalpy changes usually quoted in chemistry books are standard enthalpy changes. The standard enthalpy change of a reaction is usually written after the equation, to its right hand side and by convention it must bear a sign, either positive (if reaction is endothermic) or negative ( if reaction is exothermic).

Consider the general equations of reaction below:



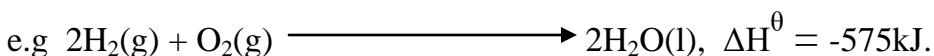
The above equation implies:

When 1 mole of A reacts with 2 moles of B to form 1 mole of C, x kJ of heat energy are given out.



The above equation implies:

When 2 moles of M react with 1 mole of J to form 1 mole of L and 1 mole of E, y kJ of heat are absorbed.



The above equation implies,

When 2 moles of hydrogen gas react with 1 mole of oxygen gas to form 2 moles of water, 575kJ of heat energy are given out .

## ENTHALPY(HEAT) OF COMBUSTION

### 1. Introduction

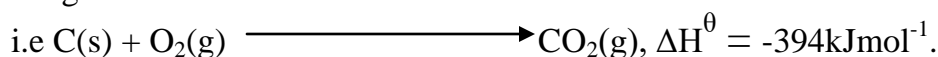
Enthalpy (heat) of combustion is the amount of heat given out when one mole of a substance completely burns in air.

The heat of combustion of a substance is usually stated in  $\text{kJmol}^{-1}$  (i.e the kJ of heat given out per mole of the substance that is completely burnt)

e.g

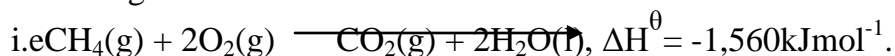
(i) The enthalpy of combustion of carbon is  $-394\text{kJmol}^{-1}$

This implies: When one mole of carbon is completely burnt in air, 394kJ of heat are given out.



(ii) The heat of combustion of methane is  $-1,560\text{kJmol}^{-1}$ .

This implies: When one mole of methane is completely burnt in air, 1,560kJ of heat are given out.



etc

### 2. Calculations Associated with Heat of Combustion

Examples:

- 1) Calculate the amount of heat given out when 18g of carbon are completely burnt in air.

( C =12, heat of combustion of carbon =  $-394\text{kJmol}^{-1}$  )

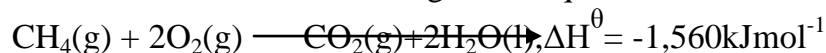
#### Solution

$$\text{moles of carbon burnt} = \left(\frac{18}{12}\right)$$

1 mole of carbon gives out 394kJ of heat

$$\left(\frac{18}{12}\right)\text{moles give out } \left(\frac{394 \times 18}{12}\right) \text{ kJ of heat}$$
$$= \underline{591\text{kJ}} \text{ of heat}$$

- 2) Methane burns in air according to the equation:



Calculate the amount of heat given out when  $2.4\text{dm}^3$  of methane gas, measured at room temperature and pressure is completely burnt in air.

( 1 mole of gas occupies  $24.0\text{dm}^3$  at room temperature and pressure)

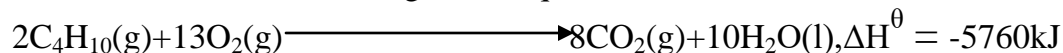
### Solution

$$\text{moles of methane burnt} = \left( \frac{2.4}{24.0} \right)$$

1 mole of methane gives out 1,560kJ of heat

$$\left( \frac{2.4}{24.0} \right) \text{ moles of methane give out } \left( \frac{2.4 \times 1,560}{24.0} \right) \text{ kJ of heat}$$
$$= \underline{156\text{kJ}} \text{ of heat.}$$

3) Butane burns in air according to the equation below:



(a) Calculate the:

- (i) heat of combustion of butane.
- (ii) volume of butane gas, measured at room temperature and pressure, required to produce 17,280kJ.  
(1 mole of gas occupies 24.0dm<sup>3</sup> at room temperature and pressure)
- (b) Given that a litre of butane costs shs 12,000, calculate the amount of money required to buy that amount of butane needed to produce 172,800kJ of heat.

### Solution

(a)(i) From the equation above,

2 moles of butane produce 5760kJ of heat

$$1 \text{ mole of butane produces } \left( \frac{5760}{2} \right) \text{ kJ of heat}$$
$$= 2880\text{kJ of heat}$$

Therefore, heat of combustion = -2880kJmol<sup>-1</sup>.

- (iii) 2880kJ of heat are produced by 1 mole of butane  
17,280kJ of heat are produced by  $\left( \frac{1 \times 17,280}{2880} \right)$  moles of butane  
= 6 moles

At r.t.p,

1 mole of butane occupies 24.0 dm<sup>3</sup>

$$60 \text{ moles of butane occupy } (24.0 \times 6) \text{ dm}^3$$
$$= \underline{144 \text{ dm}^3}.$$

(c) From a(ii) above,

172,800kJ of heat are produced by 6 moles of butane  
(144l ) of butane.

1 l of butane costs shs 12,000.

$$1,440\text{l of butane cost shs } (12,000 \times 144) = \underline{\text{shs } 1,728,000}.$$

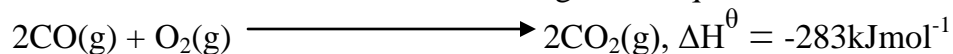
### **EXERCISE**

- 1) The heat of combustion of ethanol is  $-1367 \text{ kJmol}^{-1}$ .

Calculate the,

- (i) amount of heat evolved when 2.3g of ethanol is completely burnt in air. ( O =16, C = 12, H =1)
- (ii) mass of ethanol required to produce 27,340kJ of heat.

- 2) Carbon monoxide burns in air according to the equation below:



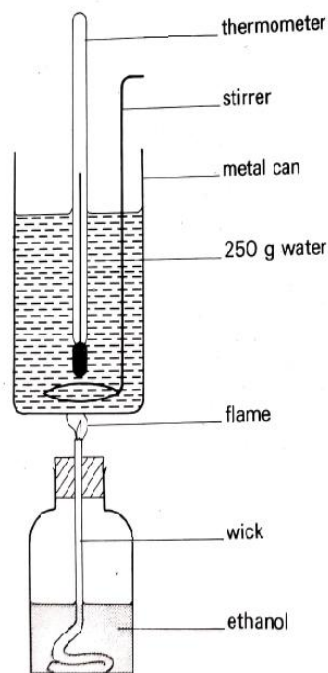
Calculate the volume of carbon monoxide, measured at s.t.p, required to produce 56.6kJ of heat.

- 3) The heat of combustion of carbon is  $-394\text{kJmol}^{-1}$ .

Given that 90kg of charcoal cost shs 60,000, calculate the amount of money required to buy charcoal that is needed to produce 197,000kJ of heat.

( C = 12 )

### **3. Experimental Determination of Heat of Combustion of Ethanol**



### Procedure:

A reagent bottle that has been fitted with a wick ( to improvise as a lamp) is half-filled with ethanol. The mass ( $m_1\text{g}$  ) of the bottle and contents is determined.

A known volume of water ( $v\text{ cm}^3$ ) is put in a thin-walled tin can. A thermometer is inserted in the water and its initial temperature (  $\theta_1^\circ\text{C}$ ) noted.

The tin is then clamped above the reagent bottle and the wick lit. The height of the tin may be adjusted to ensure that the flame just touches its base and a shield may be arranged around the bottle to ensure that the flame is steady.

As the water heats up, it is continuously stirred. When the temperature has risen substantially (through about 25°C) the flame is blown off and the final temperature ( $\theta_2$  °C) of the water noted.

The new mass ( $m_2$ g) of the reagent bottle and contents is determined.

Treatment of Results:

Density of water =  $1\text{gcm}^{-3}$

Specific heat capacity of water =  $4.2\text{Jg}^{-1}\text{K}^{-1}$

Temperature rise of water,  $\theta = (\theta_2 - \theta_1)^\circ\text{C}$

Mass of water = volume  $\times$  density

$$= v \times 1$$

$$= v \text{ g.}$$

Heat produced by burnt ethanol = Heat gained by water

But, heat gained by water = mass  $\times$  specific heat capacity  $\times$  temperature rise

$$= (v \times 4.2 \times \theta) \text{ J}$$

$$= (4.2v\theta) \text{ J}$$

Mass of ethanol burnt =  $(m_1 - m_2)\text{g}$

RMM of ethanol,  $\text{C}_2\text{H}_5\text{OH} = (12 \times 2) + 6 + 16 = 46$

$$\text{Moles of ethanol burnt} = \left( \frac{m_1 - m_2}{46} \right)$$

Hence

$$\left( \frac{m_1 - m_2}{46} \right) \text{ moles of ethanol give out } (4.2v\theta) \text{ J of heat}$$

$$1 \text{ mole of ethanol gives out } \left( \frac{46 \times 4.2v\theta}{m_1 - m_2} \right) \text{ J of heat}$$

$$= \left( \frac{46 \times 4.2v\theta}{1000(m_1 - m_2)} \right) \text{ kJ of heat.}$$

$$\text{Therefore, heat of combustion} = - \left( \frac{46 \times 4.2v\theta}{1000(m_1 - m_2)} \right) \text{ kJmol}^{-1}$$

### Specimen Results:

Volume of water =  $100\text{cm}^3$

Initial temperature of water =  $25.0^\circ\text{C}$

Final temperature of water =  $48.5^\circ\text{C}$

Mass of reagent bottle before burning =  $29.974\text{g}$

Mass of reagent bottle after burning =  $29.592\text{g}$

### Treatment of Results:

Mass of water =  $100 \times 1$

$$= 100\text{g}$$

Temperature rise =  $48.5 - 25.0 = 23.5^\circ\text{C}$

Heat gained by water =  $100 \times 4.2 \times 23.5$

$$= 9870 \text{ J}$$

Mass of ethanol burnt =  $29.974 - 29.592 = 0.382\text{g}$

RMM of ethanol,  $\text{C}_2\text{H}_5\text{OH} = (12 \times 2) + 6 + 16 = 46$

Moles of ethanol burnt =  $\frac{0.382}{46}$

$\left(\frac{0.382}{46}\right)$  moles of ethanol give out  $9870 \text{ J}$  of heat

1 mole of ethanol gives out  $\left(\frac{9870 \times 46}{0.382}\right) \text{ J}$  of heat

$$= \left(\frac{9870 \times 46}{1000 \times 0.382}\right) \text{ kJ of heat}$$

$$= 1,188.53 \text{ kJ of heat}$$

Hence, heat of combustion =  $-1,188.53 \text{ kJmol}^{-1}$

### **EXERCISE:**

In an experiment to determine the enthalpy of combustion of propanol (  $\text{C}_3\text{H}_8\text{O}$  ), 0.54g of propanol was burnt and the heat evolved raised the temperature of  $150\text{cm}^3$  of water by  $21.5^\circ\text{C}$ .

Calculate the experimental value of the enthalpy of combustion of propanol.

(  $\text{O} = 16$ ,  $\text{C} = 12$ ,  $\text{H} = 1$ ; Density of water =  $1\text{gcm}^{-3}$ , S.H.C of water =  $4.2\text{Jg}^{-1}\text{K}^{-1}$  )

### **4. Importance of Heat of Combustion:**

The heat of combustion of a substance can be used:

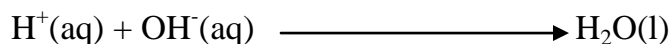
- To measure the relative effectiveness of a fuel ( via the 'calorific value' of the fuel )
- To measure the relative effectiveness of a given type of food in providing energy to the body.

## ENTHALPY ( HEAT ) OF NEUTRALIZATION

### 1.Introduction:

In a neutralization reaction, an acid reacts with a base to form a salt and water only. In this reaction, heat energy is given out.

The ionic equation for a neutralization reaction is



From the above ionic equation, we can conclude that the new substance formed in a neutralization reaction is actually water.

### 2. Definition:

Heat of neutralization is the amount of heat given out when one mole of water is formed after an acid being neutralized by a base or a base being neutralized by an acid.

Hence, as an enthalpy change, heat of neutralization is assigned a negative sign. It is usually expressed in  $\text{kJmol}^{-1}$  ( i.e the kJ of heat given out per mole of water formed.)

### 3. Determination of Enthalpy of Neutralization of Hydrochloric acid by Sodium hydroxide:

#### Procedure:

A known volume (  $v \text{ cm}^3$  ) of standard hydrochloric acid( molarity,  $m$  ) is put in a plastic beaker. An equal volume of sodium hydroxide solution, of the same molarity as the acid , is measured and put in another beaker.

A thermometer is inserted in the sodium hydroxide solution and its temperature (  $\theta_1 \text{ }^\circ\text{C}$  ) noted. The thermometer is withdrawn, its bulb rinsed and dried and then inserted in the hydrochloric acid. Hence, the temperature (  $\theta_2 \text{ }^\circ\text{C}$  ) of the acid is also noted.

The sodium hydroxide solution is then quickly (but carefully) added to the hydrochloric acid, the mixture stirred briefly to mix using the thermometer and the highest temperature attained (  $\theta_3 \text{ }^\circ\text{C}$  ) noted.

#### Treatment of Results:

Assumptions made:

- density of mixture = density of water =  $1 \text{ g cm}^{-3}$
- specific heat capacity of mixture = specific heat capacity of water =  $4.2 \text{ J g}^{-1} \text{ K}^{-1}$

$$\text{Volume of mixture} = v + v = 2v \text{ cm}^3$$

$$\text{Mass of mixture} = \text{volume} \times \text{density}$$

$$= 2v \times 1$$

$$= 2v \text{ g}$$

$$\text{Temperature rise of mixture, } \theta = \left( \theta_3 - \left( \frac{\theta_1 + \theta_2}{2} \right) \right) ^\circ\text{C}$$

$$\text{Heat produced by reaction} = \text{Heat gained by mixture}$$

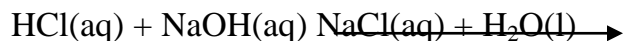
$$\text{Heat gained by mixture} = \text{mass} \times \text{specific heat capacity} \times \text{temperature rise}$$

$$= (2v \times 4.2 \times \theta) \text{ J}$$

$$= (8.4v\theta) \text{ J}$$

$$\text{Moles of HCl} = \frac{mv}{1000}$$

$$\text{Moles of NaOH} = \frac{mv}{1000}$$



$$\text{Mole ratio of HCl : NaOH : H}_2\text{O} = 1 : 1 : 1$$

$$\text{Hence, moles of water formed} = \frac{mv}{1000}$$

Therefore,

$$\frac{mv}{1000} \text{ moles of water formed with evolution of } (8.4v\theta) \text{ J of heat}$$

$$1 \text{ mole of water formed with evolution of } \left( \frac{8.4v\theta \times 1000}{mv} \right) \text{ J of heat}$$

$$= \left( \frac{8.4v\theta \times 1000}{1000 \times mv} \right) \text{ kJ of heat}$$

$$= \left( \frac{8.4\theta}{m} \right) \text{ kJ of heat.}$$

$$\text{Therefore, Heat of neutralization} = - \left( \frac{8.4\theta}{m} \right) \text{ kJ mol}^{-1}$$

Specimen Results:

$$\text{Volume of 1M HCl} = 25.0\text{cm}^3$$

$$\text{Volume of 1M NaOH} = 25.0\text{cm}^3$$

$$\text{Temperature of 1M HCl} = 24.5^\circ\text{C}$$

$$\text{Temperature of 1M NaOH} = 25.0^\circ\text{C}$$

$$\text{Maximum temperature of mixture} = 32.0^\circ\text{C}$$

Treatment of the Results:

$$\text{Volume of mixture} = 25.0 + 25.0 = 50.0\text{cm}^3$$

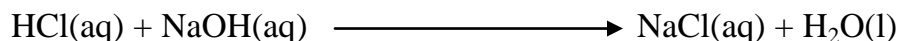
$$\text{Mass of mixture} = 50 \times 1 = 50.0\text{g}$$

$$\begin{aligned}\text{Temperature rise of mixture} &= \left( 32.0 - \left( \frac{24.5+25.0}{2} \right) \right) ^\circ\text{C} \\ &= 7.25^\circ\text{C}\end{aligned}$$

$$\begin{aligned}\text{Heat gained by mixture} &= 50.0 \times 4.2 \times 7.25 \\ &= 1,522.5\text{J}\end{aligned}$$

$$\text{Moles of HCl} = \frac{1 \times 25.0}{1000} = 0.025$$

$$\text{Moles of NaOH} = \frac{1 \times 25.0}{1000} = 0.025$$



$$\text{Mole ratio of HCl : NaOH : H}_2\text{O} = 1 : 1 : 1$$

Therefore, moles of water formed 0.025

Hence,

0.025 moles of water formed with evolution of 1,522.5 J of heat

$$\begin{aligned}1 \text{ mole of water formed with evolution of } &\left( \frac{1,522.5}{0.025} \right) \text{ J of heat} \\ &= \left( \frac{1,522.5}{1000 \times 0.025} \right) \text{ kJ of heat}\end{aligned}$$

$$= 60.9 \text{ kJ of heat}$$

Therefore, heat of neutralization =  $-60.9 \text{ kJ mol}^{-1}$

Example:

When  $50 \text{ cm}^3$  of  $0.5 \text{ M}$  hydrochloric acid was added to  $50 \text{ cm}^3$  of  $0.5 \text{ M}$  potassium hydroxide solution in a calorimeter, there was a temperature rise from  $27.5^\circ\text{C}$  to  $30.5^\circ\text{C}$ .

Calculate the heat of neutralization of potassium hydroxide by hydrochloric acid.

( density of water =  $1 \text{ g cm}^{-3}$ , specific heat capacity of water =  $4.2 \text{ J g}^{-1} \text{ K}^{-1}$  )

### Solution

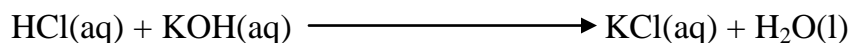
$$\text{Volume of mixture} = 50 + 50 = 100 \text{ cm}^3$$

$$\text{Mass of mixture} = 100 \times 1 = 100 \text{ g}$$

$$\text{Temperature rise} = 30.5 - 27.5 = 3.0^\circ\text{C}$$

$$\text{Heat gained by mixture} = 100 \times 4.2 \times 3.0 = 1,260 \text{ J}$$

$$\text{Moles of HCl} = \text{Moles of KOH} = \frac{0.5 \times 50}{1000} = 0.025$$



$$\text{Mole ratio of HCl : KCl : H}_2\text{O} = 1 : 1 : 1$$

$$\text{Hence, moles of water formed} = 0.025$$

Therefore,

$0.025$  moles of water formed with evolution of  $1,260 \text{ J}$  of heat

$1$  mole of water formed with evolution of  $\left(\frac{1260}{0.025}\right) \text{ J}$  of heat

$$= \left(\frac{1260}{1000 \times 0.025}\right) \text{ kJ of heat}$$

$$= 50.4 \text{ kJ}$$

Hence, heat of neutralization =  $-50.4 \text{ kJ mol}^{-1}$

### EXERCISE

1) When a solution containing 2g of sodium hydroxide was completely reacted with hydrochloric acid, 2,730J of heat was evolved.

Calculate the:

(i) number of moles of sodium hydroxide that reacted. ( Na = 23, O = 16, H = 1 )

(ii) enthalpy of neutralization of sodium hydroxide by hydrochloric acid.

( density of water =  $1\text{gcm}^{-3}$ , specific heat capacity of water =  $4.2\text{Jg}^{-1}\text{K}^{-1}$  )

2) When  $50\text{cm}^3$  of 1M sulphuric acid was added to  $50\text{cm}^3$  of 2M sodium hydroxide solution, the temperature of the resulting mixture rose by  $13.6^\circ\text{C}$ .

Calculate the heat of neutralization of sodium hydroxide by sulphuric acid.

(density of water =  $1\text{gcm}^{-3}$ , specific heat capacity of water =  $4.2\text{Jg}^{-1}\text{K}^{-1}$  )

#### **4. Temperature Measurement Experiment For Neutralization Reaction:**

The fact that heat is produced when an acid reacts with a base can be used to determine: the volume of base needed to react with a fixed volume of acid or the volume of acid needed to react with a fixed volume of base.

This is basically done by temperature measurement, when various increasingly higher volumes of acid are added to a fixed volume of base or when various increasingly higher volumes of base are added to a fixed volume of acid.

##### Procedure:

(i) A fixed volume (e.g  $20\text{cm}^3$ ) of acid (e.g hydrochloric acid) is measured using a measuring cylinder ( or a pipette ) and transferred into a plastic beaker.

(ii) A known volume (e.g  $5\text{cm}^3$ ) of base (e.g sodium hydroxide solution) is measured using another measuring cylinder (or a burette) into another beaker.

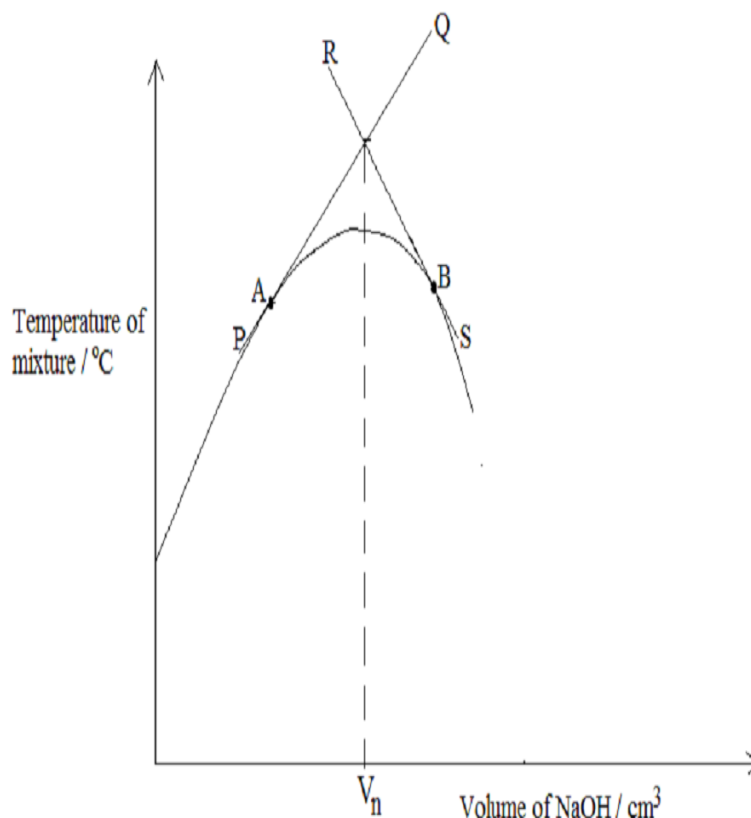
(iii) The base is quickly added to the acid, the mixture stirred briefly using the thermometer and the highest (maximum) temperature attained noted.

(iv) Procedures (i) – (iii) above are repeated several times, each time using an increasingly higher volume of base but the same volume of acid.

Treatment of Results:

A graph of (maximum) Temperature of the reaction mixture against Volume of base added is plotted.

The graph is used to determine the volume of base needed to just react completely with acid, as shown below:



Where,

- A and B are two points near the turning point of the curve and they are at the same horizontal level but on opposite sides of the curve.
- PQ and RS are tangents to the curve at points A and B respectively.

- $T_{\text{max}}$  is the actual maximum temperature attained by the mixture.
- $V_n$  is the volume of base needed to just neutralize the acid.

Hence,  $V_n$  can be used to answer the questions that follow; which can be mole concept questions or enthalpy change questions.

Note:

- The temperature of the mixture when the volume of base added is zero  $\text{cm}^3$  is the temperature of the acid, before any base is added to it.
- The procedure may be adjusted in such a way that the same mixture is used for all the various volumes of base added ( i.e. without discarding the mixture after noting the maximum temperature of a given addition of base )
- A graph of Temperature rise against volume of base added gives the same shape and should be treated in the same way as that of Temperature volume of base added.
- A similar experiment can be carried out by instead fixing the volume of base but varying the volume of acid instead.

### EXERCISE

The table below shows the maximum temperature of resultant mixture, when various volumes of 2M potassium hydroxide solution were added to  $20\text{cm}^3$  of nitric acid

Volume of KOH ( $\text{cm}^3$ )	0	5	10	15	20	25	30	35
Maximum temperature ( $^{\circ}\text{C}$ )	22.0	25.5	29.0	33.0	35.5	32.0	28.0	24.0

- Plot a graph of temperature against volume of KOH
- Using the graph, determine the:
  - maximum temperature attained by the mixture.
  - volume of potassium hydroxide required to just neutralize the acid.

(c) calculate the:

(i) molar concentration (i.e molarity) of nitric acid.

(ii) heat of neutralization of nitric acid by potassium hydroxide.

(density of water =  $1\text{gcm}^{-3}$ , specific heat capacity of water =  $4.2\text{Jg}^{-1}\text{K}^{-1}$  )

## ENTHALPY (HEAT) OF SOLUTION

### 1. Introduction:

When a salt dissolves in water, the process may either be exothermic or endothermic.

For a salt that dissolves exothermically, heat is released to the mixture (i.e the immediate environment), thus raising the temperature of the mixture.

For a salt that dissolves endothermically heat is absorbed from the mixture(i.e the immediate environment), thus lowering the temperature of the mixture.

When a salt dissolves in little water, the resulting solution is concentrated. If this solution is diluted, it undergoes a heat change(i.e a temperature rise or fall) upto some level of dilution- when there will be no further heat change. In this state, the solution is said to be infinitely dilute.

### 2. Definition:

Enthalpy of solution is the amount of heat given out or absorbed when one mole of a compound dissolves in water to form an infinitely dilute solution.

This enthalpy change can either be negative(if the compound dissolves exothermically) or positive (if the compound dissolves endothermically ). It is expressed in  $\text{kJmol}^{-1}$ ( i.e kJ of heat given out or absorbed per mole of compound that dissolves )

### 3. Determination of Heat of Solution of a Compound:

#### Procedure:

A known volume ( $v \text{ cm}^3$ ) of water is put in a plastic beaker. A thermometer is inserted in the water and its initial temperature ( $\theta_1 \text{ }^\circ\text{C}$ ) noted. A known mass ( $m \text{ g}$ ) of the compound whose heat of solution is required is introduced into the water.

The mixture is stirred using the thermometer to dissolve the compound and the final steady temperature ( $\theta_2 \text{ }^\circ\text{C}$ ) noted.

#### Treatment of Results:

##### Assumption

- Specific heat capacity of mixture = specific heat capacity of water =  $4.2 \text{ Jg}^{-1}\text{K}^{-1}$

Mass of water = volume  $\times$  density

$$= v \times 1 = v \text{ g}$$

Mass of mixture =  $(v + m) \text{ g}$

Temperature rise of mixture,  $\theta = (\theta_2 - \theta_1)^\circ\text{C}$

[ i.e assuming compound dissolves exothermically ]

Therefore,

Heat absorbed by mixture =  $[(v + m) \times 4.2 \times \theta] \text{ J}$

$$= \left( \frac{4.2\theta (v+m)}{1000} \right) \text{ kJ}$$

Hence,

$$\text{Heat of solution} = - \left( \frac{4.2\theta (v+m)}{1000} \right) \text{ kJmol}^{-1}$$

#### Note:

In case the compound dissolves endothermically, then  $\theta_2$  is less than  $\theta_1$ .

Hence, in this case, temperature fall,  $\theta = (\theta_1 - \theta_2)^\circ\text{C}$  and the heat of solution in this case would be assigned a positive value.

Example:

8.0g of ammonium nitrate were dissolved in 92cm<sup>3</sup> of water at 20°C and the final steady temperature of the solution was 14°C.

(a) What does the drop in temperature indicate about this process?

(b) Calculate the heat of solution of ammonium nitrate.

( O=16,N=14,H=1 Density of water= 1gcm<sup>-3</sup> specific heat capacity of water = 4.2Jg<sup>-1</sup>K<sup>-1</sup> )

Solution:

(a) It indicates that ammonium nitrate dissolves endothermically.

(b) mass of water = volume × density

$$= 92 \times 1 = 92\text{g}$$

Mass of mixture = 92 + 8.0 = 100g

Temperature fall of mixture = 20 – 14 = 6°C

Heat lost by mixture = ( 100 × 4.2 × 6 ) J

$$= 2,520\text{J}$$

RFM of ammonium nitrate, NH<sub>4</sub>NO<sub>3</sub> = (14 × 2 ) + (16 × 3) + 4

$$= 80$$

Therefore, moles of ammonium nitrate =  $\frac{8.0}{80} = 0.1$

Hence,

0.1 moles of ammonium nitrate absorb 2,520 J of heat

$$\begin{aligned} 1 \text{ mole of ammonium nitrate absorbs } & \left( \frac{2520}{0.1} \right) \text{ J of heat} \\ & = \left( \frac{2520}{1000 \times 0.1} \right) \text{ kJ of heat} \\ & = 25.2\text{kJ} \end{aligned}$$

Therefore, heat of solution = +25.2kJmol<sup>-1</sup>

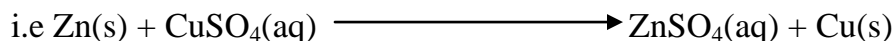
## ENTHALPY ( HEAT ) OF DISPLACEMENT

### 1. Introduction:

In a displacement reaction, a more reactive element displaces a less reactive one from its compound.

In this topic, the displacement reaction we are concerned with is that between a more reactive metal and a salt ( in solution ) of a less reactive metal.

e.g between Zinc and copper(II) sulphate solution.



In such a reaction, heat energy is always given out.

### 2. Definition:

Heat of displacement is the amount of heat given out when one mole of a metal is displaced from its salt in solution by a more reactive metal.

As an enthalpy change, it is always negative since the reaction is exothermic. It is expressed in  $\text{kJmol}^{-1}$  ( i.e kJ of heat given out per mole of the metal displaced )

### 3. Determination of Heat of Displacement of Copper by Zinc:

#### Procedure:

A known volume (  $v \text{ cm}^3$  ) of standard copper(II) sulphate solution ( molarity,  $m$  ) is put in a plastic beaker. A thermometer is inserted into the solution and its initial temperature (  $\theta_1 \text{ }^\circ\text{C}$  ) is noted.

Excess zinc powder is then added to the solution, the mixture stirred using the thermometer and the maximum temperature (  $\theta_2 \text{ }^\circ\text{C}$  ) attained by the mixture noted.

#### Treatment of Results:

##### Assumptions:

- Heat produced in reaction is gained by liquid mixture.
- Density of mixture = density of water =  $1 \text{ gcm}^{-3}$
- Specific heat capacity of mixture = specific heat capacity of water =  $4.2 \text{ Jg}^{-1} \text{ K}^{-1}$

Mass of liquid mixture = volume  $\times$  density

$$= v \times 1 = v \text{ g}$$

Temperature rise of mixture,  $\theta = (\theta_2 - \theta_1)^\circ\text{C}$

Heat gained by mixture =  $(v \times 4.2 \times \theta) \text{ J}$

$$= (4.2v\theta) \text{ J}$$

$$\text{Moles of CuSO}_4 = \frac{mv}{1000}$$



Mole ratio of  $\text{CuSO}_4 : \text{Cu} = 1 : 1$

$$\text{Therefore, moles of Cu displaced} = \frac{mv}{1000}$$

Hence,

$$\frac{mv}{1000} \text{ moles of Cu displaced with evolution of } (4.2v\theta) \text{ J of heat}$$

$$1 \text{ mole of Cu displaced with evolution of } \left( \frac{4.2v\theta \times 1000}{mv} \right) \text{ J of heat}$$

$$= \left( \frac{4.2v\theta \times 1000}{1000 \times mv} \right) \text{ kJ of heat}$$

$$= \left( \frac{4.2\theta}{m} \right) \text{ kJ}$$

$$\text{Therefore, heat of displacement} = - \left( \frac{4.2\theta}{m} \right) \text{ kJ mol}^{-1}$$

### **EXERCISE**

When excess zinc powder was added to  $100\text{cm}^3$  of  $0.2\text{M}$  copper(II) sulphate solution, the temperature of the solution rose from  $20^\circ\text{C}$  to  $30^\circ\text{C}$ . Calculate the heat of displacement of copper by zinc.

( Density of water =  $1\text{gcm}^{-3}$  , Specific heat capacity of water =  $4.2\text{Jg}^{-1}\text{K}^{-1}$  )