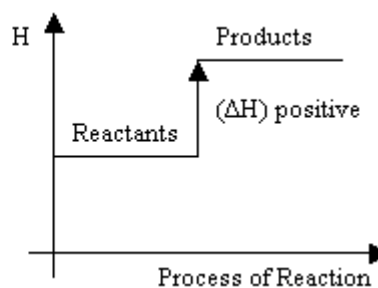
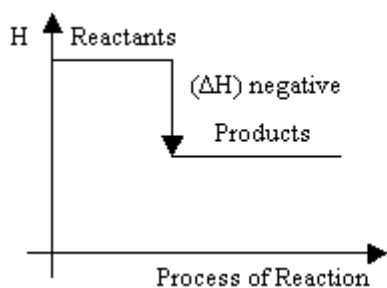


UNIT 4

INTRODUCTION TO PHYSICAL CHEMISTRY

PART 1 – ENERGY CHANGES



Contents

1. Energy Transfer in Chemical Reactions
2. Measuring Energy Changes

Key words: enthalpy, enthalpy change, exothermic, endothermic, enthalpy level diagram, molar enthalpy change, enthalpy of formation, enthalpy of combustion, enthalpy of neutralisation, enthalpy of solution, energy content

Units which must be completed before this unit can be attempted:

Unit 1 – Atomic Structure and the Periodic Table

Unit 2 – Particles, Structure and Bonding

Unit 3 – Amount of Substance

1. Energy Transfers in Chemical Reactions

Potential energy is a type of energy resulting from the attraction or repulsion between different particles.

Particles which repel each other have a positive potential energy. As repelling particles are forced closer together, their potential energy increases. As they move further apart, their potential energy decreases until they are an infinite distance apart and they have zero potential energy.

Particles which are attracted to each other have a negative potential energy. As attracting particles get closer together, their potential energy becomes more negative (ie it decreases). As attracting particles are pulled further apart, their potential energy becomes less negative (ie it increases) until they are pulled an infinite distance apart and they have zero potential energy.

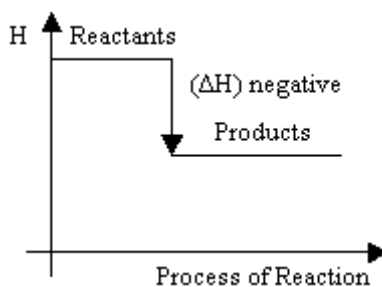
All chemical substances are held together by the attraction between protons and electrons. All chemical substances therefore have a negative potential energy (called **chemical potential energy**). The stronger the attractive forces holding the substance together, the more negative (ie the lower) the potential energy of the substance and the more stable it is.

Chemical potential energy is also known as **enthalpy** and is given the symbol H .

When a chemical reaction takes place, the products and reactants have different potential energies and thus there is a change in enthalpy. However since **total energy is always conserved**, any change in enthalpy must be balanced by an equal and opposite change in kinetic, or heat energy. The change in enthalpy during a chemical reaction is shown by the symbol ΔH .

(a) Exothermic reactions

In some reactions, the products are more stable than the reactants. The products therefore have a lower enthalpy than the reactants, and the enthalpy of the reacting species decreases. This can be shown in an **enthalpy level diagram**:



In these reactions the enthalpy decreases so there is a negative enthalpy change. ($\Delta H = -ve$). Since the total energy is always conserved, the heat energy of the species must increase by an equal amount. The surrounding temperature therefore increases.

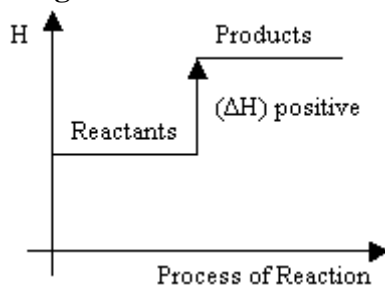
In these reactions, there is a transfer of energy from chemical potential energy to heat energy and an increase in temperature. Such reactions **give out heat** and are said to be **EXOTHERMIC**.

In practice, not all of the energy will be transferred into heat (kinetic) energy. In some cases, sound energy will be produced as well. It is also possible in some cases to produce electrical energy rather than heat energy. But the loss in chemical potential energy will always be equal to the total gain in heat, kinetic, electrical or sound energy.

(b) Endothermic reactions

In other reactions, the reactants are more stable than the products. The products therefore have a higher enthalpy than the reactants, and the enthalpy of the reacting species increases.

This can be shown in an **enthalpy level diagram**:



In these reactions the enthalpy increases so there is a positive enthalpy change. ($\Delta H = +ve$). Since the total energy is always conserved, the heat energy of the species must decrease by an equal amount. The surrounding temperature therefore decreases.

In these reactions, there is a transfer of energy from heat energy to chemical potential energy and a decrease in temperature. Such reactions **absorb heat** and are said to be **ENDOTHERMIC**.

2. Measuring Energy Changes

(a) Molar Enthalpy Changes

The enthalpy change depends on the amount of substance used. It is therefore necessary to specify the amount of reactants used when recording energy changes.

Enthalpy changes are generally measured per mole of reacting substance and typically have units of kJmol^{-1} . This is the **molar enthalpy change** of a reaction.

Given a reaction: $A + 3B \rightarrow 2C + 4D$

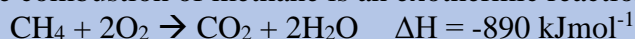
The enthalpy change for this reaction, in kJmol^{-1} , is taken to be the enthalpy change when one mole of A reacts with three moles of B to give two moles of C and four moles of D.

Eg If 0.2 moles of A react with 0.6 moles of B, 200 kJ of energy are released. What is the molar enthalpy change of the reaction?

Answer: If 0.2 moles of A releases 200 kJ, 1 mole must release $200/0.2 = 1000$ kJ
so the molar enthalpy change is -1000 kJmol^{-1}

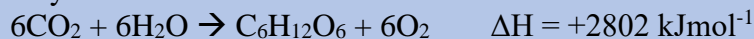
Test Your Progress: Topic 4 Part 1 Exercise 1

1. The combustion of methane is an exothermic reaction:



- What will be the enthalpy change for the following reaction? $\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_4 + 2\text{O}_2$
- Calculate the heat energy released when 100 g of methane is burned
- Calculate the heat energy released when 500 cm^3 of methane is burned at 298 K and 300 kPa
- Calculate the mass of methane required to produce 50,000 kJ of heat energy

2. Photosynthesis is an endothermic reaction:



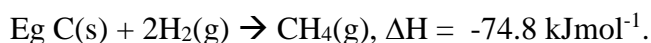
- What will be the enthalpy change for the following reaction? $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$
- Calculate the amount of light energy required to make 1000 g of glucose
- Calculate the amount of light energy required to absorb 500 cm^3 of carbon dioxide is at 298 K and 100 kPa
- Calculate the mass of glucose which can be made when a tree absorbs 10,000 kJ of light energy

(b) Definitions of special enthalpy changes

The enthalpy changes of some reactions are frequently used in chemistry and so have been given special names:

(i) Enthalpy of formation

The **enthalpy of formation** of a substance is **the enthalpy change when one mole of that substance is formed from the most stable allotropes of its elements in their standard states.**



The enthalpy of formation of methane is -74.8 kJmol^{-1} .



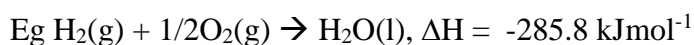
The enthalpy of formation of water is $-285.8 \text{ kJmol}^{-1}$.

The standard enthalpy of formation of all elements in their standard states is zero.

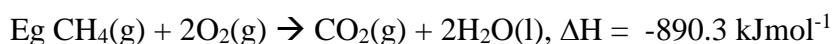
It is usually not possible to measure enthalpies of formation directly.

(ii) Enthalpy of combustion

The **enthalpy of combustion** of a substance is the enthalpy change when one mole of that substance is burned in an excess of oxygen.



The enthalpy of combustion of hydrogen is $-285.8 \text{ kJmol}^{-1}$.



The enthalpy of combustion of methane is $-890.3 \text{ kJmol}^{-1}$.

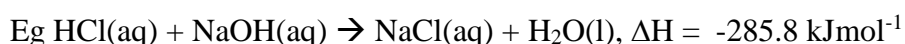
Burning a substance in oxygen is almost always exothermic, so standard enthalpies of combustion almost always have negative values.

Substances which do not support combustion, like water, carbon dioxide and most other oxides, have zero enthalpy of combustion.

It is usually possible to measure enthalpies of combustion directly.

(iii) Enthalpy of neutralisation

The **enthalpy of neutralisation** of an acid and a base is the enthalpy change when one mole of water is formed by the reaction of that acid with that base.



The enthalpy of neutralisation of HCl by NaOH is -57.3 kJmol^{-1} .

It is usually possible to measure enthalpies of neutralisation directly.

(iv) Enthalpy of solution

The **enthalpy of solution** is the enthalpy change when one mole of a substance is dissolved in an excess of water.

Eg $\text{NaCl(s)} \rightarrow \text{NaCl(aq)}$, $\Delta H = +11.1 \text{ kJmol}^{-1}$

The enthalpy of solution of NaCl is $+11.1 \text{ kJmol}^{-1}$.

It is usually possible to measure enthalpies of solution directly.

(c) Practical measurement of enthalpy changes

Enthalpy changes are generally measured by carrying out a reaction under controlled conditions in a laboratory and measuring the temperature change.

The amount of heat required to change the temperature of a system by 1K is known as the heat capacity of a system (H_c). It is measured in JK^{-1} .

The heat energy change (q) for a given reaction can therefore be calculated from the temperature change (ΔT) from the equation:

$$q = \Delta T \times H_c$$

The **specific heat capacity (c)** is the amount of heat required to heat 1g of a substance by 1K.

So heat capacity = specific heat capacity x mass

mass = volume x density

So: heat capacity = specific heat capacity x volume x density

$q = V\rho c\Delta T$ $\text{or } q = mc\Delta T$

If a reaction is taking place in solution (and therefore water is the main species present) it is reasonable to assume that the solution behaves as if it were pure water.

The density of water is 1.0 gcm^{-3} and the specific heat capacity of water is $4.18 \text{ Jg}^{-1}\text{K}^{-1}$.

The enthalpy change can then be calculated by dividing the energy change by the number of moles of reactants.

If the temperature goes up the enthalpy change is negative. If the temperature goes down the enthalpy change is positive.

Eg: Zinc will displace copper from copper (II) sulphate solution according to the following equation: $\text{CuSO}_4(\text{aq}) + \text{Zn(s)} \rightarrow \text{Cu(s)} + \text{ZnSO}_4(\text{aq})$

If an excess of zinc powder is added to 50 cm^3 of 1.0 mol dm^{-3} copper(II) sulphate, the temperature increases by $6.3 \text{ }^\circ\text{C}$. Calculate the molar enthalpy change for the reaction.

Answer: mass of solution being heated = volume x density = $1 \times 50 = 50 \text{ g}$

Heat change = $50 \times 4.18 \times 6.3 = 1317 \text{ J} = 1.317 \text{ kJ}$

Moles of $\text{CuSO}_4 = 50/1000 \times 1 = 0.05$

Molar enthalpy change = $1317/0.05 = 26.3 \text{ kJmol}^{-1}$

Temperature increased, so reaction exothermic, so sign should be -ve: **26.3 kJmol^{-1}**

Practical: determine the molar enthalpy of solution of ammonium chloride (NH₄Cl)

- 1) Place a clean, dry polystyrene cup inside a glass beaker.
- 2) Pour 100 cm³ of water into the cup using a measuring cylinder. Record the initial temperature of the water.
- 3) Use a weighing boat to weigh out approximately 5 g of ammonium chloride. Record the exact mass used.
- 4) Add the ammonium chloride to the water and stir continuously, until the temperature either remains constant for over a minute or starts to change in the opposite direction. Record the final temperature reached.
- 5) Deduce the temperature change, and hence the heat energy change q ($100 \times 4.18 \times \Delta T$, then convert to kJ).
- 6) Deduce the moles (n) of ammonium chloride used ($m/53.5$).
- 7) Hence deduce the molar enthalpy change of solution of ammonium chloride (q/n); don't forget to include a sign in your answer (-ve if exothermic, +ve if endothermic)

Practical: determine the molar enthalpy of neutralisation of hydrochloric acid by sodium hydroxide according to the equation $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$

- 1) Place a clean, dry polystyrene cup inside a glass beaker.
- 2) Pour 25 cm³ of 1 mol dm⁻³ HCl into the cup using a measuring cylinder. Record the initial temperature of the solution.
- 3) Measure out 25 cm³ of 1 mol dm⁻³ NaOH using a measuring cylinder and record the initial temperature of the solution. Hence deduce the average initial temperature of the solutions.
- 4) Add the NaOH solution to the HCl solution and stir continuously, until the temperature either remains constant for over a minute or starts to change in the opposite direction. Record the final temperature reached.
- 5) Deduce the temperature change, and hence the heat energy change q ($50 \times 4.18 \times \Delta T$, then convert to kJ).
- 6) Deduce the moles (n) of water formed ($(25/1000) \times 1 = 0.025$)
- 7) Hence deduce the molar enthalpy change of neutralisation of HCl by NaOH (q/n); don't forget to include a sign in your answer (-ve if exothermic, +ve if endothermic)

Test Your Progress: Topic 4 Part 1 Exercise 2

1. When 5.73 g of sodium chloride (NaCl) dissolves in 100 cm³ of water, the temperature of the water fell from 22.4 °C to 19.8 °C. Calculate the molar enthalpy of solution of NaCl.
2. When 2.3 g of magnesium chloride (MgCl₂) dissolves in 200 cm³ of water, the temperature rose by 3.4 °C. Calculate the molar enthalpy of solution of MgCl₂.
3. If 50 cm³ of 0.1 mol dm⁻³ HCl and 50 cm³ of 0.1 mol dm⁻³ NaOH are mixed, the temperature of the solution rises by 0.68 °C. Calculate the molar enthalpy of neutralisation of HCl by NaOH.
4. If 50 cm³ of 1.0 mol dm⁻³ NaOH is added to 25 cm³ of 2.0 mol dm⁻³ CH₃COOH, the temperature rose by 8.3 °C. Calculate the molar enthalpy of neutralisation of CH₃COOH by NaOH.

Practical: determine the molar enthalpy of combustion of ethanol (C₂H₆O)

1. Using a measuring cylinder, pour 100 cm³ of water into a copper can.
2. Mount the can on a clamp stand and record the initial temperature of the water.
3. Take a spirit burner containing ethanol, and record its mass with the lid on.
4. Remove the lid, place the spirit burner under the calorimeter and surround it with a windshield to protect it from wind currents.
5. Light the spirit burner and allow it to heat the copper calorimeter until the temperature of the water has increased by 30 °C. Record the final temperature of the water and deduce the temperature change.
6. Put out the spirit burner by putting the lid back on.
7. Weigh the spirit burner again and record the loss in mass.
8. Calculate the heat energy change (q) in the reaction (100 x 4.18 x ΔT, then convert to kJ)
9. Use the loss in mass to determine the number of moles of ethanol used (n) (m/46)
10. Hence calculate the molar enthalpy of combustion of ethanol (q/n); don't forget to include a sign in your answer (-ve if exothermic, +ve if endothermic)

Test Your Progress: Topic 4 Part 1 Exercise 3

1. A spirit burner containing ethanol (C₂H₅OH) was used to heat 100 cm³ of water in a copper can by 30 °C. As a result, the mass of the spirit burner decreased by 0.62 g. Calculate the molar enthalpy of combustion of ethanol.
2. A spirit burner containing butan-1-ol (C₄H₉OH) was used to heat 200 cm³ of water in a copper can by 20 °C. As a result, the mass of the spirit burner decreased by 0.81 g. Calculate the molar enthalpy of combustion of butan-1-ol.

(d) Using enthalpy changes

Understanding enthalpy changes is very useful for knowing how much energy it is possible to get from a certain quantity of fuel when it reacts exothermically. This quantity is known as the **energy content** of a fuel and it can be measured in kJmol⁻¹ or kJg⁻¹.

Eg wood has an energy content of 17 kJg⁻¹
 coal has an energy content of 31 kJg⁻¹
 hydrogen has an energy content of 142 kJg⁻¹

The measurement of the energy content of fuels by burning a fixed quantity of the fuel and measuring the temperature rise of a fixed amount of water is known as **calorimetry**.

It is also possible to measure the energy content of foods in the same way. Most carbohydrates have an energy content of around 17 kJg⁻¹ and most fats have an energy content of around 39 kJg⁻¹.

A typical human needs to consume around 10,000 kJ per day. This is equivalent to around 250 g of pure fat or around 600 g of pure carbohydrate.