‘A’ LEVEL

CHEMISTRY
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STUDY PACK

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S. Madzingira

Director

CHAPTER 1

Atoms, Molecules and Stoichiometry

Chemical reactions consume and produce materials. There is need at times to calculate the quantities of these materials. For example the objective of doing titrations is to enable the determination of concentrations of samples. The procedure of titration is based on the determination of reacting quantities. The chemistry concerned with the calculation of reacting quantities is called stoichiometry. To be able to do these calculations, one requires knowledge of relative atomic and molecular masses. Balanced reaction equations are crucial in stoichiometric calculations. Reactants and products are all related through the moles. The mole provides a convenient way of counting things in chemistry hence one must have sound understanding of the mole concept, relative atomic and molecular masses .

Content

2.1 Relative Masses of Atoms and Molecules

2.2 The mole concept

2.3 Relative atomic and molecular masses from mass spectra

2.4 Empirical and molecular formulae of compounds

2.5 Chemical reactions

2.6 Stoichiometric calculations

2.7 Summary

Learning outcomes

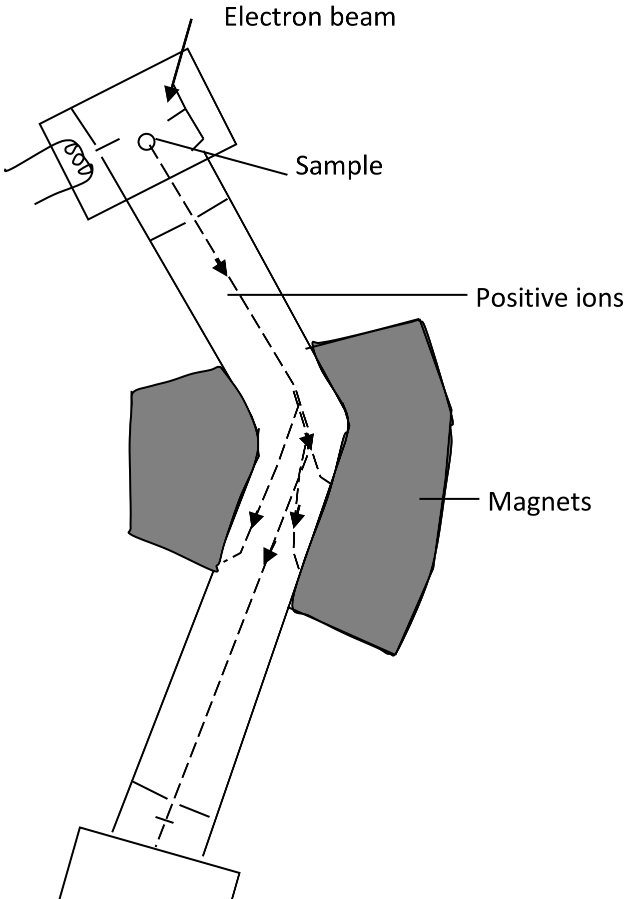
On completion of the chapter, the student should be able to:

- define relative atomic mass based on ^{12}C scale
- explain how relative atomic masses are determined
- calculate the relative atomic mass of an element given the relative abundances of the isotopes of the element
- interpret mass spectra of elements and molecular compounds

- describe the mole based on Avogadro's number
- define empirical and molecular formula
- calculate empirical and molecular formulae from combustion or composition by mass data
- balance chemical equations
- calculate masses of reactants and products
- calculate volumes of reactants and products
- determine the limiting reagent in a reaction
- calculate reacting quantities for reactions occurring in solution

1.1 Relative Masses of Atoms and Molecules

The system of atomic masses is based on ^{12}C as the standard and ^{12}C is assigned a mass of 12 atomic mass units (amu). All other atoms are given masses relative to the ^{12}C standard. The masses of atoms are compared using an instrument called a mass spectrometer. The schematic diagram of the mass spectrometer is given below.



The instrument operates as follows:

Atoms or molecules are passed into a beam of electrons moving at high speed. The electrons convert the atoms or molecules being analysed into positively charged ions by removing electrons from them. The positive ions pass through an electric field which accelerates them towards a magnetic field. Accelerating ions create their own magnetic field The interaction between the two magnetic fields results in the ion being deflected and the amount of deflection for each ion depends on its mass. The heaviest ion is deflected the least; therefore ions of different masses separate. Comparison of the areas where the ions hit the detector plate enables the accurate determination of their relative masses.

Example: When the masses of ^{12}C and ^{13}C are compared in a mass spectrometer their ratio is found to be:

$$\frac{Mass\ of\ ^{13}C}{Mass\ of\ ^{12}C} = 1.0836$$

^{12}C was assigned a mass of 12amu. If this is substituted into the above relationship, then the mass of ^{13}C can be deduced.

$$Mass\ of\ \ ^{13}C = 1.0836 \times 12amu$$

$$= \ \ 13.003\,amu$$

The masses of other atoms can be deduced in the same manner. The relative atomic mass of an element contains the same number of atoms as contained by carbon -12 in 12g of carbon-12.

Relative atomic masses for elements with isotopes

Though carbon -12 was assigned a mass of exactly 12amu, its mass number as shown in the periodic table is 12.01 or is not 12. The reason is that, the carbon found in nature is a mixture of isotopes ^{12}C, ^{13}C and ^{14}C. These have different numbers of neutrons but the same number of protons. The atomic mass of 12.01 is an average value which is calculated taking into account the relative abundances of the three isotopes. Natural carbon consists of 98.89% of ^{12}C, 1.11% of ^{13}C and the amount ^{14}C is negligible therefore only 12C and 13C contribute to the average value. The relative atomic mass is obtained as follows:

98.89% of 12amu +1.11% of 13.003

= (0.9889x12amu) + (0.011x13.003amu) = 12.01amu.

12.01 is the atomic weight of carbon.

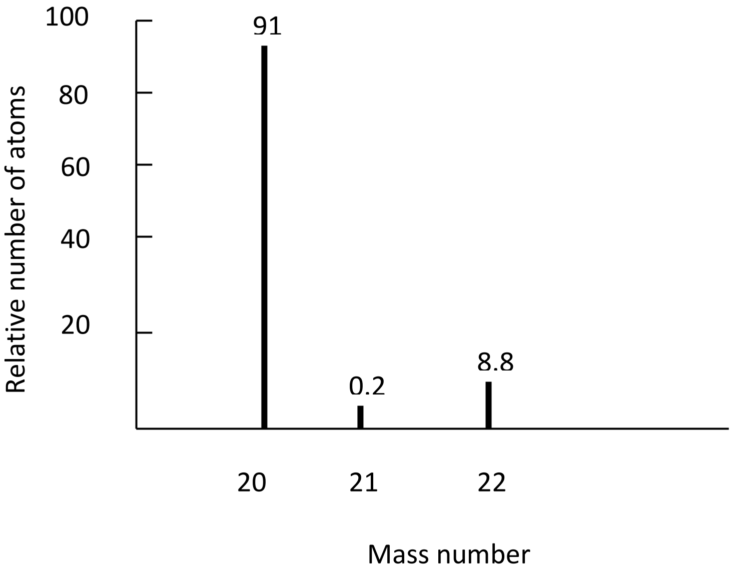
1.2 The Mole Concept

The mole is a unit of measure designed for counting atoms, molecules, electrons etc. It is defined as *the number equal to the number of particles in 12g of Carbon-12*. This number is equal to 6.022×10^{23}. It is called **Avogadro's Number**. 1 mole of aluminium means there are 6.022×10^{23} atoms of aluminum. 1 mole of water means there are 6.022×10^{23} molecules (i.e. H_2O) of water. It reduces the size of the figures to be used in calculations.

No of mols in a given mass = $\frac{mass\ given}{mass\ of\ 1\ mol\ of\ subs\tan ce}$

1.3 Relative atomic and molecular masses from mass spectra

The mass spectrometer is also used for determining the isotopes of a natural element. When a sample of a naturally occurring element is analysed in a mass spectrometer, a mass spectrum is obtained. It is a plot of the number of atoms against mass number. If the mass spectrum shows a number of peaks, then they are due to the isotopes of the element. The spectrum enables the determination of the masses of each isotope and their relative abundances. Below is a spectrum of natural neon



Therefore natural Neon has three isotopes ^{20}Ne, ^{21}Ne and ^{22}Ne. their relative abundances are 91%, 0.2% and 8.8% respectively.

The relative atomic mass of Neon is :

$0.91 x 20 + 0.002 x 21 + 0.088 x 22 \quad = \quad 20.18$

Relative Molecular Mass

The mass spectrum of a compound shows a variety of peaks that correspond to the various fragments of the molecule. The relative mass of the heaviest particle shown on a mass spectrum is that of the unfragmented particle with a positive charge. This mass is taken as the relative molecular mass of the compound. It is the sum of all the atomic masses of the elements making up the molecule.

Activity

1. Calculate the average relative atomic mass of each of the following elements:

   (a) Bromine (50.5% Bromine-79, 49.5% Bromine-81)

(b) Chromium (4.3% Chromium-50, 83.8% Chromium-52, 9.6% Chromium-53, 2.3% Chromium-54)

2. Determine the mass in grams of the following

(a) 3.0×10^{20} N_2 molecules

(b) 2.0×10^{-1} moles O_2.

3. How many moles are represented by 500.0g of Fe?

1.4 Empirical and molecular formulae of compounds

Empirical formula represents the simplest whole number ratio of the different types of atoms that make up a compound whereas the **molecular formula** represents the exact formula (if the atomic masses of the constituent elements are added, their sum is equal to the molar mass of the compound.

Two methods can be used to determine the formula of a compound. These involve the use of composition by mass data and combustion data. A weighed sample is either decomposed into its constituent elements or it is reacted with oxygen to produce CO_2, H_2O and N_2. The products are weighed. Results from such procedures provide the mass of each element in a compound which can be used to determine the composition of each element in the compound as a percentage. The following example illustrates how to deduce the formula of a compound.

Example

An organic substance is composed of carbon, hydrogen and nitrogen. When 0.1156 grams of the compound was burnt in oxygen, 0.1638g of carbon dioxide CO_2 and 0.1676g of Water H_2O were collected. Given that the molar mass of the organic compound is 62.12 deduce its empirical and molecular formulae.

Solution

Assuming all the carbon is converted to CO_2,

the fraction of carbon in terms of mass present in CO_2 is = $\frac{atomic\ mass\ of\ carbon}{molar\ mass\ of\ CO_2}$

$$= \frac{12}{44}$$

Mass of Carbon in 0.1638g of CO_2 $= \frac{12}{44} \times 0.1638 = 0.04470 g\ C$

Percentage of Carbon in the original sample $= \frac{0.04470}{0.1156} \times 100 = 38.674\%$

Mass of hydrogen in H_2O; =

$$\frac{2g\ H}{18g\ H_2O} \times 0.1676 g\ H_2O \quad = \quad 0.01862 g\ H$$

Percentage of Hydrogen in the sample $= \frac{0,01862g}{0.1156g\ org.compound} \times 100 \quad = 16.11\%\ H$

The amount of nitrogen as a percentage can now be determined.

% Nitrogen = 100% – (38.67% + 16.11%) = 45.22%

The compound contains 38.67% carbon, 16.11% hydrogen and 45.22% nitrogen.

A formula indicates the number of atoms in a compound, therefore the masses have to be converted to atoms. Since quantities are in percentages, it is convenient to assume 100g of the sample so that the percentage of each component becomes its mass. The number of atoms is calculated in mols

$$no\ of\ mols = \frac{given\ mass}{mass\ of\ one\ mol}$$

Carbon $\frac{38.67gC}{12.011gC} \times 1\ mol\ C = 3.22\ mol\ C$

Hydrogen $\frac{16.11gH}{1.008\ gH} \times 1\ mol\ H = \quad 15.98\ mol\ H$

Nitrogen $\frac{45.10g\ N}{14.007g\ N} \times 1\ mol\ N = 3.22\ mol\ N$

Therefore 100g of the sample contains 3.22 mols of carbon atoms, 16.10 mols of hydrogen atoms and 3.22 mols of nitrogen atoms.

To find the **empirical formula**, the simplest ratio in which the atoms exist in the compound has to be determined. This is done by dividing the calculated numbers of moles by the smallest number of moles i.e. 3.22

C: 3.22/3.22 = 1

H: 15.98/3.22 = 5

N: 3.22/3.22 = 1

The empirical formula is CH_5N, its molar mass is 31.06.

The **molecular formula** can also be determined since the molar mass is known. The molecular formula is a whole number multiple of the empirical formula. The number of empirical formula units in one molecule is calculated:

$$\frac{Molar\ mass}{Empirical\ \ formula\ mass}$$

The molar mass is 62.12 which is two times the molar mass of the empirical formula (i.e. 31.06). Therefore the number of atoms in the molecular formula is twice those in the empirical formula. The molecular formula is therefore $C_2H_{10}N_2$

Steps in determination of empirical formula

- Base calculations on 100g of compound. The percentage of each component becomes the mass of the element in the compound
- Determine the number of atoms (in moles) of each element present in 100g of compound : (mol =mass/molar mass)
- Divide each of the values you obtained above by the smallest value. The resulting numbers should be whole numbers. Round off if necessary. These numbers are the subscripts of the elements in the empirical formula
- If the numbers calculated above are not whole numbers, multiply each number by an integer to make them whole numbers.

Determination of molecular formula

Method 1

- Obtain the empirical formula
- Compute the empirical formula mass
- Calculate the number of empirical formula units present in one molecule
- Multiply the factor obtained in the calculation above by the subscripts in the empirical formula to obtain the molecular formula

Method 2

- Determine the mass of each element present in one mole of compound using mass percentages and the molar mass
- Determine the number of moles of each element present in one mole of compound.
- The integers from the above step form the subscripts in the molecular formula.

Activity

1. A monobasic organic acid has the composition by mass: C, 40%; H, 6.7%; O, 53.3%. What is its empirical formula?

1.5 Chemical equations

Chemical equations provide a way of describing changes that occur during a chemical reaction. An equation shows reactants and products.

$$\underbrace{H_2 \quad + \quad N_2}_{\text{Reactants}} \longrightarrow \underbrace{NH_3}_{\text{Product}}$$

Atoms are reorganized during a reaction. In the above representation,H-H and N≡ N bonds are broken and N-H bonds are formed. New products are formed during a reaction. No atoms are destroyed or created during a reaction. All atoms have to be accounted for in reactants and products. In the presentation above, there are two atoms of hydrogen yet on the right there are three hydrogen atoms. It would seem like a hydrogen has been created. Two nitrogen atoms on the left side and only one on the right again it seems as if a nitrogen atom has been destroyed. These atoms have to be accounted for by a process known as *balancing an equation*. The reaction below is balanced. The method of balancing chemical equations will be discussed later.

$$3H_2 + N_2 \longrightarrow 2NH_3$$

Often the physical states of components of a reaction are indicated. The symbols used are shown in the table below.

Table: State symbols

State	**symbol**
solid	*s*
Liquid	*l*
Gas	*g*
Dissolved in water (aqueous)	*aq*

The following reaction shows the use of state symbols. $CaCO_3$ is solid, Carbon dioxide is gaseous and so on

$$CaCO_3(s) + 2HCl(aq) \dashrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

Balancing chemical reactions

Since atoms are conserved during a reaction, their numbers must be the same in products and reactants. The formulae of reactants and products do not change during the process of balancing an equation. It follows therefore that the subscripts (numbers written in small print in front of a chemical symbol) in a formula cannot be changed. Atoms can not be added or subtracted from a formula.

Most reactions are balanced by inspection.

1. Identify the molecule with the greatest number of atoms

   For the reaction:

$$C_3H_7OH(l) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$$

Propanol (C_3H_7OH) has the greatest number of atoms

2. Balance the products that contain atoms in propanol

- Propanol contains three carbon atoms, therefore CO_2 is multiplied by 3

$$C_3H_7OH(l) \quad + \quad O_2(g) \rightarrow 3CO_2(g) + H_2O(l)$$

3 carbon atoms 3 carbon atoms

- There are eight hydrogen atoms in propanol, therefore H_2O is multiplied by 4 to give eight hydrogen atoms

$$C_3H_7OH(l) \quad + \quad O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$$

8 (i.e. 7+1) H atoms 8 (i.e. 4x2) H atoms

3. Balance oxygen atoms by considering the oxygen atoms on the right side since they are not to be disturbed. There are **10** oxygen atoms on the product side and only three on the reactants side. The O_2 on the reactants must be multiplied by a factor which will enable the oxygen atoms to be balanced. There is one oxygen atom on the propanol molecule therefore 9 Oxygen atoms are needed to make the total ten. Nine oxygen atoms can be obtained from O_2 by multiplying it by $\frac{9}{2}$.

$$C_3H_7OH(l) \quad + \quad \frac{9}{2}O_2(g) \rightarrow 3\,CO_2(g) + 4H_2O(l)$$

10 Oxygen atoms 10 Oxygen atoms

All types of atoms are now equal on either side of the arrow. The equation is balanced. However the fraction $\frac{9}{2}$ on O_2 can be eliminated without changing the way the equation is balanced. This is done by multiplying all terms by the denominator 2.

$$2C_3H_7OH(l) \quad + \quad 9O_2(g) \rightarrow 6CO_2(g) + 8H_2O(l)$$

In the reaction between Hydrogen and nitrogen to give ammonia

$$H_2(g) \quad + \quad N_2(g) \quad \rightarrow \quad NH_3(g)$$

NH_3 has the greatest number of atoms

Nitrogen is balanced by multiplying NH_3 (has less N atoms) by 2

$$H_2(g) \quad + \quad N_2(g) \quad \rightarrow \quad 2NH_3(g)$$

2 Nitrogen atoms 2 nitrogen atoms

There are now six hydrogen atoms (more H atoms) on NH_3, the hydrogen i.e H_2 is multiplied by a factor to make the total on the reactants side equal to 6 and that factor is 3.

$$3H_2(g) \quad + \quad N_2(g) \quad \rightarrow \quad 2NH_3(g)$$

6 hydrogen atoms 6 hydrogen atoms

The equation is now balanced

$$3H_2(g) \quad + \quad N_2(g) \quad \rightarrow \quad 2NH_3(g)$$

6 hydrogen atoms 6 hydrogen atoms

2 nitrogen atoms 2 nitrogen atoms

Activity

1. What information is supplied by a chemical equation:
2. Write balanced equations that describe each of the following.
    (a) Potassium metal reacts with water to produce aqueous potassium hydroxide and hydrogen gas
    (b) Barium oxide reacts with Nitric acid to produce Barium Nitrate and water.

1.6 Stoichiometric Calculations

The coefficients in chemical equations represent numbers of molecules. It is sometimes necessary to determine the amounts of reactants needed in a reaction or the amounts of products formed. These amounts may be required as mass or in terms of volume. The coefficients do not represent masses or volume but they are useful in determining the later. Stoichiometry is about the relationships found in a chemical equation.

All components in a balanced equation are related through their numbers of moles. For the reaction:

$$C_3H_8(g) \quad + \quad 5O_2(g) \quad \rightarrow \quad 3CO_2(g) \quad + \quad 4H_2O(g)$$

According to the reaction 1 mole of C_3H_8 reacts with 5 moles of O_2 to produce 3 moles of CO_2 and 4 moles of H_2O. In order to find masses of reactants or products, it is useful to be able to convert moles to mass. The coefficients only tell us the mole relationship between components. The actual moles have to be determined. The starting mass of one of the reactants must be known. Assuming that 96.1g of C_3H_8 are present at the beginning of the reaction, the number of moles of propane can be calculated;

$$moles \quad = \quad \frac{given\ mass}{molar\ mass}$$

The molar mass of propane = 44.1g

The mass present = 96.1g

Therefore $moles \quad = \quad \frac{96.1g}{44.1g} \times 1mol\ C_3H_8$

= 2.18 mol

To determine the actual number of moles of O_2 present, reference is made to the balanced reaction equation.

1 mole of propane reacts with 5 moles of oxygen

Therefore 2.18 moles of propane will react with five times as many oxygen moles

The number of moles of oxygen = mols C_3H_8 x $\frac{5mol\ O_2}{1mol\ C_3H_8}$

$= 2.18 \text{ x } \frac{5}{1}$

= 10.9 mol

This quantity can be converted into mass by multiplying mols by the molar mass of O_2(molar mass =32g).

$$= 10.9 \times 32g \qquad = \qquad 348.8g\ O_2$$

$\frac{5mol\ O_2}{1mol\ C_3H_8}$ is the Mole Ratio of the reactants

Determining the mass of CO_2

To find moles of CO_2, using the moles of propane

$$= \text{mols } C_3H_8 \times \frac{3mol\ CO_2}{1mol\ C_3H_8}$$

$$= 6.54 \text{ mol}$$

The molar mass of CO_2 is 44.0g

Therefore the mass of CO_2 produced for 96.1 g propane is 6.54 x 44g = 288g CO2.

Determining the mass of H_2O

$$\text{Moles of } H_2O = \quad \text{mols } C_3H_8 \times \frac{4mol\ H_2O}{1mol\ C_3H_8}$$

$$= \quad 8.72\text{mol}$$

Molar mass of water = 18g

Mass of H_2O produced from reaction 8.72 x 18g = 156.96g H_2O

Steps in calculation of masses of reactants and products

- Balance the equation for the reaction
- Convert known masses of the substances to moles
- Set up mole ratios from the balanced equation
- Use mole ratios to calculate the number of moles of the desired reactant or product
- Convert from moles back to grams if required from the question.

Gaseous reactants and products

Gaseous reactants and products are conveniently expressed as volume quantities. The quantity that enables volumes to be calculated is the **Molar Volume**. This is the volume occupied by one mole of any gaseous element at Standard Temperature and Pressure assuming ideal behaviour. Its value is 22.42 dm^3. From the calculations in the previous section, the number of moles of carbon dioxide produced in the reaction is 6.54 mol. The volume of CO_2 produced can be calculated thus;

Mols CO_2 x Molar volume

= 6.54 moles x 22.42 dm^3/mol

= 146.63 dm^3.

The volume of oxygen required to react with all the propane can be calculated from the number of moles of oxygen present (i.e. 10.9mol)

Moles O_2 x Molar mass

= 10.9 mol x 22.42 dm^3/mol

= 244.38 dm^3

Once the number of moles of the reactant or product has been determined the volume is obtained by multiplying the number of moles by the Molar volume.

Calculations involving limiting reagent

Normally reactants are mixed in stoichiometric amounts so that they are all used up during the reaction. In the reaction between propane and oxygen, if less than the stoichiometric amount of oxygen were supplied, not all the 96.1 grams of propane were going to react. The amount of propane that reacts is limited by the amount of oxygen present. Oxygen is said to be the **limiting reagent** and propane is in excess. The amounts of products formed depend on the quantity of the limiting reagent present.

Example

25.0g of Nitrogen and 5g of hydrogen are mixed to form Ammonia. Determine the limiting reagent and the amount of ammonia produced.

The number of moles of each reactant are first calculated. Molar mass N_2 =28.0g, H_2 = 2.016

25g N_2 x 1 mol/28.0g = 0.893 mol

5g H_2 x 1 mol/ 2.016g= 2.480 mol

The balanced reaction is

$$3H_2(g) \quad + \quad N_2(g) \quad \rightarrow \quad 2NH_3(g)$$

Nitrogen reacts with hydrogen in the ratio 1:3. The moles of hydrogen that will react with 0.893 mol of Nitrogen are :

Mols N_2 x 3

0.893 x 3 = 2.679g H_2

Only 2.480g of H_2 are available yet 2.679 are required therefore H_2 is the limiting reagent. The amount of ammonia present is determined by the amount of hydrogen present.

Moles of Ammonia present = mole ratio x mols H_2

$$= \frac{2}{3} \times 2.480 mol\ NH_3$$

= 1.653 mol

Mass of Ammonia produced = mols NH_3 x Molar mass NH_3

= 1.653 mol x 17g/mol

=28.10g

Steps in solving stoichiometric calculations involving limiting reagent

- Balance the equation for the reaction
- Convert known masses of the substances to moles
- Compare the mole ratio of reactants as per the stoichiometry of the reaction to the mole ratio of the reactants actually present. Deduce the limiting reagent.
- Calculate the number of moles of the desired component basing on the amount of the limiting reagent
- Convert moles to mass using the molar mass value or moles to volume using molar volume.

Solutions and Stoichiometry

Solutions are described in terms of volume and concentration. Concentration is the amount of solute in a unit volume of the solution. The amount in solution can be stated as a mass, in which case the units can be g/dm^3. It is very common to convert the grams to moles so that the concentration is expressed as Mol/ dm^3. When concentration is expressed in mol/dm^3 the term **Molarity** is used.

$$\text{Concentration (mol/dm}^3\text{)} \quad = \frac{moles\ of\ solute}{volume}$$

Therefore if volume and concentration of solution are known, the moles of solute can be determined.

Example

How many moles of NaOH are present in 25 ml of 0.1 mol/dm^3?

Rearranging the formula above

$$\begin{aligned}\text{Mols NaOH} &= \text{Concentration NaOH x Volume}\\ &= 0.1\text{mol/dm}^3 \text{x } 25/1000\ \text{dm}^3\\ &= 0.0025\ \text{mol}\end{aligned}$$

Moles can be converted to mass using the molar mass/ formula weight.

Example

What is the volume of 0.1mol/dm^3 H_2SO_4 required to react completely with 25ml of 0.1mol/dm^3 NaOH?

The balanced equation is:

$$H_2SO_4(aq) \quad + \quad 2NaOH(aq) \rightarrow \quad Na_2SO_4(aq) + 2H_2O(aq)$$

The moles of NaOH in 25ml have already been calculated and are equal to 0.0025. According to the equation above, the number of moles of H_2SO_4 that will react with NaOH is half those of NaOH.

Mols H_2SO_4 = Mole ratio x mols NaOH

= ½ x 0.0025 mols

= 0.00125mol H_2SO_4

From the relationship;

$$\text{Concentration (mol/dm}^3\text{)} = \frac{moles\ of\ \ solute}{volume}$$

$$volume = \frac{moles\ ofsolute}{concentration}$$

$$= \frac{0.00125}{0.1} = 0.0125\ \text{dm}^3$$

or 12.5 ml

1.7 Summary

- The relative atomic mass is the ratio of the mass of a particular atom to 1/12 of the mass of an atom of carbon -12.
- The relative atomic mass is measured using a mass spectrometer.

- The empirical formula is the simplest ratio of the different types of atoms making up a compound
- The molecular formula shows the numbers of atoms of each atom present in a formula.
- Stoichiometry is the chemistry concerned with the calculation of quantities of reactants or products.
- The reagent in short supply is the limiting reagent for a reaction.
- The amount of products produced in a reaction will depend on the amount of the limiting reagent.

Examination Type Questions

1.(a) What do you understand by the term relative atomic mass? [2]

(b) Naturally occurring Gallium, Ga is a mixture of two isotopes, gallium-69 and gallium-71. Use this information together with the relative atomic mass given in the data booklet to calculate the percentage abundance of each isotope. [4]

(c) The mass spectrum of chlorine, Cl_2 (g), consists of peaks at m/e values of 70, 72 and 74 of relative abundance 9:6:1. Explain the source of these peaks. [4]

2. When chlorine is bubbled through a concentrated aqueous solution of ammonium chloride, a yellow oily liquid, nitrogen trichloride, NCl_3, is formed, together with a solution of hydrochloric acid. Nitrogen trichloride is hydrolysed by aqueous sodium hydroxide, producing ammonia gas and a solution of sodium chlorate(I).

(a) Write balanced equations for the formation and hydrolysis of nitrogen trichloride. [2]

(b) Apart from peaks associated with solitary nitrogen (at m/e -14) and chlorine atoms (at m/e -35 and m/e-37), the mass spectrum of nitrogen trichloride contains 9 peaks arranged in 3 groups, ranging from m/e -49 to m/e-125. predict the m/e values of all 9 peaks, and suggest a formula for the species responsible for each one. [18]

CHAPTER 2

ATOMIC STRUCTURE

One of the main postulates of John Dalton (1766-1844)'s atomic theory is that matter is made up of atoms. The theory also points out that atoms of different elements are different. It does not explain in what way or how the atoms of elements differ. Therefore it is not possible to explain the behavior of matter. Further studies in this area have shed more light on the structure of the atom. It is now known that an atom has three subatomic particles: Protons, neutrons and electrons. Atoms of different elements are different because they contain different numbers of these subatomic particles. Elements are now known to interact through the electrons and their atoms and the number and arrangement of the electrons gives an element its chemistry. The aim of this chapter is to develop or make clear the concept of an atom based on the properties and arrangement of the sub-atomic particles.

Content

Learning objectives

On completion of this chapter, students should be able to:

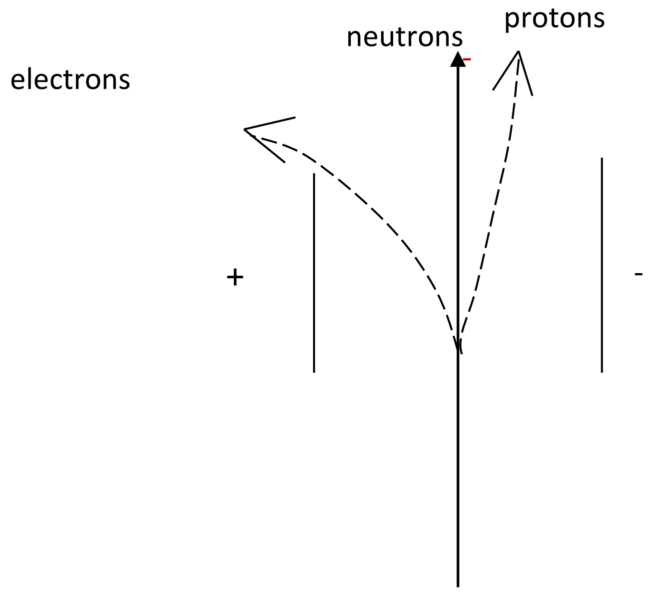
- identity protons, neutrons and electrons in terms of their relative charges and relative masses.
- deduce the behaviour of protons, neutrons and electrons in an electric field.
- represent elements using the nuclide notation.
- define the terms, atomic number, and atomic mass.
- describe the distribution of charge in an atom.
- deduce numbers of protons, electrons and neutrons in an atom.
- differentiate isotopes of an element on the basis of different numbers of neutrons present.
- explain how ions are formed.
- write electronic configuration of elements.
- describe the relative energies of orbitals.
- describe the shapes of s and of p-orbitals.
- define the term ionisation energy.
- explain trends in ionisation energy down a group and along a period.
- use successive ionisation energies to deduce the position of an element in the periodic table.
- deduce electronic configuration from successive ionisation energies.

2.1 Composition of Atoms

Atoms are the smallest units of matter. The term matter refers to anything that has mass and volume. Three fundamental particles make up the atom. These are; protons, neutrons and electrons.

2.1.2 Behaviour of sub-atomic particles in an electric field

If a beam of these particles is passed through an electric field, electrons are defected towards the anode (positive terminal), therefore electrons must carry a negative charge. Protons are deflected towards the negative terminal (cathode). They must be positively charged. Neutrons are not affected by an electric field. They are electrically neutral. The smaller the mass the greater the deflection.



The table below lists the properties of subatomic particles.

Particle	Relative mass	Relative electric charge
Proton	1	+1
Neutron	1	0
Electron	1/18 39	-1

Table 1: Properties of sub-atomic particles

Location of subatomic particles

Protons and neutrons are in the nucleus. Therefore the nucleus is positively charged. Protons and neutrons are called nucleons. Electrons are bound by the nucleus' positive charge in orbitals around the nucleus.

2.2. The Nuclide Notation

An atom is electrically neutral since the number of protons in the nucleus of an atom is equal to the number of electrons. The number of protons is the atomic number (also called proton number) of an element. It has the symbol Z. Atoms of the same element have the same atomic number. This number identifies a particular element. This is because Z determines the number of electrons an element has, its electron structure and hence its physical and chemical properties. The mass number, assigned the symbol A, is the sum of protons and neutrons in the nucleus of an atom. The mass number is also called the nucleon number. The neutron number N is the difference between the mass number and the number of protons. Only protons and neutrons contribute to the mass of an atom, the mass of electrons being negligible.

The composition of a nuclide is written alongside its chemical symbol. This is its nuclide notation and the figure below illustrates the nuclide notation of nitrogen. The chemical symbol for nitrogen is N.

$$^{14}_{7}\mathbf{N}$$

Mass number is 14 and the atomic number is 7. A nuclide is any nuclear species of given mass number (A) and atomic number (Z). For $^{208}_{82}Pb$ there are 82 protons, 82 electrons and 208-82= 126 neutrons.

2.3 Isotopes

Isotopes are atoms of the same element with different numbers of neutrons and therefore different mass numbers. Isotopes of a given element are chemically identical since they have the same number of electrons. The terms 'heavier' and 'lighter' isotope are used to distinguish between the isotope with bigger mass number and the one with smaller mass number.

Examples of Isotopes

Hydrogen has the isotopes with mass numbers 1, 2 and 3. The nuclide notations are shown below.

$^{1}_{1}H \quad ^{2}_{1}H and\, ^{3}_{1}H$

The isotopes have 0, 1 and 2 neutrons respectively. The isotopes are sometimes represented as 1_H, 2_H and 3_H or hydrogen-1, hydrogen-2 and hydrogen -3.

Sodium (Na) has two isotopes ^{23}Na and ^{24}Na with mass numbers 23 and 24. Neutron numbers are 12 and 13 respectively.
The relative atomic mass of an element is the weighted average of all the masses of isotopes present taking into account isotopic relative abundances.

2.4 Formation of ions

Ions are formed when atoms lose or gain electrons. An atom is electrically neutral before electron loss or gain. During reactions the numbers of electrons change. Electrons can be transferred form one element to another.

2.4.1 Cations

These are positive ions formed by loss of electrons. The cation will have more protons than electrons. Therefore it will carry a net positive charge. The magnitude of the charge depends on the number of electrons lost. It increases as more electrons are lost Mg^{2+} 10 electrons, 12 protons, 12 neutrons.

2.4.2 Anions

These are negative ions formed when atoms gain electrons. An anion has more electrons than protons.

${}^{35}_{17}Cl$	17 electrons 17 protons **18 neutrons**
O^{2-}	**10 electrons** **8 Protons** **8 Neutrons**

2.5 Electronic Structure Of Atoms

Electrons are arranged in energy levels or shells around the nucleus. The energy levels are energetically defined and are at a specific distance form the nucleus

Each electron in an atom occupies a particular energy level. The electrons first occupy the lowest available energy level closer to the nucleus. When the shell is full, the next electron will enter the next higher level available.

There is a maximum number of electrons that each shell can accommodate.

- The first shell can accommodate a maximum of 2 electrons.
- The second shell accommodates a maximum of 8 electrons.
- The 3rd shell will have a maximum of 18 electrons.

2.5.1 Simple Electronic configuration

If the proton number (atomic number) is known then the number of electrons can be deduced for an element. The basic electronic arrangement can be worked out.

Elements in period 1 have electronic arrangement which can be written as 1 for hydrogen and 2 for helium.

Elements in period 2 have electronic arrangement from 2,1 for Lithium up to 2, 8 for Neon

Li	2,1
Be	2,2
B	2,3
C	2,4
N	2,5
O	2,6
F	2,7
Ne	2,8

Elements in period 3 have electronic arrangements from 2.8.1 to 2.8,8. Period 4 from 2.8,8.1 to 2.8.18.8.

2.5.2 Extra nuclear structure

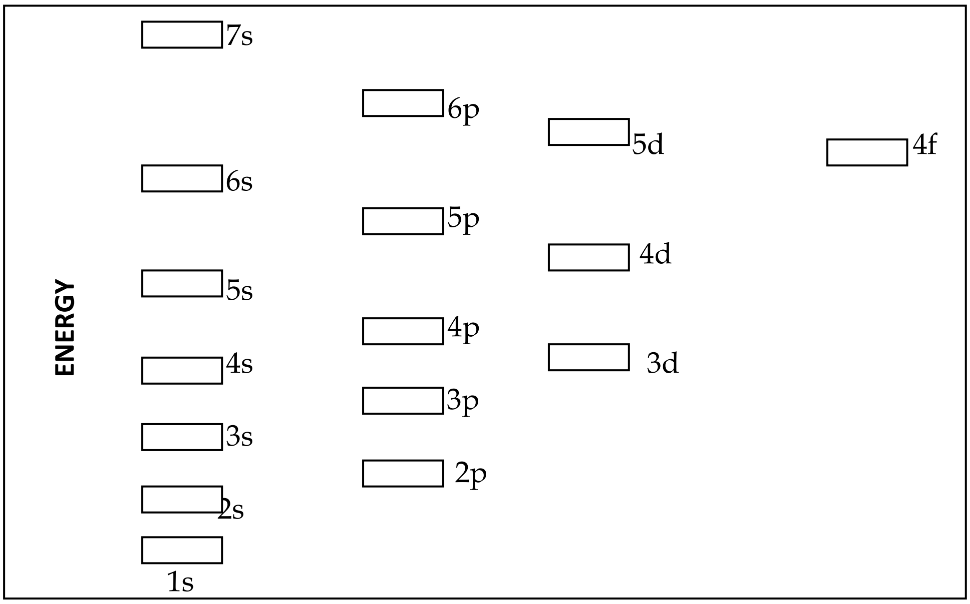
The main energy level/shell is capable of sub-division to from sub shells. It is necessary to be able to identify the various energy levels.

The number of the main energy level is called the principal quantum number and is designated the letter (n). It will have values 1, 2, 3 etc. corresponding to the shell number.

2.5.3 Relative energies of orbitals

The first shell lies at a lower energy and the electrons in it are strongly held by the nucleus than electrons in higher shells. Electrons in the highest shell are easily lost as little energy is needed to remove them. Orbitals of the same designation (i.e. s, p, d or f) are degenerate or have the same energy content. S orbitals are at a lower energy level followed by p then d and finally f. Electrons in a higher orbital are easily ionized than those in lower orbitals.

As the principal quantum number increases, the energy gap between successive shells gets smaller. Overlapping of orbitals occurs. For example the 3d is a higher energy level than the 4s orbital but below the 4p orbital.



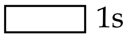
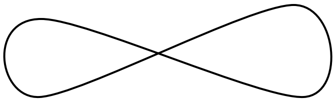


Figure 2.5.3 Orbital energies showing overlaps.

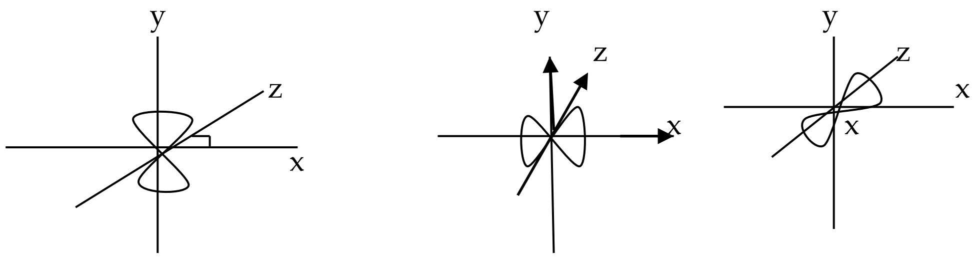
2.5.4 Shapes of orbitals

An orbital is the region around the nucleus where there is a high probability of finding electrons. The shapes of an orbital is simply a map of the electron density of an electron cloud. In an S orbital, electrons are likely to be found in a spherical region around the nucleus. An s orbital is therefore spherical, a 2s orbital being larger than a 1s; a 3s orbital in turn larger than the 2s etc.

Each of the p orbital has a dumb bell shape



There are three p orbitals and these are arranged in a three dimensional way



Py orbital Px orbital Pz orbital

They differ only in terms of their orientation in space. They lie on the different axes

2.5.5 Electronic configuration in terms of s,p,d and f

It is important to know electronic arrangements in atoms when they are in their ground state in order to establish any similarities that may exist among elements. Electron configuration is the distribution of electrons in different orbitals. The configuration indicates the principal quantum number, the orbital to which particular electrons belong and the number of electrons, e.g. $1s^2$ means principal energy level is 1. The orbital is s and there are two electrons.

Filling of orbitals is according to aufbau principle and Hund's rule.

Aufbau principle

The principle states that orbitals are occupied by electrons in order of increasing energy. This means the orbital of lowest energy will be filled first. When an orbital has the maximum number of electrons, the remaining electrons enter the next higher energy level.

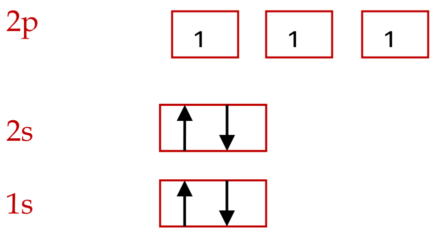
Hund's rule

This rule explains how a set of degenerate orbitals are occupied by electrons. The rule states that when filing degenerate orbitals, electrons will first occupy these orbitals singly with parallel spins before pairing.

Electronic configurations

Hydrogen has 1 proton therefore 1 electron only, the 1s orbital is available and the electron goes into this orbital. The configuration is $1s^1$. Helium, proton number 2 has one more electron, it also goes into the 1s orbital. The configuration of Helium is $1s^2$. Lithium has three electrons. The first 2 electrons go into the 1s orbital, the remaining electron goes into the next higher level (i.e. 2s). The configuration is $1s^2\ 2s^1$. This follows the aufbau principle. The 2s orbital is filled at Be . Boron with 5 electrons has the configuration $1s^2\ 2s^2\ 2p^1$.

So the p orbitals are filled from Boron to neon. Nitrogen has 7 electrons. It configuration is $1s^2$, $2s^2\ 2p^3$. The figure below illustrates how electrons are arranged in the orbitals according to Hund's rule.



Inert gas core notation

It is a shorthand method of writing electronic configurations. The electron configuration for Neon is $1s^2\ 2s^2\ 2p^6$. The next electron which will be present in sodium Na, will occupy the 3s orbital. The configuration of Na is $1s^2\ 2s^2\ 2p^6\ 3s^1$. In this configuration part of the configuration is that of Ne. That part is substituted with the representation [Ne] so that the configuration for Na becomes [Ne] $3s^1$. Mg has the configuration [Ne] $3s^2$
C1 has the arrangement [Ne] $3s^2\ 3p^5$. Ar has (Ne) $3s^2\ 3p^6$. The core [Ar] is then used for elements in the 4th energy level.
Ca= [Ar] $4s^2$. is filled before 3d. After the 4s is full, 3d orbitals are occupied so scandium will have the configuration [Ar] $4s^2\ 3d^1$. The 3d orbitals will be full at Zn. [z = 30]. The configuration is [Ar] $4s^2\ 3d^{10}$. The 3d orbitals fill up at Zinc. The next electron [of Gallum will enter the 4p orbital].

Ions

These are charged species formed by loss or gain of electrons. Hydrogen forms an ion by loss of its single electron.

$$\underset{Is^{I}}{H} \xrightarrow{-e} \underset{Is^{o}}{H^+}$$

Only a proton remains in the nucleus hence H^+ is called a proton. Mg forms Mg^{2+} ion. The electronic configuration changes from $1s^2\ 2s^2\ 2p^6\ 3s^2$ to $1s^2$, $2s^2$, $2p^6$ which is the same as that for Ne. The electronic configuration of the ion is said to be isoelectronic with that of neon. i.e. they have then same number of electrons.

Activity

1. Write electronic configurations for:
(i) A ℓ
(ii) Cl^-
iii) C
iv) Ca^{2+}

2. Write an ion that is isoelectronic with neon.

3. Use the inert gas core notation to write the electronic configurations of (i) Mn (ii) V (iii) Ge.

2.6 Ionisation Energies

Ionisation energy is the amount of energy required to remove one mole of electrons from a mole of gaseous atoms of an element.
It is the energy needed for the process:

$$X(g) \longrightarrow X^+(g) + e^-$$

Ionization energies provide useful information which can be used to verify the orbital model of the atom. The ionization energy value for a specific electron is an indication of the energy of the orbital the electron occupies in an atom.

2.6.1 Factors Influencing Ionisation Energy

1. Distance from nucleus hence atomic/ionic size
2. Charge on an ion
3. Shielding by inner electrons

Atomic size

The force of attraction between the nucleus and the outermost electrons is inversely proportional to the distance between the charges. (i.e. the nucleus is positive and electrons are negative). When the distance between the two is large (i.e. big atomic size) the electrons are loosely held and less energy is required to loose the outer electrons. More ionisation energy is required for smaller atoms.

Charge

When an ion is formed by loss of electrons, the resulting ion will have more protons than electrons. The remaining electrons become more tightly held by the nucleus. The amount of ionisation energy increases as the charge on the ion increases.

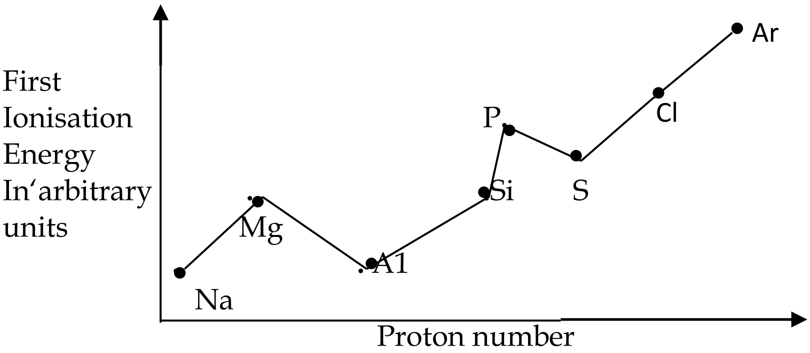
Shielding Effect

Shielding occurs due to repulsion between electrons. Inner electrons shield the outer electrons from the nuclear charge. Electrons in the same energy level do not shield each other from the nuclear charge. When there is more shielding effect less energy is require to ionize the outer electrons.

2.6.2 Trends in Ionization Energy

Across a period

Across a period, elements have the same number of occupied shells therefore the effects of shielding effect is uniform. The factor which is important is atomic size. Atomic size decreases along a period. Outer electrons become closer to the nucleus. The amount of energy required to remove outer electrons generally increases along the period. The diagram below shows variation in first ionization energies across period III.



Down a group

Atomic size increases down a group. More shells are being added down the group hence shielding effect increases downwards. Less and less energy is needed to remove outer electrons.

There is break in continuity at Mg/Al. The electron lost from Al is in a 3p orbital which is more distant from the nucleus than the 3s orbital electron lost from Mg. The Al electron experiences less attraction from the nucleus and hence is less strongly held. As such, it can be lost with less energy being used.

Another break in continuity occurs at P/S. The following electron arrangements can be used to explain. The electron lost from sulphur is in a doubly occupied 3p orbital. It suffers from repulsion from an electron occupying the same region of space hence lower first ionisation energy than that of P.

2.6.3 Successive ionization energies

These are ionisation energies for electrons removed from the same element. They are denoted as first ionisation energy; second ionisation energy, third ionisation energy and so on until all electrons have been removed.

Successive ionisation energies for aluminum are given below (only four are shown)

1st Ionisation energy IE,	580kj/mo1
2nd Ionisation energy IE2	1820kj/mol
3rd Ionisation Energy IE3	2 740kj/mol
4th Ionisation energy IE4	11 600 k/mol

Important points derived from these results are;

- in successive ionisation, the highest energy electron is removed first.
- the energy required for this change is the 1st IE.
- the electron removed is from the 3p orbital.
- the second electron is removed form the 3s orbital of $A\ell^{+}$.
- IE_1 is less than IE_2. This is due to the second electron being more strongly bound compared to the first.
- same trend observed in IE_3 and IE_4 where electrons are removed from ions $A\ell^{2+}$ and $A\ell^{3+}$.
- there is a large jump in moving from IE_3 to IE_4.
- IE_4 is removing an electron from stable shell with a noble gas core of electronic configuration $1s^2\ 2s^2\ 2p^6$ more energy is needed to disturb this configuration.
- This jump occurs whenever noble gas core electrons are removed.

If ionisation is continued, another large jump in ionisation energy will occur on IE_{12} i.e removal of an electron from $1s^2$. There will be a gradual increase in IE from IE_4 to IE_{13}. There will be 13 successive ionisation energies.

2.6.4 Atomic structure

Whenever there is a large gap in successive IE a new shell is broken/ionized. There were two large gaps in IEs, therefore the number of shells is 3. The element is in period 3. There were three successive ionisation energies at the beginning before the first large jump, therefore there are three electrons in the outer most shell. The element is in group III. Electronic configuration is 2, 8, 3, with 2 electrons in the first shell, 8 electrons in the second shell and 3 electrons in the third shell.

2.7 Summary

- Atoms are the smallest particles of matter.
- Atoms are made up of three fundamental particles; protons, neutrons and electrons.
- Electrons are deflected towards the positive terminal in an electric field.
- Neutrons are not affected by an electric field.
- Protons are deflected towards the negative terminal.
- Protons and neutrons are in the nucleus.
- Electrons orbit the nucleus in shells.
- The nuclide notation shows the symbol representing the element, the atomic number and the mass number.
- Isotopes are atoms of the same element and which differ in terms of the number of neutrons.
- Ions are formed when atoms lose or gain electrons.
- Electrons are located in an orbital of a sub shell and sub shells are relocated within an energy level.

- Ionisation energy is the amount of energy in kJ/mol needed to remove one mole of electrons from a mole of gaseous atoms of an element.
- Successive ionisation energies enable the determination of number of electrons and number of shells in an atom. The number of electrons in each shell can be deduced.

Examination Type Questions

1. The first ionisation energies in kJ mol^{-1} of group II and group III elements are given below

GROUP II		**GROUP III**	
Be	900	B	799
Mg	736	Aℓ	577
Ca	590	Ga	577
Sr	548	In	558
Ba	502	Tℓ	589

(a) (i) Define by means of an equation, what is meant by <u>first ionisation energy</u> of an element. [1]

(ii) Explain why the first ionisation energies increase in size on ascending Group II. [3]

(b) Explain why the first ionisation energy of Aluminum is less than that of magnesium. [4]

2(a) State the number, charge and location of the sub atomic particles in the atom $^{16}_{8}O$ [9]

(b) Calculate the number of each sub atomic particle in an atom of $^{74}_{32}Ge$ and give its electronic configuration. [4]

3(a) Describe the relative charges and masses of the three types of particles contained within the atom and explain how these particles behave in an electric field. [3]

b) The first eight successive ionisation energies of an element E are as follows:
703, 1610, 2460, 4350, 5400, 8500, 10300 and 12300 Kj mol^{-1}.

State giving reasons, the group of the periodic table to which E is likely to belong. [3

CHAPTER 3

Chemical bonding

There are three types of primary bonds which are covalent, ionic and metallic bonds. Primary bonds are formed between atoms. For some substances primary bonding occurs throughout the substance. However for covalent compounds primary bonding occurs for some molecules but not for others. Some covalent compounds exist as simple molecular compounds. A different type of bonding exists between the molecules. The intermolecular bonding is referred to as secondary bonding. The existence of different types of bonds gives rise to substances with different chemical and physical properties. The structure of a substance is important in explaining its physical properties.

This chapter describes the various types of bonds and attempts to relate the properties of substances to the type of bonding present.

Content

3.1	Ionic bonding
3.2	Covalent bonding
3.3	Intermolecular forces
3.4	Formation of sigma and pi bonds
3.5	Shapes of molecules
3.6	Metallic bonding
3.7	Summary

Learning Outcomes

On completing this chapter the student should be able to:

- describe ionic bonding using ‘dot and cross’ diagrams.
- describe ionic structures through the use of coordination numbers.
- explain the properties of ionic compounds.
- use ‘dot and cross’ diagrams to describe covalent bonding. Explain the differences between various types of covalent bonds.
- relate bond energy and bond length to the reactivity of covalent molecules.
- describe Van der Waals forces.
- explain the nature of hydrogen bonding.
- relate properties of covalent compounds to the types of bonding present in the molecule.
- explain shapes of molecules using VSEPR theory.
- describe metallic bonding in metals.
- explain the properties of metals with reference to metallic bonding.

3.1 Ionic Bonding

Ionic bonds are formed between metals and non-metals. Electrons are transferred from metal atoms to non-metal atoms. The metal atom after losing one or more electrons forms a positive ion (cation) and the non-metal atom after gaining one or more electrons forms a negative ion (anion). Electrostatic attraction between the oppositely charged ions constitutes the ionic or electrovalent bond.

3.1.1 *NaCl* (Sodium Chloride)

When sodium metal is reacted with chlorine gas, an ionic compound, sodium chloride is formed. A sodium atom transfers one electron to a chlorine atom. The ions that are formed, have the noble gas configuration and are therefore stable.

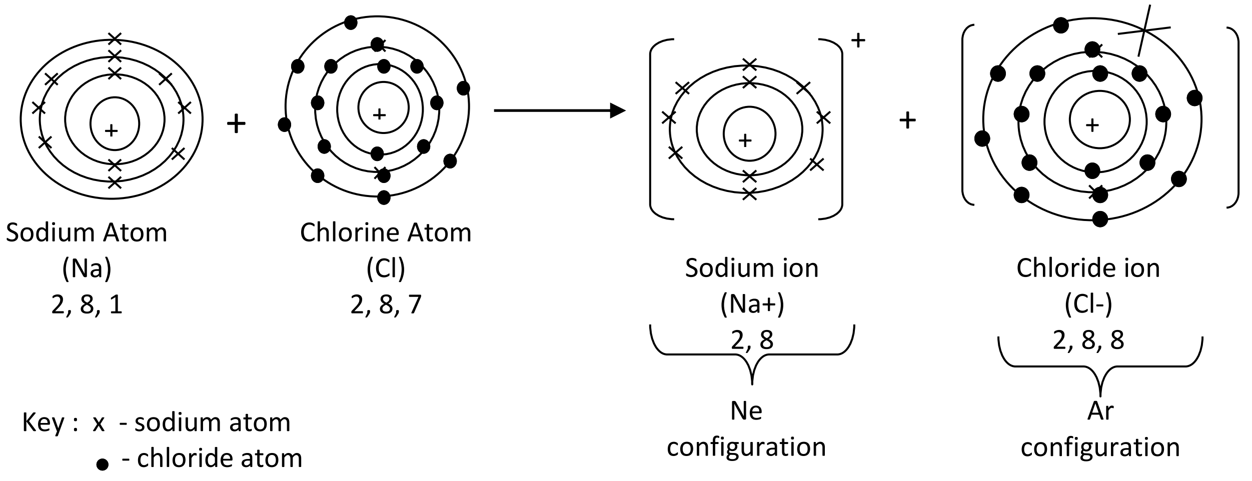


Fig 3.1.1.1 Ionic bonding configuration

The formation of a positive ion is governed by the ionisation energy. This is the amount of energy needed to remove one mole of electrons from one mole of gaseous atoms. This corresponds to:

$$M_{(g)} \longrightarrow M^{+}_{(g)} + e$$

Where M is a metal. The removal of further electrons becomes difficult since the remaining electrons are held strongly by the nucleus. Ions with a charge of more than 3+ are not common due to the high ionisation energy requirements.

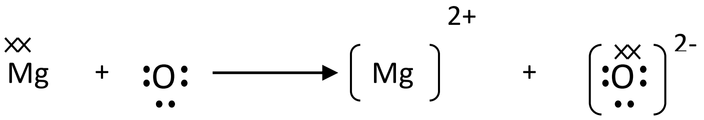
On the other hand, when a non-metal gains electrons it becomes negatively charged. The energy change that occurs, when an electron is attached to an atom is called electron affinity. The first electron affinity is the energy change that occurs when one mole of gaseous atoms accepts one mole of electrons.

$$A_{(g)} + e^{-} \longrightarrow A^{-}_{(g)}$$

The second electron affinity would be the energy required for one mole of gaseous A^- ions to accept a mole of electrons. This is not easy since there will be repulsion between electrons. It follows therefore that formation of anions with a higher charge is energetically unfavourable. Anions of 3- charge and above are not common. Doubly charged ions are quite common.

Mg O (Magnesium Oxide)

In the structure below, only outer electrons are shown.



Magnesium Atom (Mg)	Oxygen atom (O)	Magnesium oxide MgO

Since the formation of multiply charged ions is difficult, it follows therefore that ionic compounds are most likely formed by metals far to the left in the periodic table and non-metal elements far to the right in the periodic table especially group 7 elements.

3.1.2 Ionic Structure

Ionic compounds consist of giant lattice/ionic structures. The number of ions in the structure is not specified. In sodium chloride, each Na^+ ion is surrounded by six chloride ions and each chloride ion is surrounded by six sodium ions. The numbers are called coordination numbers. Sodium chloride is a 6,6 structure.

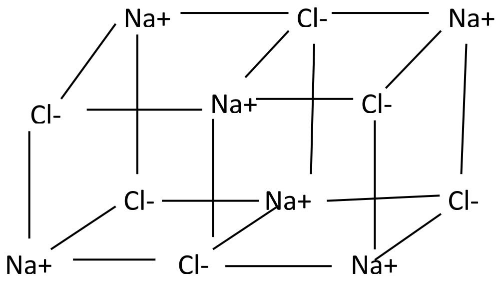


Fig 3.1.2.1 NaC1 Structure

CsCl

Cs^+ has an ionic radius of 0.169 nm compared to 0.095nm for Na^+. The lattice structure of *CsCl* has a coordination of 8.8. Eight Cl^- ions surround an ion of Cs and eight Cs^+ ions surround a Cl^- ion.

Activity

1. Explain why the melting point of NaC1 (801℃) is lower than that magnesium oxide (2640℃).

2. Given the following information about the ionic radii of Cs^+, Na^+ and Cl^- predict the lattice structure of KCl and suggest the coordination number of each ion in the structure you propose.

Table: Ionic radii of some ions

Ion	**Ionic radius nm**
Cs+	0.169
Na+	0.095
Cl^-	0.181
K+	0.133

3.1.3 Properties of ionic compounds

1. They have high melting and boiling points.
   The ionic bonds are very strong and a lot of energy s required to break them. The strength of the ionic bonds depends on
   - (i) The size of the charges on the ions. The greater the charges the stronger the bonds e.g. MgO with charges of 2+ and 2- has a stronger ionic bond than *NaCl* with ionic charges of 1+ and 1-.
   - (ii) The size of the ions: small ions pack closely and the electrostatic attractions are greater. CsI has ions bigger than those in NaC1. CsI is expected to melt at a lower temperature.
2. Ionic compounds are brittle. If ion layers are hammered into different positions, ions of the same charge are brought side by side and repulsion takes place.

3. Many ionic compounds are soluble in water. This is because for the compounds that are soluble the energy given out when ions are surrounded by water molecules is enough to overcome the attraction between ions.

4. Ionic compounds are insoluble in organic solvents since the interaction of organic solvent and ions is not strong enough to break the ionic bonds.

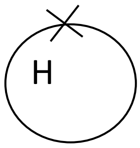
5. Solid ionic compounds do not conduct electricity. The ions are fixed and do not move in response to an electric field.
6. Molten and aqueous solutions of ionic compounds conduct electricity. The ions are mobile and migrate to electrodes of opposite polarity.

3.2 Covalent bonding

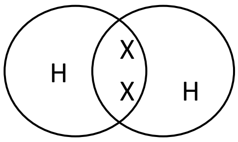
3.2.1 Covalent bond

Atoms can also gain the noble gas configuration by sharing electrons. The bond formed by sharing of electrons is called a covalent bond. The nuclei of the atoms involved in covalent bond attract the shared pair(s) of electrons. Non-metallic elements from covalent bonds.

H_2 molecule



Hydrogen atoms



Hydrogen molecule

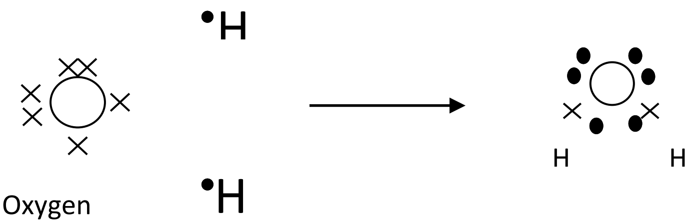
The shells of hydrogen overlap to form a molecular orbital. The nucleus of each hydrogen is surrounded by 2 electrons. The shared pair of electrons constitutes a single covalent bond. A single bond is shown by means of a single line.

$$H — H$$

While the nuclei are attracted to the electrons, there is repulsion between the positively charged nuclei. Therefore the distance between the nuclei of the hydrogen atoms (bond length) represents a balance between the attractive and repulsive forces.

Water molecule H_2O

The elements involved are hydrogen and oxygen. Oxygen needs 2 electrons to achieve a noble gas structure while hydrogen needs one electron to achieve a noble gas structure. Therefore, one oxygen atom will share two of its electrons with two hydrogen atoms.



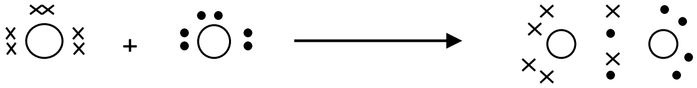
Oxygen

Hydrogen atoms

Water molecule (H_2O)

3.2.2 **Multiple Covalent bonds**

Multiple covalent bonds are formed by sharing more than one pair of electrons. If two covalent bonds are formed between two atoms, then the bond is called a double bond e.g in a molecule of Oxygen (O_2) each oxygen requires two electrons to achieve a stable outer electronic configuration. The two atoms will therefore share 2 pairs of electrons.



Oxygen atoms (O)

Oxygen molecule (O_2)

The double bond is represented by two parallel lines.

$$\mathrm{O}=\mathrm{O}$$

Sharing of 3 pairs of electrons results in a triple bond .

Activity

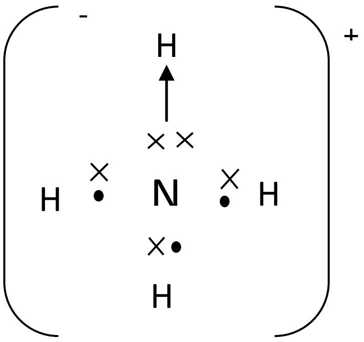
Use dot and cross diagrams to show the structures of the following molecules.
(i) Chlorine
(ii) Hydrogen chloride
(iii) Carbon dioxide
(iv) Methane
(v) Ethene

3.2.3 Types of Covalent Bonds

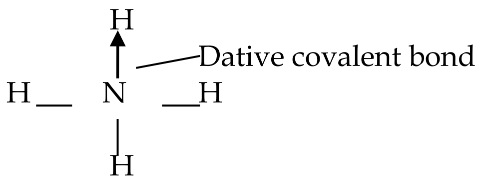
1. Non-polar covalent bonds - These are formed by atoms with equal or similar electro negativities (the tendency to pull shared electrons). The bonded pairs are shared equally between the atoms forming the covalent bond e.g. 0_2.

2. Polar covalent bonds - elements involved in the bond have different electronegativities. The bonded electrons are not shared equally. They are close to one of the atoms than the other. In HCl, Cl is more electronegative than H. Therefore the covalent bond in HCl is polar

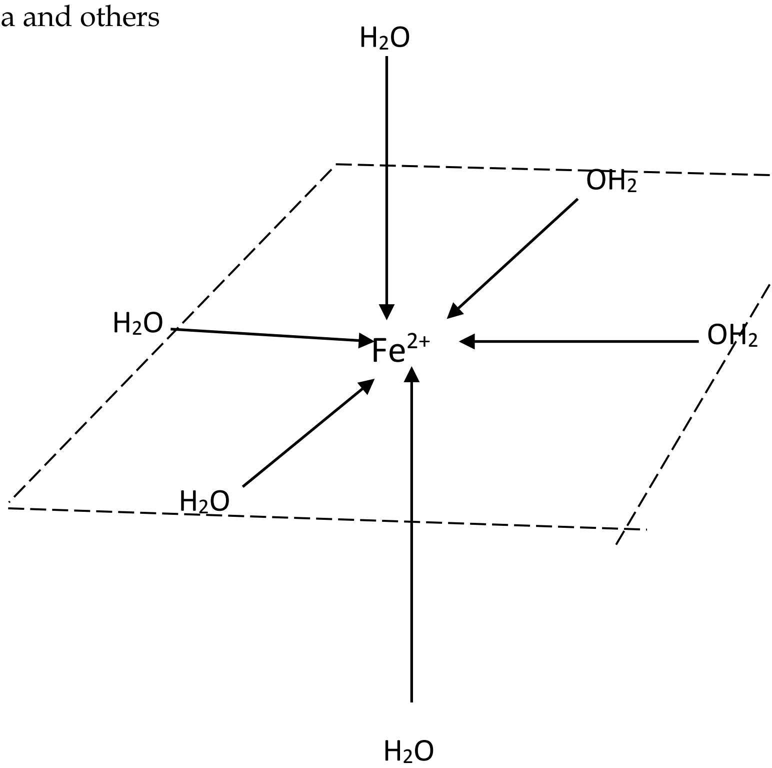
3. Coordinate (dative covalent) bonding
   In this type of covalent bonding the shared electrons come from the same atom rather than both atoms contributing equally. In the ammonium ion NH_4^+, 3 N-H bonds are formed by equal sharing of electrons between nitrogen and the three hydrogen atoms. The fourth N- H bond is formed by unbonded electrons on nitrogen and a proton. Nitrogen donates the bonded pair of electrons.



The dative covalent is indicated by an arrow pointing from the electron pair donor to the recipient.



Transition metal ions form coordinate bonds with liquids (electron pair donors) such as water ammonia and others



3.2.4 **Bond energy and bond length**

The reactivity of covalent molecules depends on the ease with which the covalent bond can be broken. The amount of energy required to break one mole of bonds is called bond dissociation energy or simply bond energy. A weak bond has low bond energy. It is easy to break and the molecule is fairly reactive than one with a high bond energy.

Bond lengths depend on the size of atoms forming the covalent bond. Bonds formed between large atoms are longer and bonds between small atoms are short.

The more electrons shared between atoms, the shorter the bond length. The table below shows bond energies and bond lengths for some bonds.

Table 3.2.4 Bond energies and lengths

Bond	**Bond energy length**(Kj mo1^{-1})	**Bond (nm)**
C- H	413	0.108
C-O	358	0.143
C≡O	805	0.116
C= C	612	0.134
C= C	838	0.120
O- H	464	0.096
O= O	498	0.121
N- H	390	0.101
N≡N	994	0.110

Activity

Show the bonding in the following molecules

(i) Carbon monoxide

(ii) Al_2Cl_6

3.2.5 Covalent Structures

Covalent compounds exist as simple molecular compounds or giant molecular compounds. In simple molecular compounds, atoms are joined through covalent bonds within the molecule (intramolecular) but different type of forces exist between the molecules (intermolecular force). The intermolecular forces are weaker than covalent bonds.

In giant covalent structures, all atoms are joined by covalent bonds.
Simple molecular compounds are characterized by low values of physical properties such as melting points or boiling points. Giant covalent compounds have strong bonds throughout. Examples are diamond, graphite and polymers.

3.2.6 Properties of covalent compounds

- Simple molecular compounds have low melting and boiling points due to weak intermolecular forces between molecules.
- Giant molecular substances have high melting and boiling points because the bonds being broken are strong covalent bonds.
- Covalent solids do not conduct electricity because the electrons are localized i.e are not able to move in response to an electric field.
- Molten compounds do not form ions therefore do not conduct electricity.
- Generally covalent compounds do not dissolve in water.

3.3 Intermolecular forces:

3.3.1 Van der Waals forces

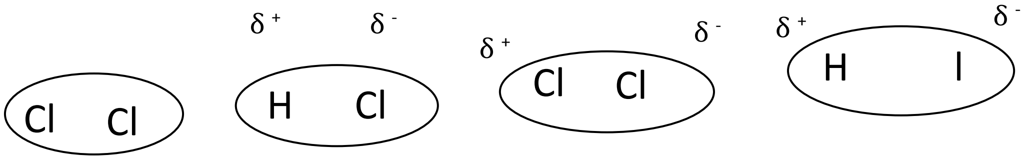
Molecules with polar bonds have an end with a partial negative charge (δ-) and an end with a partial positive charge (δ^+)
e.g

$$\overset{\delta^+}{H} - \overset{\delta^-}{Cl}$$

Such a molecule has a permanent dipole or it is permanently polarized. The difference in electronegativities of H and *Cl* causes the dipole. Such molecules can attract each other through appositively charged ends.

$$\overset{\delta^+}{H} - \overset{\delta^-}{Cl} \ldots\ldots \overset{\delta^+}{H} - \overset{\delta^-}{Cl} \ldots\ldots \overset{\delta^+}{H} - \overset{\delta^-}{Cl}$$

The interactions are <u>permanent dipole-permanent dipole attractions.</u> Molecules with non-polar bonds are also able to interact with each other. Molecules such as $C1_2$ gain polarity when close to a polarized molecule e.g *Cl* .



Not polarized

polarized

$C1_2$
Induced dipoles by
the attraction of electrons
on $C1_2$ to the partially
positive side of HCl

The form of interaction in such a case, is a <u>permanent dipole- induced dipole attraction</u>
<u>Induced instantaneous dipole.</u>

Electrons in a non- polar molecule are always in motion. They are not always evenly distributed within the molecule. This causes instantaneous dipoles which in turn induces polarity in a neighbouring molecule. The interaction in non- polar molecules and atoms of group O are <u>instantaneous dipole- induced dipole attractions.</u> The size of induced dipoles varies with the number of electrons. The more electrons there are, the bigger the size of the induced dipoles.

Activity

1. Which of these molecules have permanent dipoles.
   (i)Br_2, (ii) HBr, (iii) N_2 (iii) CH_3 C00H

2. What physical properties of covalent substances depend on the types of interactions described above?

3.2.3 Hydrogen bonding

The hydrogen bond is a type of permanent dipole-permanent dipole interaction but takes place in molecules with a hydrogen atom bonded to a highly electronegative element. In this case highly electronegative refers to three elements Nitrogen, Fluorine and Oxygen. There is a big difference in electro-negativity between these elements and hydrogen. This results in the attraction of hydrogen to the electro negative element on neighbouring molecule.

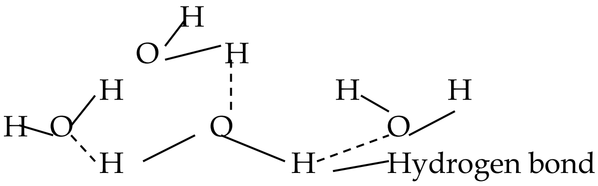


Fig 3.3.2.1- Hydrogen bonding in H_2O.

Activity

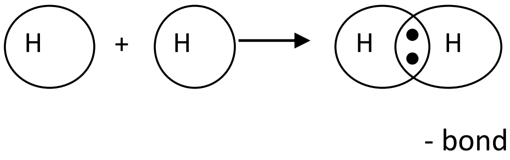
Which of the molecules below are likely to exhibit hydrogen bonding.

(i) $C_3 H_8$
(ii) $CH_3 0H$
(iii) HF
(iv) HCI

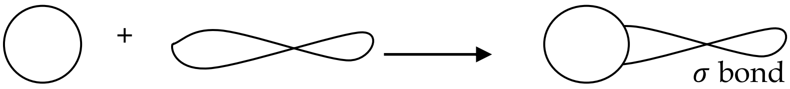
The hydrogen bond causes stronger interactions between molecules than Van der Waals forces. The bond energy for a hydrogen bond is about 25kj/mol. It is much more than that of Van der Waals' forces. The strong interactions due to hydrogen bonding causes hydrogen bonded compounds to have unusually high boiling points e.g. the boiling point of water is 100°C the boiling points of the hydrides: NH_3, HF are higher than those other hydrides in their respective groups.

3.4 Formation of Sigma (δ) and pi (π) bonds

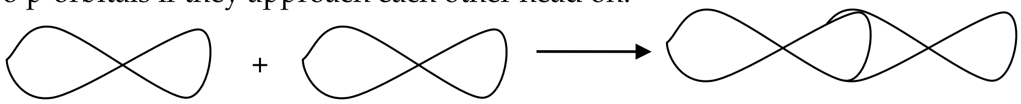
Sigma bonds are formed by the overlap of s orbitals



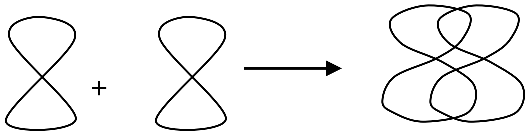
Or by an s- orbital and a p orbital.



Or two p-orbitals if they approach each other head on.



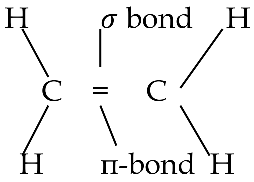
If the p-orbitals approach each other side ways, a pi σ bond is formed.



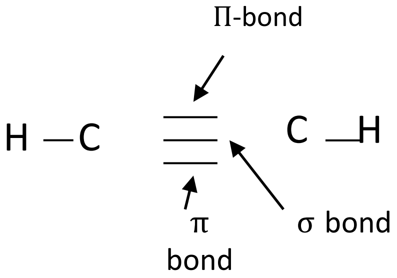
π-bond

In multiple bonds, it is possible to form two pi bonds by the overlap of two atomic orbital. In ethene, one sigma bond is formed by the head-on overlap of two p orbitals, one from each carbon atom, a pi bond is formed by the sideways overlap of p orbitals from carbon atoms.

Carbon atom

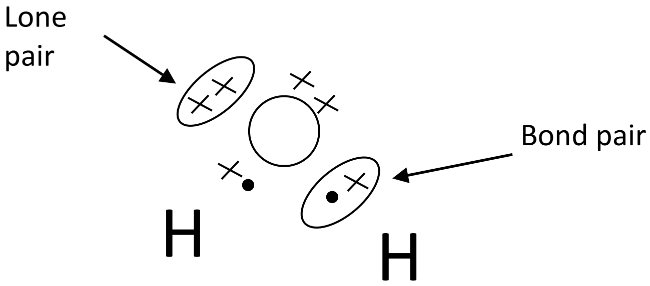


In ethyne, one sigma bond and two pi bonds are formed.



3.5 Shapes of molecules

The bonds of a covalent nature are directional. This causes molecules to have definite shapes. Covalent molecules have bonding electron pairs and non-bonding (lone) pairs, e.g. for a water molecule, the dot and cross diagram is as follows:

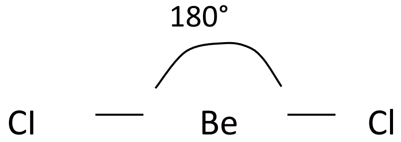


There are two lone pairs and two bonding pairs of electrons. These electrons repel each other. The shape of a molecule results from a structure in which the repulsions are minimized. This is the valence shell electron pair repulsion theory (VSEPR), and it states that:

> **"Non-bonding electrons have greater repulsion than bonding pairs. Lone pair-lone pair repulsions are greater than lone pair-bonding pair repulsions. Shapes of molecules can be explained using the repulsion theory".**

4.5.1 Linear molecules

$BeCl_2$ There are two bonding pairs which repel each other. There are no lone pairs on Be. The shape that minimizes repulsion between the pairs of bonding pairs is a linear one. The bond angle is 180^0.



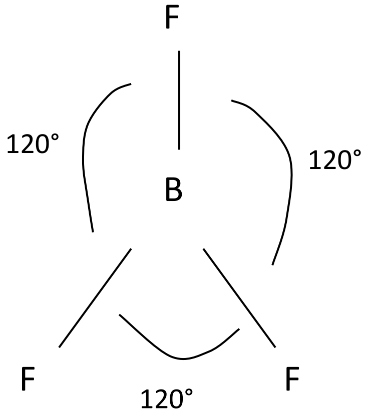
CO_2- the molecule has multiple bonds

O= C= O

Double and triple bonds are regarded as single bonds. No lone pairs are present on carbon so a linear shape results.

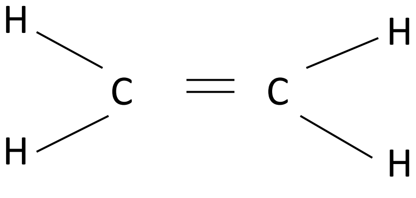
3.5.2 Planar molecules e.g. BF_3

There are three pairs of electrons (bonding) around the boron atom B. There are no lone pairs on Boron. The arrangement that will minimize repulsions is if the three bonds are uniformily distributed. This is achieved with a bond angle of 120^0 (ie 360/3)



Trigonal planar

Ethene

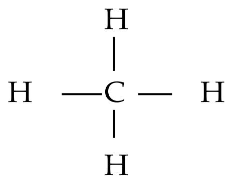


The double bond is treated as a single bond with no lone pairs on either of the carbon atoms.

The shape at each carbon atom is trigonal planar with a bond angle of 120^0.

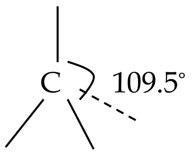
3.5.3 Three dimensional structure

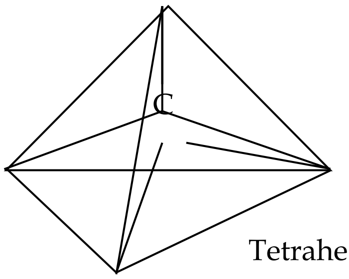
Methane



$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H$$

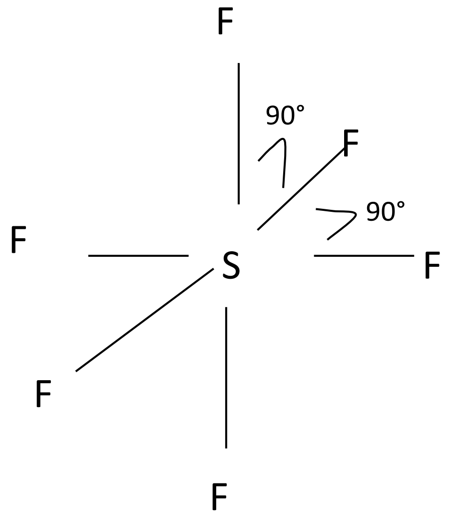
There are four bonding pairs of electrons around the carbon atom. The bonds cannot be in one plane. A three dimensional structure is formed. A tetrahedral arrangement is formed with H- C- H bond angle of 109.5^0.

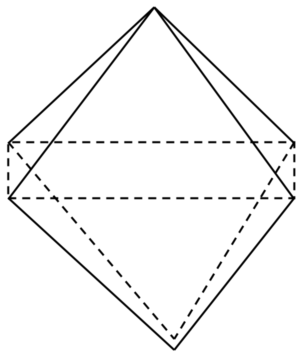




Tetrahedron

SF_6 has six bonding pairs of electrons and no lone pairs around the S atom. The shape that gives minimum repulsion is an octahedral with a bond angle of 90^0.

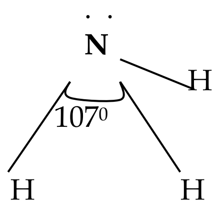




Octahedral

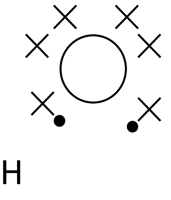
3.5.4 Molecules with lone pairs.

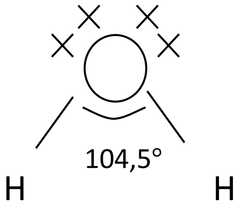
NH_3



There are three bonding pairs of electrons and one lone pair of electrons. Since there are four pairs of electrons around the nitrogen atom, a tetrahedral shape would be expected (as in CH_4). The lone pair repels strongly the bonded pairs and forces them to come closer. The pyramidal shape results with a bond angle of 107^0,

H_2O





There are two lone pairs which repel strongly the bonding pairs forcing the bond angle to reduce to 104.5^0. The water molecule has a bent or non-linear shape.

Activity

Suggest shapes and bond angles for the following molecules

(i) SiH_4 (ii) NH_4^+ (iii) H_2S

3.6 Metallic bonding

3.6.1 Metallic bond

Metal atoms lose their valence electrons and form positive ions. The electrons lost are embedded in the lattice structure formed by positive ions. The electrons are mobile and form a sea of electrons which bonds the positive ions together. This is the metallic bond. It is electrostatic in nature.

One of the important factors that determine the strength of a metallic bond is the number of valence electrons contributed to the sea of electrons. The metallic bond in aluminum is stronger than in magnesium since each aluminum atom contributes 3 electrons to the sea of electrons while magnesium contributes only two. The melting point of Al is 660.5^0C while the melting point of magnesium is 649^oC (weaker bond).

3.6.2 Properties of metals

- They have high boiling and melting points since electrostatic attraction between positive ions and delocalized electrons is strong.
- They conduct electricity. The delocalized electrons move in response to an electric field.
- They are malleable and ductile: positive ions can slide over one another without breaking the metallic bond, so they can be hammered into different shapes and be pulled into wires and rods.
- Metals have high densities since atoms are closely packed.

4.7 Summary

- Ionic or electrovalent bonding: This is a bond formed by the electrostatic attraction between oppositely charged ions.

- Covalent bonding: bonding atoms share a pair or pairs of electrons

- Dative or coordinate bonding: It is covalent bonding in which all the shared electrons come from one of the bonding atoms.

- Hydrogen bonding: A fairly strong intermolecular bonding which confers anomalous characteristics to some molecular compounds e.g. high boiling points. It is formed between a hydrogen atom bonded to a highly electronegative atom (N, O or F) and a highly electronegative element on another molecule.

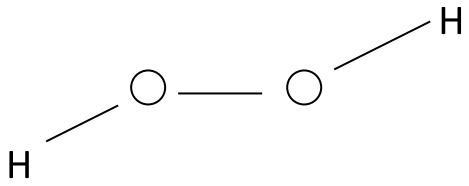
- Van der Waals forces: Very weak intermolecular forces arising from dipole- dipole interactions.

- Valence shell electron pair repulsion (VSEPR): the theory is used to explain shapes of molecules based on the repulsion of bonding and non-bonding pairs of electrons.

- Metallic bonding: The bonding that occurs in metals. Positive metal ions are electro statistically attracted to a sea of electrons derived from the valence shells of metals.

Examination Type Questions

1. The structure of hydrogen peroxide is shown below.



a) Draw the lone pairs in appropriate positions on the oxygen atoms.
b) Show the size of one of the bond angles in the molecule above.
c) What is the nature of intermolecular force between hydrogen peroxide molecules?
d) What is the property of hydrogen peroxide that arises from the force identified in (c)?

2. Describe with the use of diagrams the structures of NaC1, diamond and iodine. Explain how the properties of the compounds differ as a result the structures.

CHAPTER 4

STATES OF MATTER

This chapter explores the three states of matter i.e. gases, liquids and solids. The kinetic theory of matter is important in explaining the structure and properties of matter. Gases respond to changes in temperature, pressure and volume. Liquids and solids are not affected by pressure and changes in volume. This behavior will be explained in terms of the kinetic theory of matter. For solids and liquids, it is those properties that respond to the flow of energy through the substance that will explored e.g. melting points and evaporation. The latter properties are dependent upon the structure of these substances. Issues of the nature of bonding in liquids and solids are therefore very important.

Content

Learning outcomes

On completion of this chapter, the student should be able to:

- state the assumptions of the Kinetic theory of matter.
- describe the three states of matter in terms of the kinetic theory of matter.
- outline the gas laws.
- calculate pressure, volume or temperature at new conditions by applying the gas laws.
- derive the ideal gas equation form the gas laws.
- calculate number of moles and relative Molar mass using the ideal gas equation.
- describe enthalpy change of fusion and enthalpy of vaporization of a liquid.
- describe vapour pressure of a liquid.
- explain conditions necessary for ideal behavior.
- describe the structures of various types of solids (i.e. ionic, molecular, giant molecular, hydrogen bonded and metallic.
- describe the structure of ceramics.
- explain the properties of ceramics.
- relate the uses of metals and alloys to their properties.
- explain the importance of recycling materials.

4.1 The Gaseous State

4.1.1 The Kinetic theory of matter

The kinetic theory of matter provides a means of relating the properties of solids, liquids and gases to the way particles are arranged in the three states of matter. The following points are the main ideas of the kinetic theory of matter.

- All matter is composed of small particles.

- The particles of different substances are different and have different sizes.
- The particles are in constant motion. The energy of movement (Kinetic energy) increases as temperature increases.
- The movement of particles is in three forms: vibrational, rotational and translational.
- Movements in gases and liquids is in the three forms stated but in solids, movement is in the form of vibrational and rotational.
- At a given temperature, heavier particles move slower than lighter particles.

4.1.2 The States of Matter

In a solid particles are strongly bonded to each other, therefore the particles are close together. The particles are arranged in a specific manner since movement is limited to vibrational. The manner in which the particles are packed depends mainly on particle size. The solid has therefore orderly arrangement of particles giving rise to regularly shaped crystals in some solids. The shapes of the crystals differ from substance to substance.

In a liquid particles are still held together by some forces, but these forces permit particles to move about within the liquid state. Particles move in a random manner and collide against each other. They have more kinetic energy than particles in a solid. Since particles can move about, there is short range order within a liquid.

In a gas, particles are relatively free. There is no association of particles. As a result, individual particles can move about randomly but within the confines of the container. The particles in a gas have more kinetic energy than particles in liquids and solids

4.1.3 Gas laws

The gaseous state is affected by changes in temperature, volume and pressure. The independence of temperature, pressure and volume was investigated and a variety of laws were established.

Boyle's law

The relationship between pressure and volume was investigated at constant temperature. Boyle's law states that;

> **"At constant temperature, the pressure of a fixed amount of gas is inversely proportional to the volume"**

$P \propto \frac{1}{V}$ at constant Temperature

Removing the proportionality sign

$P = \frac{k}{v}$ k is a constant

Or Pv= Constant

This relationship is useful in calculating the p or V under changed conditions.

Condition 1 $P_1 V_1$= Constant

Condition 2 $P_2 V_2$= Constant

At the constant temperature, the two constants are equal therefore.

$$\boxed{P_1 \; V_1 = P_2 \; V_2}$$

Activity

1dm^3 of H_2 at a pressure of 0.5 atm is allowed to expand so that the final volume is 2.0 dm^3. What is the final pressure?

Charles's Law

The law focuses on the dependence of volume on temperature at constant pressure. The law states that;

> **"At constant pressure, the volume of a fixed amount of gas is directly proportional to the absolute temperature".**

$V \propto T$ at constant pressure

Therefore $\frac{V}{T} = \text{Constant}_2$

The volume or temperature of a gas can be determined if any of the two variables is adjusted to a new value at constant pressure.

$$\frac{V_1}{T_1} = \frac{V_z}{T_z}$$

The Pressure law

It states that;

> **"At constant volume the pressure of a fixed quantity of gas is directly proportional to its absolute temperature".**

$P \propto T$ at constant volume

$$\frac{P}{T} = \text{Constant}$$

$$:- \quad \frac{P_1}{T_1} = \frac{P_z}{T_z}$$

Combining the gas laws;

$PV = \text{Constant}$ (at Constant T)

$\frac{P}{T} = \text{Constant}$ (at Constant V)

$\frac{V}{T} = \text{Constant}$ (at Constant P)

Combining the above laws results in the following expression:

$$\frac{PV}{T} = \text{Constant}$$

The following condition also applies

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

If the conditions change it is possible to determine the values of the new conditions given relevant information.

Activity

A bulb has a volume of 180cm^3 and contains argon gas at a pressure of 300 mm Hg when the temperature is 27^{o}C. When the bulb is switched on, the pressure of the gas reaches 550mm Hg. What is the temperature of the gas in the bulb?

Avogadro's law

It states that;

> **"Equal volumes of gases at the same temperature and pressure contain the same number of moles".**

Mathematically this is given as:

$V = an$ V = Volume of gas
a = Proportionality Constant
n = Number of moles

Gases at low pressure nearly obey this law.

4.1.4 The ideal gas law

From Boyle's law $PV = \text{Constant}$ (at Constant T and n)

From Charles's law $\frac{V}{T} = \text{Constant}_2$ (at Constant P and n)

From Avogaro's law $V = an$ (at Constant P and T)

Combining theses gives;

$$V = \frac{R\,(Tn)}{P}$$

R= proportionality Constant called the universal gas Constant

R has the value of 0.08206 L atmK^{-1} mol^{-1}. if pressure is in atmospheres whilst
-Its value is 8.31 J molK-1 if pressure is in kPa.

The above relationship can be expressed as

$$\boxed{PV = nRT}$$

The equation is the Ideal gas law or the equation of state. It can be used to determine new set of conditions in the form.

$$\frac{PV}{T} = nR$$

Which leads to $\frac{P_1V_1}{T_1} = nR = \frac{P_zV_z}{T_z}$

$$\frac{P_1V_1}{T_1} = \frac{P_z V_z}{Tz}$$

Example

A sample of hydrogen gas (H_2) has a volume of $8.56m^3$ at 273.15K and a pressure of 1.5atm. How many moles of hydrogen are present in the sample?

Solution: From the ideal gas law,

$n= \frac{PV}{RT}$ P= 1.5atm, T= 273.15

V= 8.56cm3 $R = 0.08206 \frac{L\ atm}{Kmol}$

$$n = \frac{1.5 \times 8.56}{0.08206 \times 273.15} = \underline{0.57mol}$$

4.1.5 **Conditions for ideal behavior**

An ideal gas should obey the ideal gas equation i.e. PV when plotted against temperature, should give a straight line for gases to behave ideally;

i) - there should be negligible forces between particles
   -particles occupy negligible volume
ii) -the volume and pressure decrease linearly or temperature and become zero at absolute zero

Real gases have forces of attraction between particles and this is evidenced by the fact that gases can be liquefied

- Particles do occupy space (volume) since the gases can be liquefied to form incompressible liquids and solids.

Under suitable conditions, gases do behave ideally. The conditions that promote ideal behavior are those that do not promote liquefaction of gases. Such conditions guarantee that particles have sufficient energy to overcome forces of attraction between them. The conditions also ensure that the size of the particles of the gas is very small in relation to the volume of the gas.

Therefore, the temperature of the gas must be above its critical temperature. The pressure should be below the critical pressure.

Simply stated, ideal behavior is promoted by high temperature and low pressure.

Determination of Molar mass from

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

But n, the number of mole is given by

$$n = \frac{M}{M_r} \qquad M = \text{given mass} \quad M_r = \text{Molar mass.}$$

Substituting for n in $n = \frac{PV}{RT}$

$$\frac{M}{M_r} = \frac{PV}{RT}$$

:- Molar Mass, $M_r = \frac{MRT}{PV}$

Activity

An investigator collected 0.299g of a gas in a 4×10^{-4} m^3 container. The pressure exerted by the gas was 4.2×10^4 Pa and its temperature was 298.15K what is the molar mass of the gas?

4.2 The Liquid state

4.2.1 Liquids

The properties of liquids are intermediate between those of a solid and those of a gas e.g. particles in a liquid are joined together by intermolecular forces just like in a solid yet the arrangement is as random as in gases. The properties of interest are those that are affected by the flow of energy into a liquid.

Considering ice if it is heated, its particles gain kinetic energy and they vibrate vigorously, the volume of solid increases. If the energy supplied makes the solid reach is melting point, then further heating supplies particles with enough energy to overcome forces limiting them to vibrational movement. The ice melts i.e. changes form solid to liquid). The energy required to melt a solid at its melting point is called, the enthalpy change of fusion for ice. Fusion occurs at 0^{o}C.

$$H_2O_{(s)} \rightarrow H_2O(\ell)\Delta Hfus = 6,02kJ/mol$$

If heating is continued, the temperature of liquid water will rise until it is 100^{0}C (boiling point of water) At this temperature, the water molecules would have gained enough kinetic energy so that further addition of energy causes particles to break away from each other. The gas phase is formed. The energy required to convert liquid water into vapour at the boiling point is called the enthalpy change of vapourisation.

For water, the enthalpy change of vapourisation

$$H_2O(\ell) \rightarrow H_2O(g); \Delta Hvap = 40.7 kJmol^{-1}$$

The higher enthalpy change of vapourisation than the enthalpy change of fusion indicates the strength of intermolecular bonds in water (Hydrogen bonds.)

4.2.2 Vapour Pressure

If a liquid is placed in a closed container, its level is observed to decrease and then becomes constant. The decrease in the level of the liquid initially is due to the evaporation of the liquid. There is a net transfer of particles from liquid to the vapour phase. As the particles in the vapour increase, the reverse process to evaporation takes place, i.e. condensation. Vapour particles come together to reform the liquid. A state is eventually reached when the rate of condensation equals the rate of evaporation. The amounts of vapour and liquid phases remain constant. A state of equilibrium is reached.

The pressure of the vapour at equilibrium is called the vapour pressure of the liquid. The vapour pressure of a liquid is dependent on the strength of the forces holding particles together. Liquids with strong intermolecular forces have low vapour pressures and liquids with weak intermolecular forces have high vapour pressures.

4.3 The Solid state

4.3.1 Solids

There are two major categories of solids; crystalline solids and amorphous solids. Crystalline solids have long range order and are characterized by having crystals. Amorphous solids have a disorderly structure.

Crystalline solids have a lattice structure consisting of three diamensional arrangement of particles. The particles could be atoms, ions or molecules. The basic unit that repeats itself in a lattice structure is a unit cell. Common unit cells are;

(i) simple cubic. Which consists of particles fixed at the corners of a cube.

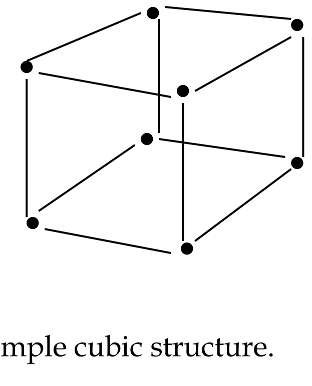


Fig 4.3.1.1 Simple cubic structure.

(ii) Body centred cubic- in addition to particles at the corners of a cube, another particle is at the centre of the cube.

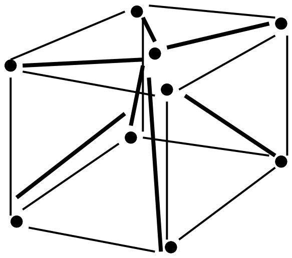


Fig 4.3.1.2. Body centred cubic lattice.

(iii) Face centred cubic- there are particles at the corners and then a particle at each face.

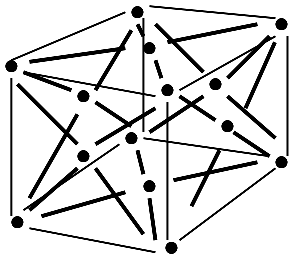


Fig 4.3.1.3. Face centred Cubic lattice

The types of crystalline solids

There are three types of crystalline solids and they are:

Ionic solids- Solids that produce ions when dissolved in a solvent e.g. Sodium chloride

Molecular Solids- Solid consisting of molecules in the unit cell e.g. iodine

Atomic solids These have atoms occupying lattice points e.g. graphite, boron, silicon and all metals.

The properties of a solid are determined by the nature of forces holding the particles together. Substances with similar lattice structures may differ markedly in their properties. Argon and Copper Are atomic solids. Argon has a very low melting point (-189°C) because atoms of Argon are held in the solid by weak Van der Waals forces whereas copper has a melting point of 1083°C because atoms are held more strongly through metallic bonds. Argon does not conduct electricity, its electrons are not mobile. Copper has delocalized valence mobile electrons and conducts electricity.

4.3.2. Ionic solids.

Lattice positions are occupied by ions in an ionic solid. The ions in the lattice are bonded through ionic bonding. This type of bond is very strong hence ionic substances have high melting and boiling points. They are also brittle.

NaCl Structure

Electronic attraction exists between Na$^+$ and CI$^-$ ions. Each Na$^+$ ion is surrounded by six CI$^-$ and each CI$^-$ ion is surrounded by six Na$^+$ ions.

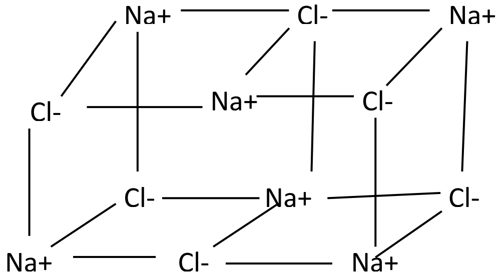


Fig 4.3.2.1 structure of $NaCl$ **.**

$NaCl$ has a 6,6 coordination i.e. number of ions surrounding each ion in 6. Ionic solids conduct electricity when molten or when in solution because the mechanism of conduction relies on mobility of ions.

The arrangement in other ionic solids depends on the ions in the solid. Where the ions are large the coordination changes e.g. it is 8,8 in $CsCl$. Melting points and boiling points of ionic solids are determined by ionic charge and radius. Smaller highly charged ions form strong ionic bonds.

4.3.3 Molecular Solids

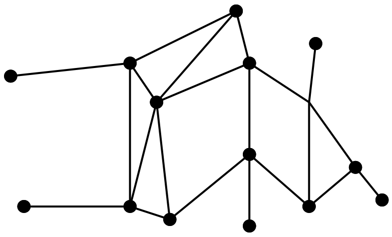
These are solids with molecular units at each lattice position. E.g. I_2, S_8, P_4. The forces between the molecules are Van der Waals forces or hydrogen bonds. In I_2, London dispersion forces exist, in HCl, permanent dipole- permanent dipole interactions occur which are stronger than the forces in I_2. In H_2O, stronger interaction occurs in the form of hydrogen bonding. Molecular solids are characterized by being soft, having low melting and boiling points. They are non-conductors of electricity and heat.

4.3.4 Giant molecular structures

Lattice positions have atoms joined throughout by covalent bonds. All bonds are directional and electrons are localized. These solids are insulators and have very high melting and boiling points.

Diamond

Each carbon atom is tetrahedrally surrounded by four carbon atoms. Covalent bonds exist throughout.

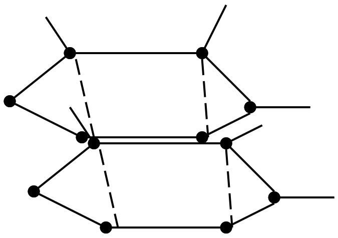


- Very hard
- Very high mp and bp due to strong covalent bonds
- Does not conduct electricity since all electrons are localized in covalent bonds.
- Hardest material hence used for making oil prospecting borers and engraving tools

Fig 4.4.4.1 Diamond

Graphite

Forms two dimensional layers held together by weak forces.



-weak Van der Waals bonds between layers

-so layers can slide easily over each other

-Hence graphite is slippery

-One electron per atom not used in bonding

-Such electrons conduct electricity.

Fig 4.3.4.2 Graphite

4.3.5 Hydrogen bonded. Lattice structure

These are simple molecules with covalent bonds between atoms. Molecules are held together by hydrogen bonds.

Ice

Hydrogen bonds exist between a hydrogen atom and a highly electronegative atom on another molecule.

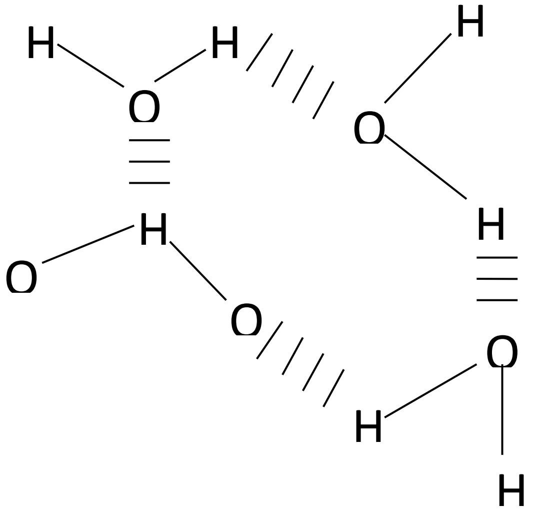


Fig. 4.3.5.1 Hydrogen bonding in H_2O

Hydrogen bonds are relatively stronger than Van der Waals forces. Compounds with hydrogen bonds show anomalously high melting and boiling points e.g. b.p of water is 100°C.

4.3.6 Metallic structure

The metallic structure consists of an array of cations held together by a sea of mobile electrons.

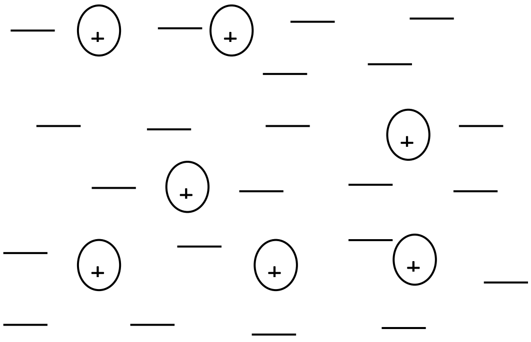


Fig 4.3.6.1 Metallic bonding.

The bonds are non directional. The valence electrons contribute to the sea of electrons. These are mobile and are responsible for thermal and electrical conductivity since they are mobile. The non-directional bonds makes it possible for particles to slide over each other without breaking so that metals are both ductile and malleable.

The particles in a metal are uniform in terms of size. They are packed in a manner that efficiently uses available space. This is called close packing. The particles are packed in layers in a variety of ways e.g. cubic close packing, hexagonal close packing.

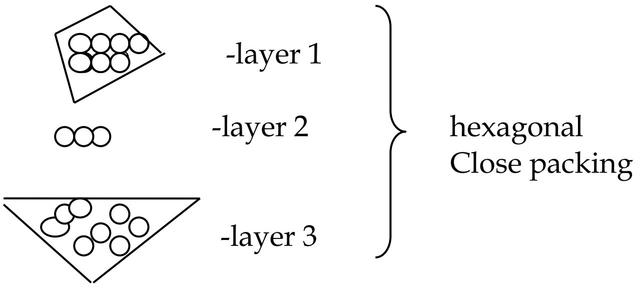


Fig 4.3.6.2 Hexagonal close packing.

The smaller the particles, the closer, they pack and the higher the density.

Alloys

Alloys are mixtures of elements and have metallic properties. There are two types of alloys:

- Substitutional alloys: some of the metal atoms are replaced by other metals atoms of comparable size. e.g. Brass- a third of copper atoms are substituted with zinc atoms.

- Interstitial alloys- empty spaces within the metallic structure are occupied e.g. spaces within iron in the formation of various grades of steel. The presence of non-metallic atoms in iron improves the directional nature of bonds. This makes steel to be harder and less ductile and malleable than pure iron. Steel can therefore be used for making tools.

Pure aluminum is a light, reactive metal with good thermal and electrical conductivity. It is not good in tensile strength. Duralumin is an alloy containing Al, Mg and Cu. It is light and strong. Magnalium Al/Mg, is another alloy involving aluminum. It is also light and strong. They are both used in the construction of aircraft and ships.

Copper has a high melting point and a density of about 8.94 gcm^{-3}. It is very malleable and ductile with excellent thermal and electrical conductivities. It has many uses; it is used for ornamental plaques because of its attractive colour and resistance to corrosion. Copper is used for making dynamo windings and for conveying electrical power because of its ductility and electrical conductivity.

Brass, is an alloy of copper and zinc. It has improved resistance to corrosion. It is used for making cartridge containers, head lamp reflectors and the working parts of watches.

4.3.7 Recycling materials

Mineral resources from which metals come are a finite resource, that is, a time will come when the minerals will be exhausted. To prolong the lifespan of these resources, it is necessary to recycle materials e.g. metals, plastics and glass. This also helps to reduce incidences of land pollution.

4.3.8 Ceramics

Are made from clays which are hardened by firing at high temperatures. The clays contain silicates based on SiO_4^{4-}.

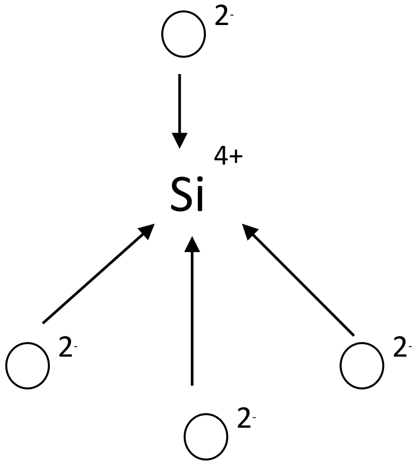


Fig 4.3.8.1 Silicate anion

Such units join up to form a network structure through covalent bonds.

Once a ceramic is hardened it it is resistant to high temperatures. Ceramics have very high melting points. The bonding within ceramics is covalent throughout. The electrons are localized so that ceramics are insulators. Ceramics are based on the clay called feldspar. It is a mixture of silicates with empirical formula such as $K_2OAlO_3SiO_2$ and $Na_2OA_2O_3.6SiO_2$.

-This clay is useful in the making of crockery.

-sodium based silicates are used for making glass. Ceramics based on magnesium oxide are used as furnace linings because of their high melting points.

4.4 Summary

- The kinetic theory of matter is important in explaining the properties of solids, liquids and gases.
- Boyle's law-states that the pressure of a fixed mass of a gas is inversely proportional to its volume at constant temperature.
- Charle's law states that the volume of a fixed quantity of gas is directly proportional to its temperature at constant pressure.
- The pressure law says that the pressure of a fixed amount of gas is directly proportional to its temperature at constant volume.
- Avogadro's law

  At constant temperature and pressure, equal volumes of gases contain the same number of moles.

  V= an
- The ideal gas equation is PV= nRT. It is nearly obeyed at low pressure and at high temperature
- Liquids respond to changes in temperature like gases which also respond to changes in pressure and volume.
- In a closed vessel, liquid evaporates to form vapour and the vapour also condenses to form liquid.
- When the rate of evaporation equals rate of condensation equilibrium is established
- The vapour pressure of a liquid is the pressure of the vapour at equilibrium
- The properties of a solid depend on the nature of forces holding particles in a solid.
- Ionic solids- produce ions when dissolved in a solvent e.g. $NaCl, MgO$
- Molecular solids- have molecules at lattice points e.g. I_2, H_2O.
- Atomic solids- have atoms at lattice points e.g. graphite, diamond, all metals.
- Alloys are mixture of elements
- Ceramics are giant molecular materials based on silicate anions
- Ceramics have very high melting points.

Examination Type Questions

1(a) What are the assumptions made in the kinetic theory of gases? [6]

(b) Under what conditions do gases behave ideally? Explain. [6]

(c) Describe the lattice structure of

(i) Sodium chloride

(ii) iodine and show how they can be used to explain two characteristic physical properties of each of these substances [8]

2. A container is filled with an ideal gas at a pressure of 40. 0 atm at 0^0C.

(a) What will be the pressure in the container if it is heated to 45^0C?

(b) At what temperature would the pressure be 1.50 x 10^2 atm?

(c) At what temperature would the pressure be 25.0 atm

CHAPTER 5

CHEMICAL ENERGETICS

Reactions are always accompanied by energy changes. The energy is mostly in the form of heat hence the reference to energy as enthalpy (heat). Chemical energetics is the study of energy transfers during a reaction. Some energy changes can be directly determined experimentally while others cannot .The chapter aims to show how calorimetry is used to determine enthalpy changes and also through Hess's law show how those enthalpies that cannot be determined directly can be calculated using information based on known enthalpy changes.

Content

5.1 Enthalpy changes
5.2 Standard conditions
5.3 Measurement of enthalpy changes
5.4 Hess's law
5.5 Formation of ionic compounds (Born Haber Cycle)
5.6 Lattice energy
5.7 Enthalpy changes in solution formation
5.8 Summary

Learning outcomes

On completion of this chapter, the student should be able to:

- explain the terms exothermic and endothermic using energy profile diagrams.
- state standard conditions for solutions and gases.
- calculate enthalpy changes using the equation $q = MC\Delta T$
- define standard enthalpy changes of neutralisation and formation.
- construct energy cycle based on Hess's law.
- calculate enthalpy changes using energy cycle.
- calculate enthalpy of reaction using bond energies.
- explain enthalpy changes that take place during the formation of an ionic compound.
- calculate enthalpy of lattice energy using the Born Haber cycle.
- define enthalpies of atomisation and formation.
- explain the factors that determine the size of lattice energy.
- explain the enthalpy changes that accompany the formation of a solution.

5.1 Enthalpy changes

5.1.1. Exorthemic and endothermic processes

Chemical reactions are always accompanied by energy changes. Reactions that give out energy to their surroundings are called exothermic reactions and reactions that absorb energy from their surroundings are endothermic reactions. Reactions and products have potential energy in the form of stored chemical energy.

In an exothermic reaction, the potential energy of reactants is lowered as the products are formed. The potential energy is converted into thermal energy or heat (enthalpy).The state of low potential energy is more stable than a state of high potential energy. The change from high potential to low potential is accompanied by change in enthalpy (H). The change in enthalpy is denoted by ΔH.

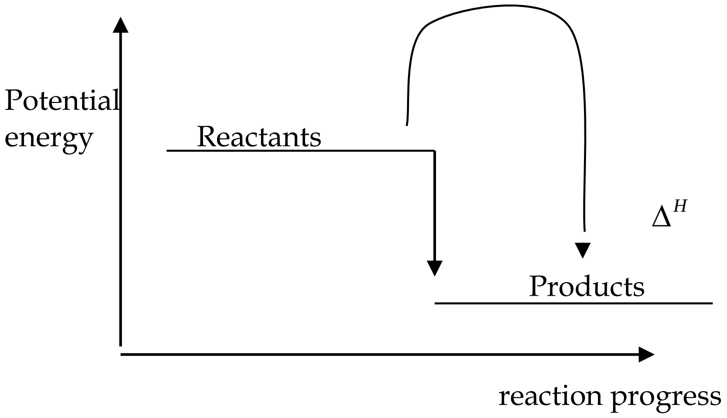


Fig. 5.1.1 Exothermic Process

In an endothermic process, energy from the environment is used to increase the potential energy of the system.

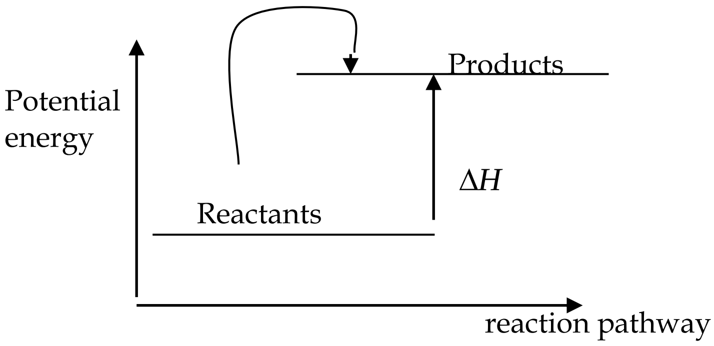


Figure 5.1.2 Endothermic Process

ΔH is negative in an exothermic reaction because energy is lost from the system to the surroundings. The following reaction shows how an exothermic reaction is written.

$$3H_{2(g)} + N_{2(g)} \rightarrow 2NH_{3(g)}; \Delta H = -92kjmol^{-1}$$

To show that the reaction is endothermic, ΔH is positive.

$$6CO_{2(g)} + 6H_2O(\ell) \rightarrow C_6H_{12}O_6(aq) + 6O_{2(g)} \ \Delta H = +2802.5 \, {}^{kj}\!/_{mol}$$

Energy is gained from the surroundings.

5.2 Standard conditions

Enthalpy change values depend on the conditions under which the measurements are done. In order to compare enthalpy changes, it is necessary to carry out the enthalphy change measurements at the same conditions. The conditions under which the measurements are done are called standard conditions. They are normally stated as.

A pressure of 1 atmosphere
Temperature of 298K
Concentration of $1moldm^{-3}$

More precisely, for a gas the standard state is a pressure of 1 atmosphere. For a solution, the concentration of exactly $1moldm^{-3}$. For a pure substance in liquid or solid state the standard state of the pure liquid or solid. The standard state of an element is the state in which it exists at standard conditions i.e. 1 atmosphere and 298K. The symbol ΔH^{θ} is used to denote standard enthalpy.

5.5 Measurement of enthalpy changes

1. Standard enthalpy change of combustion; it is the enthalpy change when one mole of a substance is completely burnt in oxygen under standard conditions.

$$eg.CH_3OH + 1\frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O \ \Delta H^{\theta} = -726kJmol^{-l}$$

A weighed fuel is used in a burner to heat up a fixed volume of water from temperature T_1, to temperature T_2.

The mass of the fuel is determined after T_2 is reached. The following data is obtained:

Mass of fuel burned = $Mf\left(g\right)$
Volume of water = $V_w cm^3$
Temperature rise T2-T1 = ΔT
Specific heat Capacity of water $= 4.2Jg^{-1}K$
Molecular Weight of fuel = $M_{r(fuel)}$

The energy(q) transferred to the water $= MC\Delta T$
M= mass, C= specific heat capacity ΔT = temperature rise

In terms of the experimentally determined data
$q = vx4.2x\Delta TJoules$

The number of moles of fuel $\frac{Mf}{M_{r(fuel)}} = n_{fuel}$

To calculate the enthalpy change of combustion per mole q is divided by the moles of fuel burned.

$$\Delta H_c = \frac{q}{n_{fuel}} Joules/mol$$

This determination assumes that there is no heat loss. Accurate values of ΔH_c are obtained using a bomb calorimeter.

<u>The standard enthalpy change of neutralization:</u> $\Delta H^{\varnothing}_{neut}$ is the enthalpy change when one mole of H^+ ions is neutralized under standard conditions.

$$H^+{}_{(aq)} + OH^-{}_{(aq)} \rightarrow H_2O(\ell)\Delta H^{\theta} = \frac{-57.5kJ}{mol} mol^{-1}$$

The enthalpy of neutralisation is determined by mixing equal volumes of 1 moldm^{-3} hydrochloric acid and 1 moldm^{-3} of sodium hydroxide solution. The temperature rise is measured. The heat produced Q is calculated using

$$Q = \text{Total mass of solution} \quad x \, 4{,}2 \, x \quad \Delta \, T$$

The value of $4{,}2Jg^{-1}K^{-1}$ is used as the specific heat capacity of water because the properties of dilute solutions approximate the properties of pure water. The total volume of solution is used as its mass because the density of a dilute solution approximates the density of pure water.

<u>Standard enthalpy change of formation:</u> $\Delta H^{\theta}{}_{f}$: is the enthalpy change when one mole of compound is formed from its elements in their standard states under standard conditions.

$$C(graphite) + 2H_{2(g)} \rightarrow CH_{4(g)}; \Delta H^{\theta}{}_{f} = -74.8KJmol^{-1}$$

$\Delta H^{\frac{\theta}{f}}$ is calculated indirectly from other measured enthalpies.

5.4 <u>Hess' law</u>

The law is derived from law of conservation of energy. It states that:

> **"The enthalpy change of a reaction is independent of the route taken provided the initial and final conditions are the same".**

Using Hess' law to construct energy cycles;
A reacts or is converted into B

A $\underline{\Delta H}$ B

A can be turned into B through the formation of intermediates C and D.

$$A \xrightarrow{\Delta H_1} C \xrightarrow{\Delta H_2} D \xrightarrow{\Delta H_3} B$$

The two alternate routes can be combined in an energy cycle

$$\begin{tikzcd}
A \arrow[rr, "\Delta H"] \arrow[d, "\Delta H_1"] & & B \\
C \arrow[r, "\Delta H_2"] & D \arrow[ur, "\Delta H_3"'] &
\end{tikzcd}$$

According to Hess's law, the shorter route is equal to the longer route.

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

ΔH can be calculated if $\Delta H_1, \Delta H_2$ and ΔH_3 are known.

Example

Given that

$$C(graphite)_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \Delta H^{\theta} = -393kJ\big/_{mol}$$

$$C(diamond)(s) + O_{2(g)} \rightarrow CO_2; \Delta H = -395kjmol^{-1}$$

Calculate the enthalpy change of the following reaction

C (graphite)(s) → C (diamond) (s)

The energy cycle is:

C (graphite) $\xrightarrow{\Delta H}$ C (diamond)

ΔH_1 □ ΔH_2 □

$CO_{2(g)}$

$$\Delta H = \Delta H_1 + \Delta H_2$$
$$\Delta H_1 = -393kjmol^{-1}$$

The reaction C (diamond) $\rightarrow CO_2$ is reversed in the cycle so its enthalpy is reversed (only the sign).

$$\therefore \Delta H_2 = +395kjmo^{-1}$$
$$\therefore \Delta = (-393 + 395)kJmol^{-1} = 2kJmol^{-1}$$

Activity

Given that

$$\Delta H^{\theta}{}_c(H_2) = -286kjmol^{-1}$$
$$\Delta H^{\theta}{}_c(C) = -393kjmol^{-1}$$
$$\Delta H_c^{\theta}(CH_4) = -890kjmol^{-1}$$

Determine enthalpy change of formation of methane

$$C_{(s)} + 2H_{2(g)} \xrightarrow{\Delta H_f^\theta} CH_{4(g)}$$

Standard enthalpy change of reaction (ΔH_r^θ)

(use of standard enthalpies of formation ΔH_f^θ)

ΔH_r^θ is the enthalpy change when the amount of reactants shown in the given chemical equation react together under standard conditions to give the products in their standard states.

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O; \Delta H_{rxn}^\theta = -286 kJmol^{-1}$$

if the reaction is written as

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O$$

Two moles of water are formed therefore the standard enthalpy of reaction $\Delta H_r^\theta = -572kj$

Calculation of enthalpy of reaction

The energy cycle has the format:

Reactants $\xrightarrow{\Delta H}$ Products

ΔH_1 □ □ ΔH_2

Elements in
their standard states

ΔH_1 = sum of enthalpies of formation of reactants

ΔH_2 = sum of enthalpies of formation of products

ΔH = enthalpy of reaction

$$\therefore \Delta H_r = \Delta H_2 - \Delta H_1$$

Example

Given that:

$\Delta H_f^\theta(CaCO_{3(s)}) = -1207 kjmol^{-1}$

$\Delta H_f^\theta(CaO(s)) = -635 kjmol^{-1}$

$\Delta H_f^\theta(CO_{2(g)}) = -394 kjmol^{-1}$

Calculate enthalpy change for the reaction below:

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

Hess's energy cycle for this reaction is as follows:

$$\begin{tikzcd}
CaCO_{3(s)} \arrow[rr, "\Delta H_r^\theta"] & & CaO_{(s)} + CO_{2(g)} \\
& Ca_{(s)} + \frac{3}{2}O_2 + C_{(s)} \arrow[ul, "\Delta H_f^\theta (CaCO_3)"] \arrow[ur, swap, "\Delta H_f^\theta (CaO) + \Delta H_f^\theta (CO_2)"] &
\end{tikzcd}$$

Applying Hess' s law

$$\Delta H_f^\theta (CaCO_3) + \Delta H_r^\theta = \Delta H_f^\theta (CaO) + \Delta H_f^\theta (CO_2)$$
$$-1207 + \Delta H_r^\theta = -635 + -(394)$$
$$\Delta H_r^\theta = +178 kjmol^{-1}$$

Bond dissociation enthalpy (bond enthalpy)

It is the energy needed to break a mole of covalent bonds between two atoms in a gaseous molecule. Bond breaking implies separating atoms to an extent that they do not interact in any way.

The bond dissociation enthalpy of the C- C bond is $+347 kJmol^{-1}$ This is the energy that has to be taken in to break the C-C bond. The process of bond breaking is endothermic. The same amount of energy is given out if a C-C bond were formed. The process of bond making is exothermic. Some bond energies are listed in the table below.

Table 5.4.1 bond energies

Bond	Bond enthalpy $(kjmol^{-1})$
C-C	+347
C≡ C	+612
C= C	+838
C-H	+413
C-O	+358
C=O	+805
O= O	+498
O- H	+464
N≡N	+994

Bond energies can be used to calculate enthalpy changes of reaction. A reaction involves bond breaking and bond formation. The enthalpy of reaction is the difference between the exothermic bond making process and the endothermic bond breaking process.

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$$

Bonds broken	Bonds formed
C- H x 4	C = O x 2
O = O x 2	O – H x 4

Using bond energies from the table:

Energy required for bond breaking	Bond formation
$+413 X 4 = 1652 kJmol^{-1}$	$805 X 2 = 161O \, {}^{kJ}\!/_{mol}$

$+498X2 = 996kJmol^{-1}$ $\qquad$ $464X4 = 1856\,{}^{kJ}\!/_{mol}$

Total $= 2648kJmol^{-1}$ $\qquad$ $3466kJmol^{-1}$

$\Delta H_{non} = 2648 - 3466 = -782kjmol^{-1}$

5.5 Formation of ionic compounds (Born Haber cycles)

The formation of ionic compounds involves transfer of electrons from a metal to a non-metal. The important energy changes are:

Enthalpy of atomisation, ionisation energy, electron affinity and lattice energy.
These energy changes can be shown on a Born-Haber Cycle for the formation of sodium chloride

$$Na_{(s)} + \frac{1}{2}C1_{2(g)} \xrightarrow{\Delta H_f^\theta} NaCI_{(s)}$$

The longer route involves converting sodium metal to sodium ions and chlorine gas to chloride ions and then the electrostatic attraction of the oppositely charged ions.

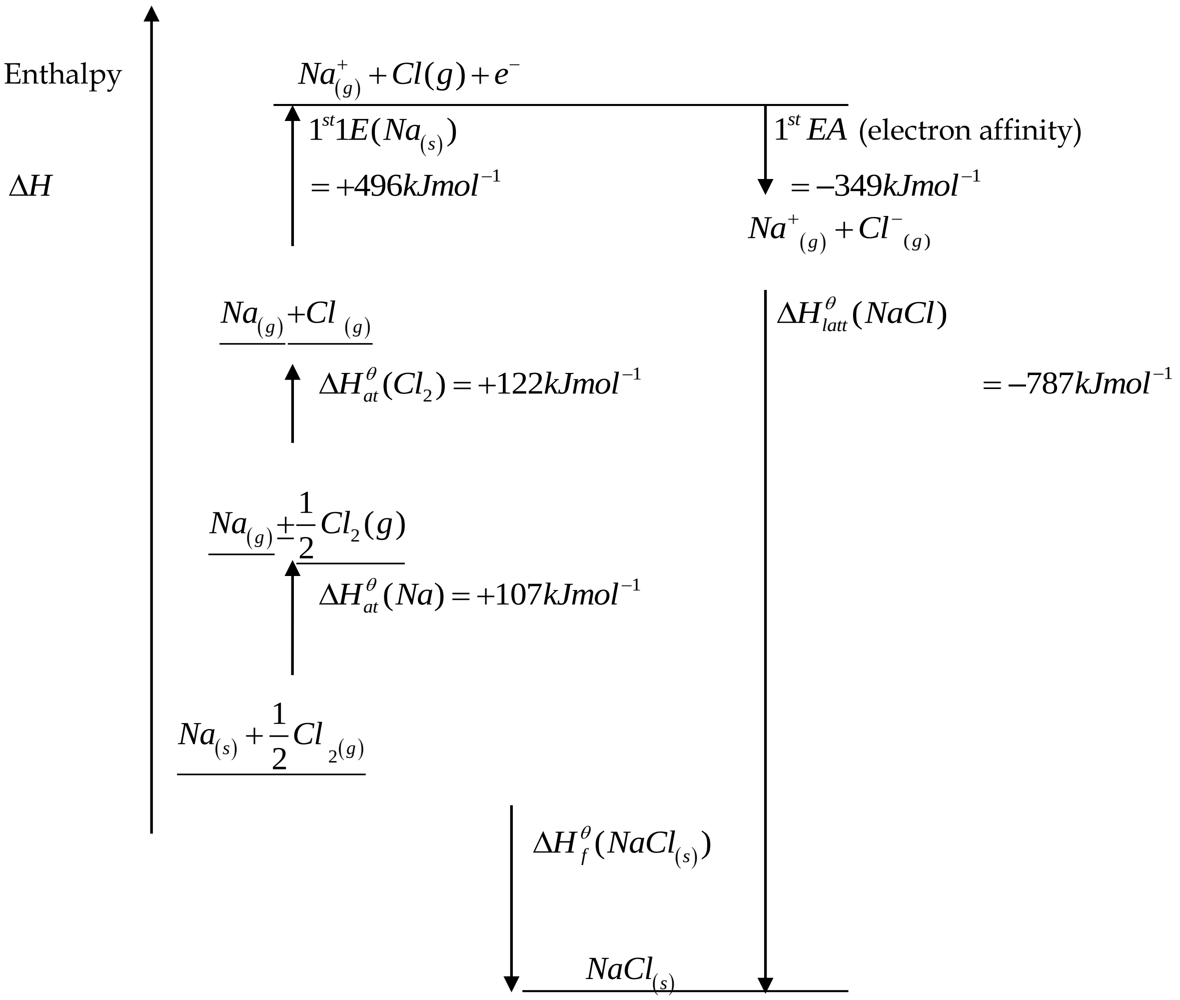


Fig 5.5.1 Born Haber Cycle for formation of $NaCl_{(s)}$

In the cycle, all endothermic enthalpy changes have arrows pointing upwards. All exothermic processes have arrows pointing downwards.

$$\Delta H_f^\theta = \Delta H_{at}^\theta(Na_{(s)}) + \Delta H_{at}^\theta(\frac{1}{2}C1_{2(g)}) + 1E(Na_{(g)}) + EA(Cl_{(g)}) + \Delta H_{1at}^\theta(NaCl_{(s)})$$

$$\Delta H_f^\theta(NaCl_{(s)}) = 107 + 122 + 496 + (-349) + (-787)$$

$$\Delta H_f^\theta(NaCl_{(s)}) = -411 kjmol^{-1}$$

Enthalpy change of Atomisation ΔH_{at}^θ

The standard molar enthalpy change of atomization is the enthalpy change when one mole of atoms of an element in the gas phase is obtained from the element under standard conditions.

Ionisation energy ΔH_{ion}^θ

Is the energy required to remove one mole of electrons from one mole of gaseous atoms (1st IE) or one mole of gaseous ions (for 2nd, 3rd et IE).

Enthalpy change of lattice formation ΔH_{latt}^θ - is the enthalpy change when one mole of ionic compound is formed from its gaseous ions under standard conditions.

Electron affinity (EA) is enthalpy change when one mole of electrons are added to one mole of gaseous atoms.

$$X_{(g)} + e^- \rightarrow X^-{}_{(g)}$$

Activity

Given the following enthalpy changes

Process		**Energy change kJmol^{-1})**	
Li (s)	$\longrightarrow$	Li(g)	-161
Li(g)	$\longrightarrow$	Li$^+$(g) + e	-520
½ F$_2$(g)	$\longrightarrow$	F (g)	-77
F(g) + e-	$\longrightarrow$	F$^-$(g)	-328
Li$^+$(g) + F-(g)	$\longrightarrow$	LiF(s)	-1047

(a) Identify the enthalpy changes represented by the processes above
(b) Draw a Born-Haber Cycle for the formation of LiF(s)
(c) Calculate $\Delta H_f{}^\theta$ (LiF(s))

5.6 Lattice energy

(Effect of ionic Charge and radius)
The table below lists some lattice enthalpies

Compound	Lattice Enthalpy Kj mo1^{-1}	Compound	Lattice energy Kj/mol
NaF	-918	MgF_2	-2957
NaC1	-780	Ca F_2	-2630
NaBr	-742	MgO	-3791
NaI	-702	Mg S	-3299

Table: 861 Lattice Energies

Column 1 shows lattice energy dependence on anionic radius. As the size of the anion increases, lattice energy decreases. In MgF_2 and CaF_2, it's the cationic size that is increasing. Again the size of the lattice energy decreases. The effect of charge is noticeable in NaF and MgF_2. The cationic charge increases and so does the lattice energy. Also in MgF_2 and MgO, the anionic charge increases and so does the lattice energy. Therefore the amount of force of attraction between ions varies directly as the charges on the ions and inversely as the distance between the charged ions.

$$F = k\frac{Q_1Q_2}{r^2}$$

Q_1 and Q_2 are the charges on ions
r = is the distance between the ions
k = proportionality constant.
The lattice energy depends on F. The higher the value of F the higher the lattice energy. Therefore, lattice energy is affected by the size of the ions since they affect the value of r and the ionic charges since they determine the product Q_1Q_2.

5.7 Enthalpy changes of solution formation

The formation of a liquid solution involves three steps.

(1) expanding the solute
- solute is broken into smallest units

(2) expanding the solvent
- accommodation of solute particles into solvent by breaking up solvent molecules or forces between them.

(3) interaction between solute and solvent

The first two steps are endothermic since they require energy first, to break up solute units and secondly to overcome the forces holding solvent molecules. The third step involves bond formation, and is therefore exothermic.

The overall process represents the enthalpy change of solution, $(\Delta H_{so\ln})$. It is the sum of the enthalpy changes taking place in the three steps above.

$$\Delta H_{soin} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

For the solubility of $NaCl$ in water

Δ H_1- is the energy required to separate Na^+ and $C1^-$. It is the reverse of lattice energy. It is positive.
ΔH_2- is the energy required to break hydrogen bonds within water
These bonds are quite strong soΔ H_2 is large and positive. ΔH_3 is the energy given out when solute ions associate with water molecules. $\Delta H_2 and \Delta H_3$ is represented by the change.

$$H_2O(\ell) + Na^+{}_{(g)} + Cl^-{}_{(g)} \rightarrow Na^+(aq) + Cl^-(aq)$$

The reaction above encompasses expansion of the solvent and the interaction of ions with water.

Δ H_2 and Δ H_3 combined form enthalpy of hydration.

$$NaCl_{(s)} \rightarrow Na^+{}_{(g)} + Cl^-(g) \Delta H_1 = 786 {kJ}/{mol}$$

$$H_2O(\ell) + Na^+_{(g)} + Cl^-{}_{(g)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

$$\Delta H_2 + \Delta H_3 = \Delta Hhyd = -783 kJmol$$

$$\Delta Hson = \Delta H_1 + \Delta H_{hyd}$$
$$= 786 + (-783)$$
$$= \underline{\underline{3 kJmol^{-1}}}$$

5.8 **Summary**

- Chemical reactions are accompanied by energy changes.
- Exothermic reactions give out energy to their surroundings.
- Endothermic reactions take in heat from their surroundings.
- The standard conditions are pressure- 101kPa Temperature- 298K, concentration- 1mol dm^{-3}
- Calorimetry is used to determine enthalpy changes and is based on heat transferred given by $q=MC\Delta T$.
- Standard enthalpy of neutralisation is the enthalpy changes when one mole of H^+ ions are completely neutralised under standard conditions.
- Standard enthalpy of formation ΔH_f^θ, is enthalpy change when one mole of a compound is formed from its elements in their standard states under standard conditions.
- Hess' law- states that the enthalpy change in a reaction is independent of the route taken, if the initial and final conditions are the same.
- Energy cycles are an application of Hess' law and are used to indirectly determine those enthalpy changes that cannot be experimentally determined.
- Bond dissociation energy- is the enthalpy needed to break a covalent bond. Bond energies can be used to calculate the enthalpy of reaction.
- Standard enthalpy of reaction is the enthalpy change when molar quantities of reactants react together under standard conditions.
- Formation of ionic compounds involves formation of oppositely charged ions and association of the ions. Enthalpy changes involved are; enthalpy of atomisation, enthalpy of ionisation, enthalpy of electron affinity and lattice energy.

- Amount of lattice energy is determined by (i) ionic radius and (ii) ionic charge
- Enthalpy change of solution is the sum of the reverse of lattice energy and enthalpy of hydration.

Examination Type Questions

1(a) Define: (i) enthalpy change of formation. [1]

(ii) Enthalpy of combustion [1]

b) When 12.00g of each of carbon and hydrogen are completely burnt in oxygen, 393,5kj and 1715,4kj are evolved respectively. Calculate the enthalpies of combustion of carbon and hydrogen.

2. Calculate the enthalpy change of the following reaction, using the data below;

$$P_4O_{10(s)} + 6H_2O(\ell) \rightarrow 4H_3PO_{4(s)}$$

Data: The enthalpies of formation of $P_4O_{10(s)}, H_2O(\ell)$ and $H_3PO_4(\ell)$ are- 2984, -285,9 and $-1279kJmol^{-1}$ respectively.

CHAPTER 6

ELECTROCHEMISTRY

Electrochemistry is a two faceted area of study. First, oxidation–reduction reactions are used to generate electrical energy. The devices used to convert chemical energy to electrical energy are called Galvanic or electrochemical cells and these batteries are used to power watches, radios, shavers etc. Secondly electrical energy is used to bring about oxidation – reduction reactions. The latter process is called electrolysis. Electrolysis is useful in such processes as charging of batteries, extraction of reactive metals, refining of metals and electroplating.

This chapter will look at the following; the nature of oxidation – reduction reactions, galvanic cells and electrolysis. Reduction and oxidation will be defined. The various types of galvanic cells will be described. Electrolytic processes will be described including the calculation of amounts of products discharged at electrodes.

CONTENT

1.1 Reduction and oxidation
1.2 Galvanic cells
1.3 Electrolysis
1.4 Summary

LEARNING OUTCOMES

On completing this chapter students should be able to:

- define reduction and oxidation in terms of electron transfer.
- define reduction and oxidation in terms of change of oxidation state.
- calculate the oxidation states of elements given the formula of a compound or ion.
- describe a galvanic cell using a diagram.
- describe a galvanic cell using a shorthand notation.
- identify the reduction and oxidation half cells of a galvanic cell.
- explain how standard electrode potentials are determined.
- describe the standard hydrogen electrode.
- describe electrode systems for (i) metals or non – metals in contact with their ions (ii) ions of the same element in different oxidation states.
- calculate the potential of a cell.
- predict the feasibility of a reaction from its cell potential.

- explain the dependence of an electrode potential on concentration.
- describe primary , secondary and fuel cells.
- define electrolysis.
- predict the reaction at an electrode from E^{Φ} values.
- predict electrode reactions by considering concentration of competing ions.
- describe the electrolysis of brine using a diaphram cell.
- describe the extraction of aluminium.
- explain the process in electro-refining of copper.
- calculate the amount of product formed at an electrode from the total charge passed into an electrolyte.

6.1 Reduction and oxidation

Reactions in which one or more electrons are transferred are called oxidation – reduction reactions. In the reaction below magnesium metal loses its electrons to oxygen.

$$Mg_{(s)} + \frac{1}{2}O_{2\ (g)} \rightarrow Mg^{2+}O^{2-}{}_{(s)}$$

Magnesium loses two electrons resulting in the formation of Mg^{2+} ions.

$$Mg_{(s)} \rightarrow Mg^{2+} + 2e^{-}$$

Oxygen accepts a pair of electrons to form the oxide anion.

$$O + 2e \rightarrow O^{2-}$$

6.1.1 Reduction and oxidation in terms of electron transfer

Gain of electrons is reduction, therefore oxygen undergoes reduction in its reaction with magnesium. Loss of electrons is oxidation. Magnesium is oxidised.

ACTIVITY

Identify the substance that is reduced and the one that is oxidised in the following reactions.

$$Na_{s} + \frac{1}{2}Cl_{2(g)} \rightarrow NaCl_{(s)}$$

$$Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$$

6.1.2 Reduction and oxidation in terms of oxidation state

The oxidation sate of an element is an imaginary charge on an atom assuming that if the atom were bonded to another atom, then electrons used in bonding would belong to the more electronegative element.

The oxidation numbers are assigned as follows:
An element, when isolated or in elementary form, is assigned an oxidation state of zero.

Cl and Cl_2 have oxidation states of zero
S or S_8 have oxidation states of zero

The oxidation state of a mono-atomic ion is equal to the charge on the ion.
Na^+ Oxidation state is +1
S^{2-} Oxidation state $is - 2$

- Hydrogen has an oxidation of +1 except in its binary metal hydrides. Its oxidation state is -1 in the binary metal hydrides.
- The oxidation state of oxygen is -2 in many of its compounds. The oxidation state in peroxides is -1 and is - ½ in super-oxides e.g. in NaO_2.
- Fluorine has an oxidation number of -1 .
- Chlorine, bromine and iodine normally have an oxidation sate of -1 except when they are combined with more electronegative elements. They tend to have positive oxidation states, e.g. in ClO^- the oxidation state of Cl is Cl +1.
- The sum of oxidation numbers in a molecule should add up to zero and in a molecular ion the sum adds up to the charge on the ion.
- During a reaction reduction can be defined as a decrease in oxidation state and oxidation as an increase in oxidation state. In the reaction between magnesium and oxygen, the oxidation state of oxygen changes from zero to -2 therefore reduction takes place. The oxidation state decreases. The oxidation state of magnesium increases from 0 (zero) to +2 . Oxidation takes place. The oxidation state refers to a charge on an element, not a group of element. The sign is always written first thus the oxidation number for Mg^{2+} is +2. The charge on an ion has the number first then the sign.

ACTIVITY

1. Calculate the oxidation number of the underlined elements.
   (i) $KMnO_4$
   (ii) $S_2O_6^{2-}$
   (iii) ClO_4^-

2. Identify the oxidising agent and the reducing agent in each of the following reactions
   $SiCl_4 + 2Mg \rightarrow 2MgCl_2 + Si$
   $Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$

6.2 Galvanic cells

From the section above it was noted that, whenever an oxidation – reduction reaction takes place, the reducing agent transfers its electrons to the oxidising agent. The chemical energy associated with the reaction is lost as heat. This energy can be harnessed and be used profitably. This is achieved by separating the half reactions so that the electrons from the reducing agent can be made to travel to the oxidising side through an external circuit. This flow of electrons through a conductor constitutes an electrical current. This current can be made to do useful work such as lighting a bulb or turning an electrical motor. The separation of the oxidation and reduction processes is achieved through construction of a Galvanic cell.

6.2.1 Galvanic cell

Zinc and silver ions react by oxidation and reduction. Zinc loses electrons to silver ions. The products are zinc ions and silver metal.

$$Zn_{(s)} + 2Ag^{+}{}_{(aq)} \rightarrow Zn^{2+}{}_{(aq)} + 2Ag_{(s)}$$

The two half reactions that take place are

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^{-} \quad ;\text{Oxidation}$$

$$Ag^{+}{}_{(aq)} + e^{-} \rightarrow Ag_{(s)} \quad ;\text{Reduction}$$

The oxidation is made to occur in separate vessel to that in which reduction takes place. The two vessels are connected in the following ways (i) using an external conductor or wire to transfer electrons from the zinc half cell to the silver half cell. (2) Using a salt bridge to complete the circuit. See diagram below. Without a salt bridge the reaction will cease after a short time due to polarisation. Excessive mixing of solution is prevented.

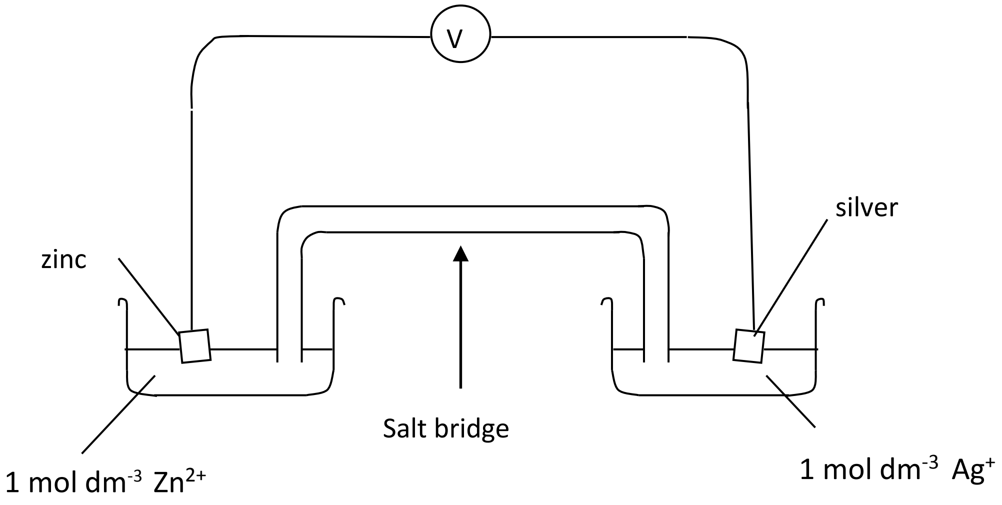


Figure 6.2.1 galvanic cell

The terminals used for transfer of electrons in containers are called electrodes. The solutions containing the metal ions are eletrolytes. The latter are liquids that conduct electricity.

6.2.2 Half cell notation

The cell above can be represented using short hand notation as shown below

Zn | Zn ; Z$_{n}^{2+}$ ¦ Ag+; Ag | Ag

ACTIVITY

Use the short hand notation to represent galvanic cells formed from the following reactions

$$Ni_{(s)} + 2Ag^{+}{}_{(aq)} \rightleftharpoons Ni^{2+}{}_{(aq)} + 2Ag_{(s)}$$

$$Zn_{(s)} + Cu^{2+}{}_{(aq)} \rightleftharpoons Zn^{2+}{}_{(aq)} + Cu_{(s)}$$

6.2.3 Cell potential

In the galvanic cell described above, electrons are transferred from the reduction half cell to the oxidation half cell. The force with which electrons are driven from one half cell to the other is the electromotive force (emf) or cell potential (E_{cell}) . The cell potential or emf is measurable using a voltmeter and its unit is the Volt (V) 1 volt = 1 joule of work per coulomb of charge transferred. The cell potential. depends on the two half cells connected together.

6.2.4 Standard electrode potentials

An electrode potential is the emf measured when a galvanic cell is constructed from a particular half cell and a reference electrode. The potential measured is assigned to the half cell which is not the reference electrode. If the measurements are done under standard conditions of pressure of 10^{5}Pa, temperature 25^{o}C and 1mol dm^{-3} concentration of the electrolyte solutions, the potentials are called standard electrode potentials.

The standard electrode or reference electrode is the electrode against which all other electrode systems are measured. It is assigned a potential of 0,0 V so that any voltage measured can be attributed to the other half cell.

An example of a reference electrode is the Standard Hydrogen Electrode. The diagram shows the construction of the Standard Hydrogen Electrode (SHE).

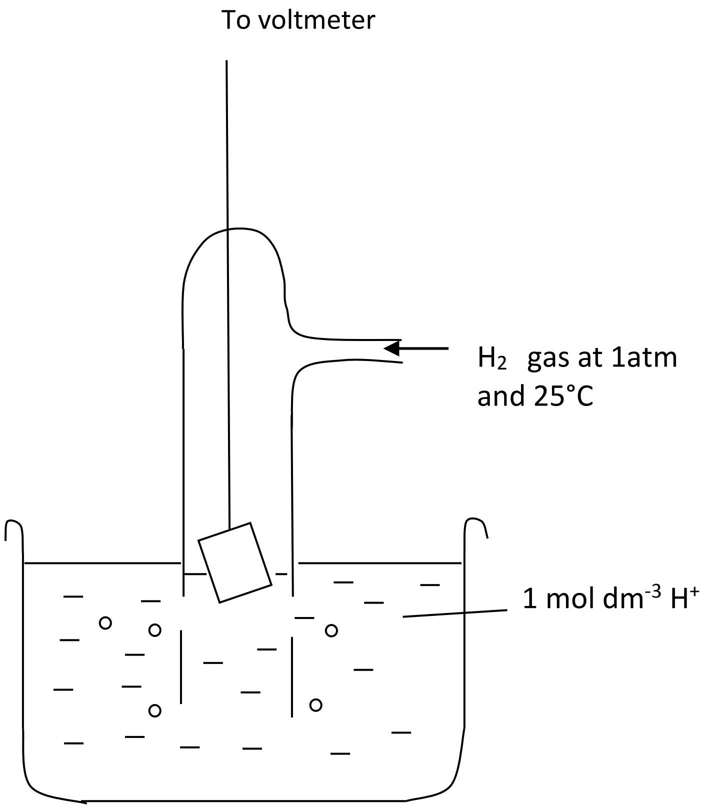


Fig 6.2.4.1 Std hydrogen electrode

It is made up of a platinum electrode which is in contact with 1M H^+ ions. Hydrogen gas is bubbled into the electrolyte. Platinum is chemically inert and serves only to transfer electrons into or out of the electrolyte. The reaction that occurs in the half cell is.

$$2H^+_{(aq)} + 2e \rightleftharpoons H_{2(g)}$$

6.2.5 Determination of standard electrode potentials $\left(E^{\Phi}\right)$

The standard hydrogen electrode is assigned an electrode potential of 0.00V, that is if a cell is constructed by combining two standard hydrogen electrodes the observed cell potential is 0.00V. Therefore the standard electrode potential of a given half cell is obtained by connecting the half cell to a standard hydrogen electrode half cell .For example to find the standard electrode potential of zinc, the half cell is constructed by immersing zinc metal
(electrode) into a solution that is IM in zinc ions . The solution is an electrolyte eg. $ZnSO_4$. This half cell is then connected to the standard hydrogen electrode half cell as shown below.

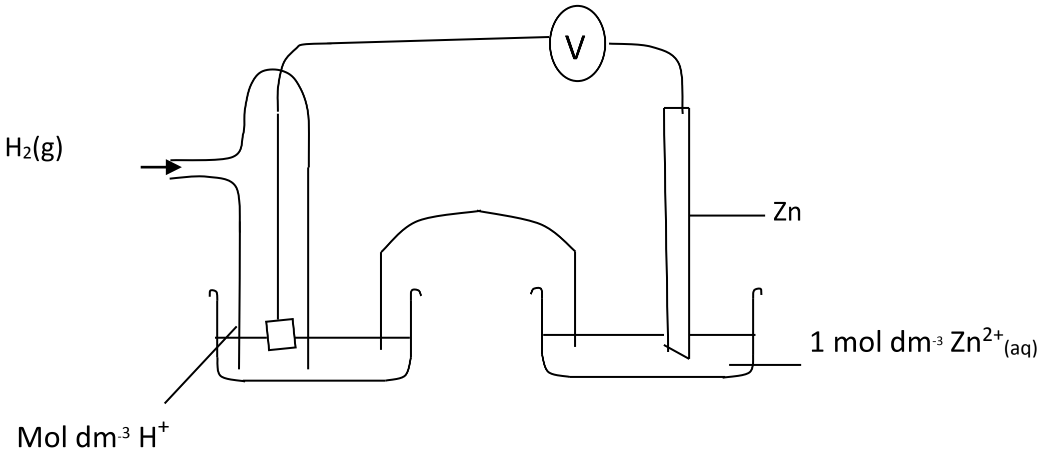


Fig 6.2.5.1 Standard cell potentials

The observed cell potential (0.76V) is assigned to the zinc half cell.

$Zn^{2+} + 2\bar{e} \rightarrow Zn$ -0.76V standard electrode potential $\left(E^{\Phi}\right)$

The electrode potential is assigned a minus sign and this means that , when a zinc half cell is connected to hydrogen half cell , it is the one that supplies electrons to hydrogen . Note also that the electrode process is written as a reduction process. The oxidation state of zinc is decreasing from +2 in the ion to zero in metallic zinc. Therefore the electrode potentials, are specifically referred to as standard reduction potentials. A positive $\left(E^{\Phi}\right)$ means the half cell accepts electrons from SHE. Reduction potentials for other elements are determined in a similar manner for metallic systems.

6.2.6. **Metal / metal ion electrodes** – the metal in contact with a solution of cations derived from the metal forms the half cell. The zinc half cell is an example of such an electrode system. For a metal M which forms an ion M^{2+} half cell representation is:

$M \left| M; m^{2+}_{(aq)} \right.$

Non –metal electrodes

Metal electrodes are used indirectly to measure the $\left(E^{\Phi}\right)$ values for anions. For the electrode to work, the metal used as the electrode must react to form a partially soluble precipitate or stable complexes with the metal ion. Silver metal can be used to determine the $\left(E^{\Phi}\right)$ value for Cl. $AgCl_{(s)}$ is formed which sets up the following equilibrium.

$AgCl_{(s)} + e^{-} \rightleftharpoons Ag_{(s)} + Cl^{-}$

6.2.7 **Electrons for redox systems**

Redox systems involve a change such as from Fe^{2+} to Fe^{3+}, i.e. where there is change in oxidation state. Inert electrodes are used and there are metals such as platinum, gold, palladium or carbons which do not react and they will measure the potentials of redox change only. Pt can be used in a Fe^{3+} / Fe^{2+} half cell. The representation is

$$Pt / Fe^{2+}{}_{(aq)}, Fe^{3+}{}_{(aq)} \vdots H^{+}{}_{(aq)} / H_{2,}Pt$$

Thus $Fe^{3+}{}_{(aq)} + e^{-} \rightarrow Fe^{2+}{}_{(aq)} E^{\theta} = +0,77V$

6.2.8 Standard reduction potentials

The table below lists standard reduction potentials for some half reactions.

Half reaction	$\left(E^{\Phi}\right)$**V**
$K^{+} + e \rightarrow K$	**-2.92**
$Ca^{2+} + 2e \rightarrow Ca$	**-2.76**
$Na^{+} + e \rightarrow Na$	**-2.71**
$Mg^{2+} + 2e \rightarrow Mg$	**-2.37**
$Al^{3+} + 3e \rightarrow Al$	**-1.66**
$Zn^{2+} + 2e^{-} \rightarrow Zn$	**-0.76**
$Ni^{2+} + 2e \rightarrow Ni$	**-0.23**
$2H^{+} + 2e \rightarrow H_{2}$	**0.00**
$Cu^{2+} + 2e \rightarrow Cu$	**+0.34**
$Fe^{3+} + e \rightarrow Fe^{2+}$	**+0.77**
$Ag^{+} + e \rightarrow Ag$	**+0.80**

6.2.9 Calculation of cell potential

One of the uses of standard electrode potentials is to enable the calculation of the cell potential constructed from a given pair of half cells. The electrode where oxidation takes place is called the anode and the electrode where reduction takes place is called the cathode. The cell potential is obtained in two ways:.

Using the formula $E^{\Phi}{}_{cell} = E^{\Phi}{}_{reduction} - E^{\Phi}{}_{oxidation}$
The standard electrode potentials are used as they are in the table of reduction potentials without changing the signs.

Example: in the reaction between zinc and copper ions.

$$Zn_{(s)} + Cu^{2+}{}_{(aq)} \square\ \square\square\ Zn^{2+}{}_{(aq)} + Cu_{(s)}$$

Zn undergoes oxidation and Cu^{2+} ions are reduced. The reduction potentials are:

Oxidation $Zn^{2+} + 2e^{-} \rightarrow Zn$ E$^{\sigma}$ = -0,76 V
Reduction $Cu^{2+} + 2e \rightarrow Cu$ E$^{\sigma}$ =+0.34 V

$$E_{cell} = E^{\Phi} reduction - E^{\Phi} oxidation$$
$$= +0.34 - (-0.76)$$
$$= 1.10V$$

(2) adding two potentials of the half reactions after reversing the one that undergoes oxidation (if electrode potentials are given as reduction potentials)

In the reaction of zinc and copper ions zinc undergoes oxidation, therefore, its electrode potential sign changes to + 0.76V

Thus $Zn \rightarrow Zn^{2+} + 2e^{-}$ E$^{\theta}$ = + 0.76V
$Cu^{2+} + 2e \rightarrow Cu$ E$^{\theta}$ = +0.34V

The overall reaction is obtained directly by adding the two half reactions . Their E^{Φ} values are also added to get the overall cell potential.

$$E_{cell} = E_{reduction} + E_{oxidation}$$

= 0.34 + 0.76

= 1.10V

6.2.10 Predicting the feasibility of a reaction

A reaction is feasible if the calculated cell potential is positive . It means the reaction takes place in the manner it is written. In the example given above , zinc metal is the one that supplies electrons to copper ions. Electrons flow from the anode to the cathode.

Suppose the reaction of zinc is written the other way round, that is copper metal supplying electrons to zinc ions:

	E^{θ}/V
$Cu \rightarrow Cu^{2+} + 2e$	- 0. 34
$Zn^{2+} + 2e \rightarrow Zn$	-0.76

The cell potential is

E$^{\sigma}_{cell}$ = -0.34 + (-0.76)

= -1.10V

A negative cell potential means that the reaction does not take place as written.

Activity

1. Predict the feasibility of the following reactions

$$Ca^{2+}_{(aq)} + 2Fe^{2+}_{(aq)} \rightarrow Ca_{(s)} + 2Fe^{3+}_{(aq)}$$
$$Mg_{(s)} + 2Ag^{+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + 2Ag_{(s)}$$

6.2.11 Dependence of electrode potential on concentration

The dependence of electrode potential on concentration can be deduced using the Nernst equation. Considering the following half reaction

$$Zn^{2+}_{(aq)} + 2e\square\ \square\square\ Zn_{(s)}$$

The Nernst equation has the form

$$\mathrm{E} = \mathrm{E}^{\sigma} - \frac{0,0591}{n}\log Q$$

where Q is conc and n is number of electrons transferred in the half cell reaction.

Suppose $\left[Zn^{2+}\right] = 1$

Then

$$E = E^{\Phi}$$

Because $\frac{-0.591}{2}\log 1 = 0$

If the concentration of $Zn^{2+} = 0.1M$ then the Nernst equation becomes.

$$E = -0.76 - \frac{0.0591}{2}\log\left(\frac{1}{0.1}\right)$$

$$= -0.76 - \frac{0.0591}{2} \times 1$$

$$E = -0.79V$$

Cell potential at non-standard concentrations

$$Zn_{(s)} + Cu^{2+}_{(aq)}\square\ \square\square\ Zn^{2+}_{(aq)} + Cu_{(s)}$$

$$Q = \frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]}$$

The Nernst equation is

$$E_{Cell} = E^{\theta}{}_{Cell}\,\frac{0.0591}{2}\log\frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]}$$

ACTIVITY

Calculate the cell potential for the reaction

$$Zn_{(s)} + Cu^{2+}{}_{(aq)} \rightleftharpoons Zn^{2+}{}_{(aq)} + Cu_{(s)}$$

If the concentration of Zn^{2+} is 0.5M and the concentration of Cu^{2+} is 1M.

6.2.12 Electrochemical Cells and batteries

Cells are classified into three categories. Primary cells : are those that cannot be recharged e.g. Leclanche , alkaline cell, lithium battery, button cell. Secondary cells: are rechargeable e.g. Lead – acid battery, Nickel- cadmium cell and Vanadium redox battery. Fuel cells have continuous supply of reactants and they operate continuously e.g. Hydrogen – oxygen fuel cell batteries are made from cells that are connected in series. i.e. Negative terminal of one cell connected to the positive terminal of the next cell. This allows for the creation of higher voltages.

Description of cells

Primary cells: three primary cells are described below,.

1. **Lenclanche or Dry cell**
The anode (negative terminal) is made of a zinc case and during discharge the following reaction takes place
$Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^{-}$
The cathode (positive terminal) consists of a carbon rod that is in contact with carbon and manganese dioxide $\left(MnO_2\right)$ .The following reaction takes place.

$$NH^{+}{}_{4(aq)} + MnO_{2(s)} + e^{-} \rightarrow NH_{3(aq)} + MnO(OH)$$

The electrolyte is a paste of $NH_4Cl, ZnCl_2$, The voltage produced by the dry cell is 1.5volts. This type of cell is used with electrical gadgets that do not draw a lot of current e.g. Radios, torches, liquid crystal calculators and toys.

The cell diagram is represented as follows:

$Zn/(ZnCl_2),: NH_4Cl;/MnO_{2.}C$

2. **Alkaline cell**
   The anode is a brass rod in contact with powdered zinc. The following reaction takes place

   $Zn_{(s)} + 2OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^-$

   The cathode is a paste of potassium hydroxide (it is an alkaline electrolyte). The cell produces a voltage of 1 volt. It is used where high current is drawn, e.g. electronic photographic flash units tape recorders, radios, shavers etc. Its cell representation is

   $Zn, ZnO / KOH(paste) / MnO_2, C$

3. **Mercury button cell**

   The anode consists of a steel cap in contact with powdered zinc. The anode reaction is:
   $Zn_{(s)} + 2OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^-$
   The cathode is a steel case in contact with powdered mercury oxide (HgO). The cathode reaction is

   $HgO_{(s)} + H_2O_{(l)} + 2e \rightarrow Hg_{(l)} + 2OH^-{}_{(aq)}$
   The electrolyte is a paste of KOH . The cell produces 1.3 volts. It is used in watches.

Secondary cells

1. **Lead – acid battery or accumulator**

   The anode is made of lead plates. The reaction below takes place at the anode

   $Pb_{(s)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4(s)} + 2e^-$
   The cathode is made of lead plates coated with lead oxide PbO_2
   $PbO_{2(s)} + 4H^+{}_{(aq)} + SO_4{}^{2-}{}_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O(l)$

   The electrolyte is $4MH_2SO_4$. Each cell produces 2 Volts. Six cells are connected in series to give a total of 12volts. Used in motor vehicle batteries. During recharging the following reaction takes place

   $2PbSO_{4(s)} + 2H_2O_{(l)} \rightarrow PbO_{2(s)} + Pb_{(s)} + 4H^+{}_{aq} + 2SO^{2-}{}_{4(aq)}$

   The cathode and anode are renewed and the concentration of the electrolyte is restored.

2. **Nickel – cadmium cell**
The anode consists of Cadmium on a suitable support the anode reaction is;

$$Cd_{(s)} + 2OH^{-}{}_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^{-}$$

The cathode is a grid covered with nickel hydroxide. The cathode reaction is;
$NiO(OH)_{(s)} + H_2O_{(l)} \rightarrow Ni(OH)_{2(s)} + OH^{-}{}_{(aq)}$
The electrolyte is potassium hydroxide. Voltage generated is 1,25 Volts. The cell is used in video cameras, phones, cordless drills, laptop computers.

Fuel Cells
They show promising future with higher efficiencies compared to coal or gas fired power stations. They are non – polluting. They are expensive since they are fed with fuel continuously. They require catalysts. A variety of fuels can be used eg, H_2, CH_4, C_3H_8.

1. **Alkaline Fuel cell**
Anode is porous carbon with catalyst in contact with $H_{2(g)}$ the anode reaction is:
$H_{2(g)} + 2OH^{-}{}_{(aq)} \rightarrow 2H_2O_{(l)} + 2e^{-}$.
Cathode is porous carbon with catalyst in contact with $O_{2(g)}$. The reaction at the cathode is
$O_{2(g)} + 2H_2O(l) + 4e \rightarrow 4OH^{-}{}_{(aq)}$
The electrolyte is hot potassium hydroxide. The cell products 1 volt

2. **Acid fuel cell**
Anode is porous carbon with catalysts in contact with hydrogen gas. The following reaction takes place.

$H_{2(g)} \rightarrow 2H^{+}{}_{(aq)} + 2e^{-}$
The cathode is also porous carbon but the catalyst is in contact with $O_{2(g)}$
$O_{2(g)} + 4H^{+}{}_{(aq)} + 4e^{-} \rightarrow 2H_2O(l)$
. The voltage produced is 1 volt.

6.3 Electrolysis

In Galvanic cells spontaneous reduction - oxidation reactions produce electrical current. Electrolysis is the reverse of what happens in Galvanic cells. A current that is forced into an electrolyte results in reactions at the electrodes which would not occur spontenously. Practical use of electrolysis include (a) charging batteries
(b) metal extraction
(c) metal plating
(d) electro refining of metals

6.3.1 Electrolytic cell

An electrolytic cell has the structure:

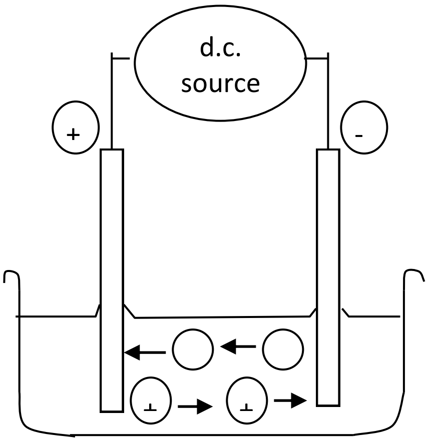


Figure 9.3.1.1 Electrochemical cell set up

Cathode reaction

$Zn^{2+} + 2e^{-} \rightarrow Zn$

Anode reaction

$Cu_{(s)} \rightarrow Cu_{(aq)}^{2+} + 2e^{-}$

The overall reaction is

$Zn_{(s)} + Cu^{2+}{}_{(aq)}$ □ □□ $Zn^{2+}{}_{(aq)} + Cu_{(s)}$

It is the opposite of what happens in the galvanic cell. The anode and cathode are reversed in the electrolytic cell.

6.3.2 Predicting electrode reactions

It is very easy to predict the products or reactions of electrolysis of binary molten salts. Only two ions are present e.g. In molten $NaCl$, only Na^{+} and Cl^{-} ions are present and they react the appropriate electrodes producing sodium metal and Cl_2 gas.

Cathode $Na^{+}{}_{(l)} + e^{-} \rightarrow Na_{(l)}$

Anode $2Cl^{-}{}_{(l)} \rightarrow Cl_{2(g)} + 2e^{-}$

There are no competing ions.

6.3.3 Electrolysis of aqueous solutions

Water has the potential to split during electrolysis thereby increasing the number of ions in solution. It becomes difficult to predict the reactions at the electrodes. If water reacts at the electrodes, the following reactions take place.

Anode $2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e$

Cathode $4e^- + 2H_2O + O_2 \rightarrow 4OH^-$

6.3.4 Electrolysis of mixtures of ions

The standard reduction potentials are important tools in predicting the order in which ions are plated on to an electrode. At a cathode two cations could compete for reactions e.g. Na^+
and Al^{3+}
The reduction potentials are:

$Al^{3+}_{aq} + 3e^- \rightarrow Al_s$ E$^\sigma$ -1.66V

$Na^+_{(aq)} + e^- \rightarrow Na_{(s)}$ -2.71V

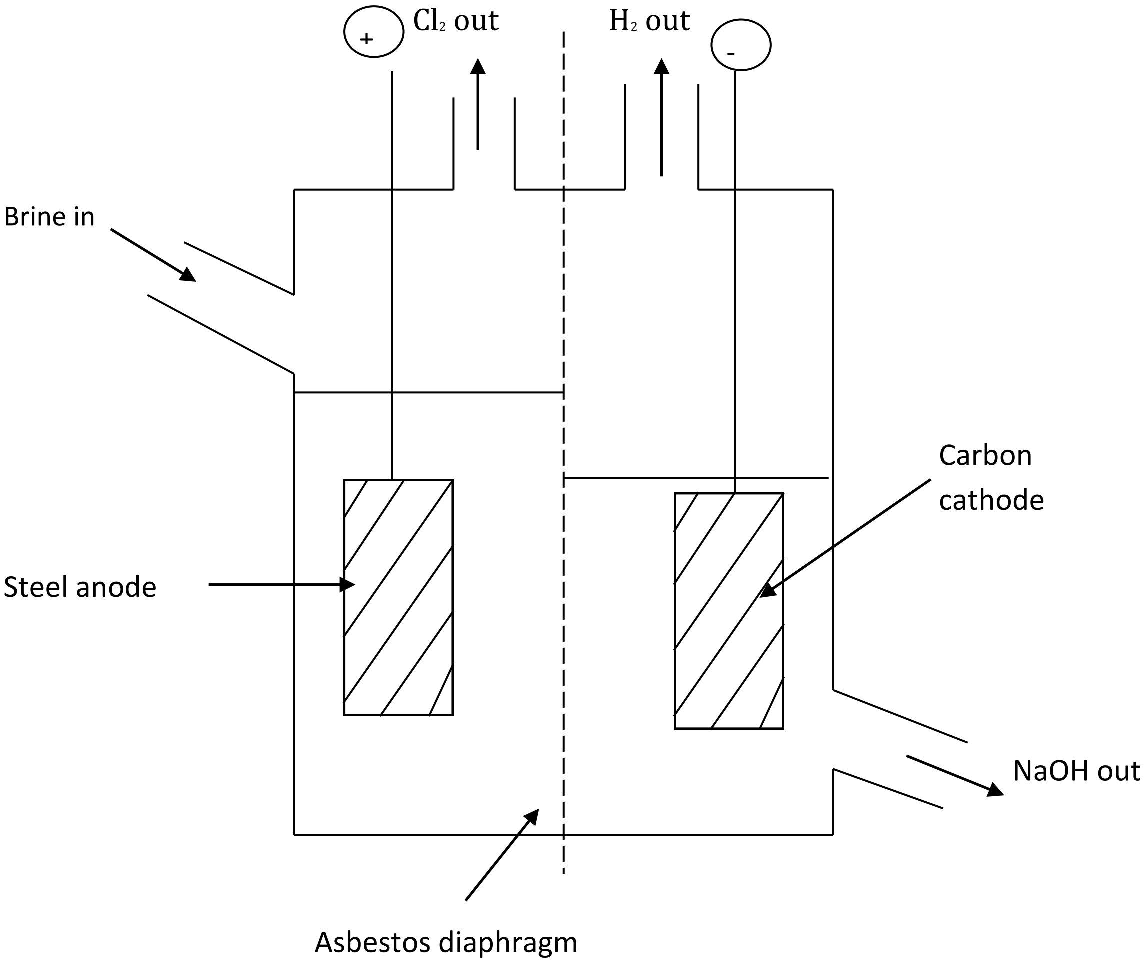
At the cathode these ions react by accepting electrons. The electrode system that is more positive is better at accepting electrons than the other. Therefore if the voltage is gradually increased, $Al_{(s)}$ is discharged.

6.3.5 Concentration

The ions of a salt are likely to react when a solution is concentrated. The probability of these ions coming into contact with the electrode is high. When a dilute solution is electrolysed, water will react at the electrodes.

6.3.6 Industrial electrolytic processes

Electrolysis of brine



- The diaphragm prevents OH^- ions from entering anode compartment and prevents Cl^- entering cathode compartment.

- Anode reaction

$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$

Cathode reaction

$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$

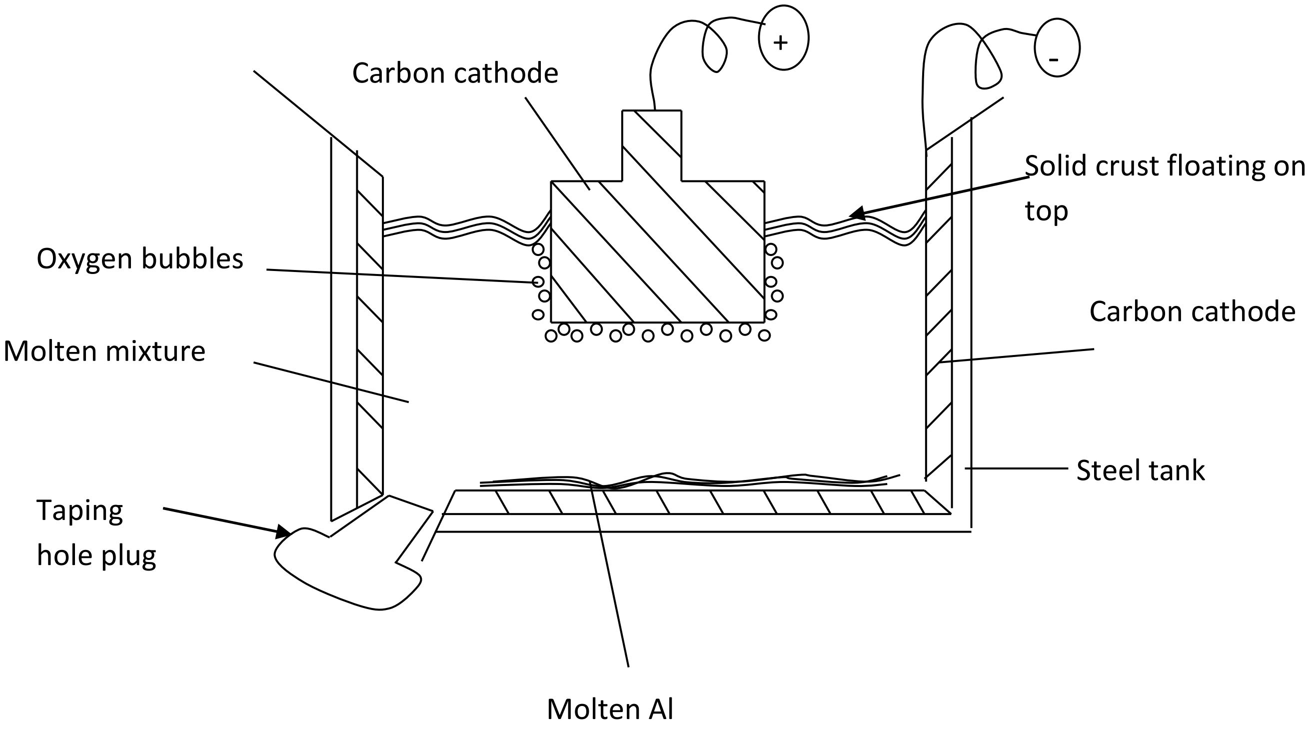
Na^+ Migrates across diaphragm to cathode compartment, combines with OH^- to form $NaOH$.

- Overall reaction
- $2H_2O_{(l)} + 2Cl^-_{(aq)} + 2Na^+_{(aq)} \rightarrow 2Na^+_{(aq)} + 2OH^-_{(aq)} + H_{2(g)} + Cl_{2(g)}$

- Product contains $NaCl$ and NaOH can be crystallized out.

Extraction of aluminium

Aluminium is a very reactive metal and exists in nature as aluminium oxide. The ore that contains the aluminium oxide is called bauxite. Production of aluminium by less vigorous means like reduction is not feasible as the ionic bonds in aluminium oxide are very strong. Electrolysis is used for the extraction of aluminium. However, aluminium cannot be obtained from the aqueous solution since water has a less negative reduction potential than Al^{3+}. Hydrogen will be discharged at the cathode. Molten aluminium oxide is used in the electrolysis process but the melting point (2050°C) is too high. A lot of energy would be needed to melt the oxide. The melting point is reduced to about 1000°C by mixing aluminium oxide with cryolite $\left(Na_3AlF_6\right)$. It is this molten mixture that is electrolysed to produce aluminium.



Electrode reactions

Cathode reaction

$$Al^{3+}{}_{(l)} + 3e^- \rightarrow Al_{(l)}$$

Anode reactions

$$2O^{2-}_{(l)} \rightarrow O_{2(g)} + 4e^-$$
$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

Effects on Electrodes

Electrolytic purification of copper

Copper is extracted by chemical reduction of its ore . The copper produced this way often contains impurities in the form of other metals. The copper is cast in thick slabs which are used as the anodes in an electrolytic cell. Pure copper is used as cathodes. Thin slabs are used. The electrolyte is copper sulphate solution.

Anode reactions

Oxidation takes place at the anode and the main reaction is

$Cu_{(s)} \rightarrow Cu^{2+}{}_{(aq)} + 2e^-$

Other reactive metals present are oxidised

$Zn \rightarrow Zn^{2+} + 2e^-$
$Fe \rightarrow Fe^{2+} + 2e^-$

Inactive metals are not oxidised and they fall to the bottom of the cell. These include silver , gold and platinum.

Cathode reaction

$Cu^{2+}{}_{(aq)} + 2e \rightarrow Cu_{(s)}$

The cathode grows thick with time while the anode gets thinner and thinner. 99,9% pure copper is obtained at the cathode.

6.3.7 Calculations on electrolysis

1. Calculations involving electrolysis are usually concerned with the mass or volume of a substance liberated during electrolysis. In such cases it is important to know the quantity of charge passed during electrolysis. If the current and duration of passing that amount of current are known, the quantity of charge in coulombs (C) can be calculated as follows:

   $C = I \times t = current\left(I\right)_A \times time\left(t\right)_s$

2. Since electrode reactions involve electron transfer, the next step would be to determine the moles of electrons transferred by the amount of charge passed into the electrolyte during electrolysis. In this case, the amount of charge carried by one mole of electrons must be known. The charge on an electron (e) was experimentally determined and is $1.6028 \times 10^{-19} C$. One mole of electrons are equal in number to the Avogadro's constant or number i.e. 6.02214×10^{23} . The total charge carried by one mole of electrons is.

   Avogadro's number x charge on an electron = Le

   The total charge carried by one mole of electrons is called a Faraday or Faraday's constant
   $\therefore F = Le$
   Substituting L and e , gives 96 485 Coulombs
   $\therefore$ One faraday = 96 485 C

To obtain the number of moles of electrons transferred during electrolysis. The total charge obtained from C = It is divided by the Faraday's constant.

Thus moles of electrons $= \frac{It}{F}$

3. Using the stoichiometry of the reaction, the number of moles of electrons is related to the moles of product, e.g. in the half reaction,

   $Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$

   The moles of Zn formed will be equal to half of the moles of electrons calculated in the step above , because the ratio of electrons to product is 2 : 1.

4. The product is required as mass or volume

- To convert the moles of product to mass the number of moles are multiplied by atomic mass or molecular mass.
- To convert moles of product to volume, the moles of product are multiplied by the molar volume.

Example

A constant current of 0.8A was maintained in a solution for 15,2 min. Calculate the mass of copper deposited at the cathode and the volume of O_2 evolved at the anode.

Solution

Total charge passed into electrolyte;
= 0.8 x 15.2 x 60
$= 729.6C.$

Cathode

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

Moles of electrons transferred $= \frac{Coulombs}{Faraday}$

$= \frac{729.6}{96485} = 7.56 \times 10^{-3}$

Moles of $Cu_{(s)}$ formed = ½ x7.56 x 10^{-3}
= 3. 78 x 10^{-3}

This is because 2 moles of electrons come from one mole of copper atoms. To convert moles to mass the atomic mass of Cu is required i.e. 63,55.

Mass of copper = moles Cu x atomic mass Cu
= 3,78 x 10^{-3} x 63,55
= 0,240g

$4H_2O_{(l)} \rightarrow O_{2g} + 4H^+_{(aq)} + 4e^-$

Total charge passed = 729.6 C

Mols of electrons transferred $= \frac{729.6}{96485} = 7.56 \times 10^{-3} mol$

Mols of O_2 formed = $\frac{1}{4} \times 7.56 \times 10^{-3} mol$

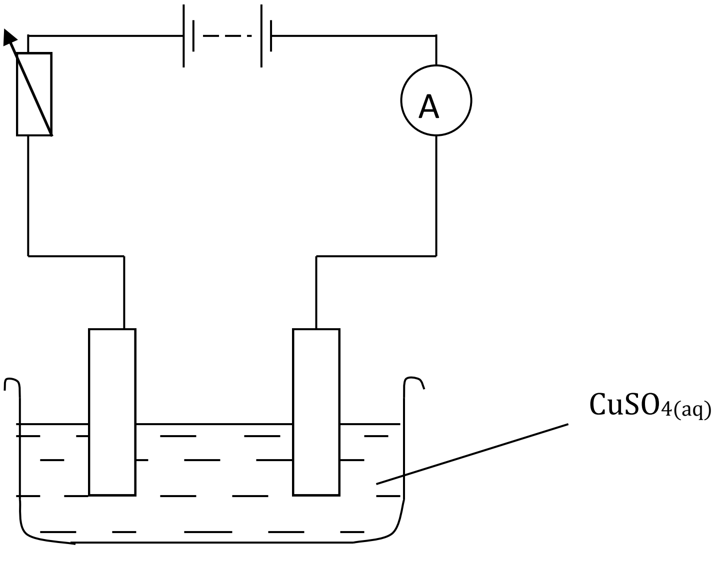
$= 1.89 \times 10^{-3}$

1 mol of gas occupies 22,4 dm dm3 (molarvolume)

$\therefore$ Volume occupied = 1.89 x $10^{-3} mol \times 22,4 dm^3$

$= 0.04 dm^3$

6.3.8 Determination of Avogadro's constant.



Apparatus is set up as shown. The masses of copper electrodes are weighed before the determination. The electrodes are dipped in $CuSO_4$ (aq) solution. The circuit is closed, time is noted and current is noted from an ammeter . The rheostat is adjusted to maintain a steady current. After time t the circuit is switched off. The electrodes are washed and reweighed.

If gain in mass = Mg

Total charge $= I \times t = It$

Moles of copper deposited $= \frac{M}{63.5} mol$

Charge required to deposit I mol of copper

$$= \frac{It}{mol} = \frac{It}{\frac{m}{635}} = \frac{It \times 63.5}{m}\ faraday$$

This is equal to the charge of 2 moles of electrons

$1.60 \times 10^{-19} \times 2 \times L$ L = Avogadro's constant

$$F = Le$$

$$\frac{63.5 \times It}{m} = L \times 2 \times 1.60 \times 10^{-19} \qquad L = \frac{1.98 \times 10^{20} \times It}{m.}$$

Summary

- Reduction is gain of electrons or a decrease in oxidation state.
- Oxidation is loss of electrons or an increase in oxidation state.
- Galvanic cells produce electricity from oxidation reduction reactions.
- Standard electrode potentials are obtained by measuring a given half cell against a standard hydrogen electrode.
- The cell potential is obtained by adding the potentials of the two half cells making up that cell.
- A reaction is only feasible or spontaneous if its calculated cell potential is positive.
- The dependence of electrode potential on concentration can be determined using Nernst equation

$$E = E^{\Phi} - \frac{0.0591}{n}\log Q$$

- Primary cells are not rechargeable
- Secondary cells are rechargeable
- Fuel cells work continuously and require a continuously supply of reactants.
- In electrolysis, an electrical current is forced through an electrolyte and it causes oxidation – reduction reactions at the electrodes.

Examination Type Questions

1 (a) Define standard electrode potential. [1]

(b) Using a suitable diagram, explain how the electrode potential of copper can be Determined. [6]

(c) Use standard electrode potential values from the data booklet to calculate the standard e.m.f. of the following cell.

$Zn_{(s)} / Zn^{2+}{}_{(aq)} // Ag^{+}{}_{(aq)} / Ag(s)$ and write the overall balanced reaction equation for the cell. [4]

CHAPTER 7

EQUILIBRIA

Introduction

Equilibrium implies a state of balance. In chemistry it applies to those reactions that do not go to completion. Such reactions have a forward reaction and a backward reaction. If a reaction is carried out in a closed system, a state is reached whereby the rate of the forward reaction equals the rate of the backward reaction, hence equilibrium is established in terms of the reaction rates. The position of equilibrium is of interest to the chemist.

It determines the yield of the reaction. Its position is determined by external variables such as temperature. One objective, therefore, of studying equilibrium is to find out how the system responds to changes of variables with a view to enhance the system and to decide on the best operating conditions for an industrial process.

The study of equilibrium enables an understanding of regulatory processes in biological systems such as buffering action of blood. It makes it possible to understand why some substances can be used to indicate the end of a reaction in acid base titrations.

Content

7.1 Reversible reactions

7.2 Types of equilibria

7.3 Le Chatelier's principle

7.4 Acids and bases

7.5 Acid-base indicators

7.6 Buffer solutions

7.7 Solubility equilibria

7.8 Summary

Learning objectives

On completion of the chapter, students should be able to:

- describe the term "reversible reaction".
- explain the state of dynamic equilibrium.
- write the equilibrium constant expression given a reaction equation.
- calculate using equilibrium concentrations, the equilibrium constant stating its units.

- write equilibrium expressions for gaseous systems.
- explain what is meant by homogeneous equilibrium in terms of the physical states of reactions and products.
- explain what is meant by heterogeneous equilibrium.
- state Le Chatelier's principle.
- explain the effect of changing concentration of reactions or products, using Le Chartelier's principle.
- explain the effect of changing temperature of a system at equilibrium.
- explain the effects of changing pressure to a gaseous system.
- explain how a catalyst affects an equilibrium system.
- justify the conditions employed in the Haber process.
- define acids and bases according to the Bronsted-Lowry theory of acids and bases.
- distinguish between strong acids and weak acids, strong bases and weak bases
- describe conjugate acids and bases.
- calculate pH of acids and bases.
- draw titration curves for acid base titrations.
- describe the equivalence point.
- explain the shapes of the titration curves.
- describe indicator action.
- deduce through calculation, the pH of an indicator at the equivalence point.
- explain how a suitable indicator can be selected for a particular type of acid-base titration.
- describe the composition of a buffer.
- explain the mechanism of buffer action.
- Calculate the pH of a buffer system.
- explain solubility product.
- calculate solubility of a solid given its solubility product and vice versa.
- show through calculation the effect of a common ion on the solubility of a substance.

7.1 Reversible reactions

When performing stoichiometry calculations, it is assumed that reactions proceed to completion. While this is true for a number of reactions, there are many reactions that do not go to completion. An example is the formation of ammonia.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

The sign $\rightleftharpoons$ indicates that the reaction is reversible. The system consists of a forward and a backward reaction which takes place at the same time. After sometime the concentration of both reactants and products becomes constant. The reaction appears to have stopped. At this point the reaction has achieved chemical equilibrium. The later refers to a state where the concentrations of reactants and products remain constant with time.

An equilibrium is achieved if the reaction is carried out in a closed vessel. If at equilibrium, there are more reactants than products, the position of equilibrium lies far to the left, and lies to the right if there are more products than the reactants at equilibrium.

7.1.1 The equilibrium condition

Equilibrium is not static. The forward reaction and the backward reaction continue to take place but at an equal rate such that there is no change in the amounts of reactants and products. The condition where the rate of the forward reaction is equal to the rate of the backward reaction is called dynamic equilibrium since reactions continue to take place. In the formation of ammonia initially there is no ammonia, and the concentration of the reactants is high. With time, the concentration of reactants gradually decreases to a constant value, similarly the concentration of ammonia builds up to a constant level. Equilibrium is reached when the concentrations of both components level off. This is shown diagrammatically below.

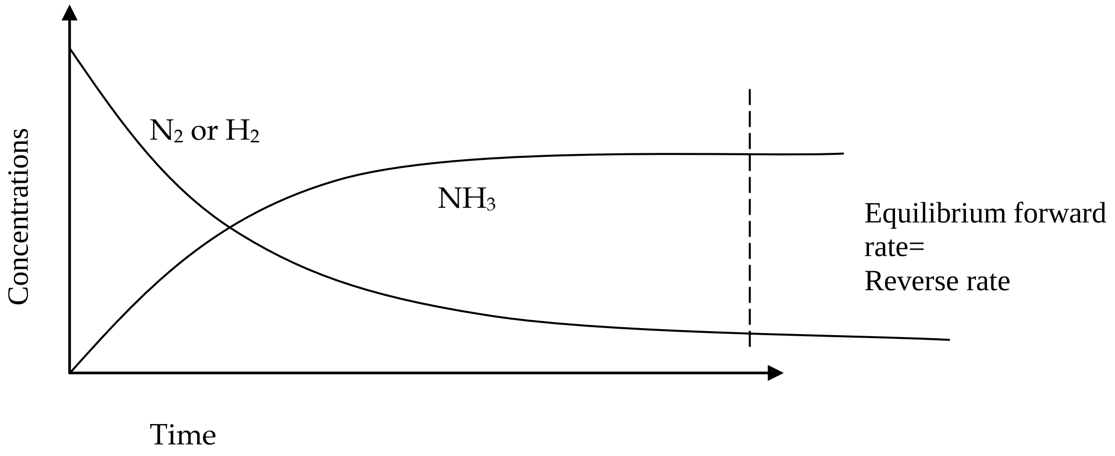


Figure 7.1 Change of concentration with time.

7.1.2 The equilibrium constant

At a given temperature the ratio of the product of the concentration of products to the product of the concentration of the reactants raised to their stoichiometric coefficients is a constant. For a reaction of the type:

$$aA + bB \rightleftharpoons cC + dD$$

where A and B are reactants and C and D are products a, b, c and d are coefficients in the balanced equation. The ratio of products to reactants is;

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

This equilibrium expression is a representation of the law of mass action. Square brackets indicate concentrations in mol dm^{-3}. K is called the equilibrium constant. K is calculated using concentrations of species at equilibrium.

Activity

Write the equilibrium expression for the reaction

$$N_{2(g)} + 3H_{2(g)} \leftarrow 2NH_{3(g)}$$

When the reaction takes place in solution, the species in the equilibrium expression are in aqueous state. The equilibrium constant is denoted as K_c since concentration terms are used.

7.1.3 Equilibrium constants for gaseous reactions

It is more convenient to use pressure terms in the equilibrium expression. Partial pressures are used for a reaction of the type,

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$$

The equilibrium constant is denoted by K_p

$$K_p = \frac{P_c.P_d}{P_a.P_b}$$

P_A means (partial pressure due to A) in the mixture. The system has a pressure = P_T i.e. P_{Total}.

For the gaseous reaction:

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

The equilibrium expression is expressed as:

$$K_p = \frac{P^2_{(NH_3)}}{P^3_{H_2} x P_{N_2}} atm^{-2}$$

7.2 Types of equilibrium

When both reactants and products are in the same phase, the type of equilibrium is called homogeneous equilibria. Formation of ammonia is an example of homogenous equilibria since all components are in the gas phase.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Many equilibria involve more than one phase. The type of equilibria in this case is called heterogeneous equilibria. The reaction below illustrates heterogeneous equilibrium.

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

The position of heterogenous equilibria is not affected by the amounts of pure solids or liquids present. The solid and liquid components do not appear in equilibrium expression of a heterogenous system.

The equilibrium expression initially is:

$$K = \frac{[CaO]\ [CO_2]}{[CaCO_3]}$$

CaO and $CaCO_3$ are pure solids and they are assigned values of 1 in the equilibrium expression since they have constant densities and hence concentrations regardless of their amounts. Thus

$$K = \frac{1\ [CO_2]}{1} = [CO_2]$$

But CO_2 is a gas. Therefore, partial pressure is used instead of concentration

$$K_p = P_{CO2}$$

For the reaction;

$$NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$$

$$K_p = P_{NH_3}.P_{HCl}$$

NH_4Cl is a solid and does not appear in the equilibrium expression.

Activity

For the reaction $H_{2(g)} + F_{2(g)} \rightleftharpoons 2HF_{(g)}$ the equilibrium constant has the value 1.15×10^2 In an experiment, 3mols of each component were added to a 1.5 dm^3 flask. Calculate the equilibrium concentrations of all species.

7.3 Le Chatelier's principle

The principle states that, if a change in conditions is imposed on a system at equilibrium, the equilibrium position will shift in a direction that tends to reduce that change in conditions.

According to the principle, the position of chemical equilibrium is determined by certain conditions. Three factors or conditions that are important are (i) change in concentration or (ii) change in pressure or (iii) change in temperature.

7.3.1 Effect of change in concentration

Change in concentration can be achieved by adding or removing a substance from a chemical reaction. The value of the equilibrium expression will no longer be equal to the equilibrium constant. The system will adjust in order to restore the value of the equilibrium constant. Using Chatelier's principle, one can predict the manner in which the reaction will adjust. Consider the reaction below:

$$A + 2B \rightleftharpoons C + D$$

If the concentration of A is increased, according to Le Chatelier the system should change in such a way as to lower the concentration of A. The position of equilibrium moves to the right i.e. reaction from left to right is temporarily favoured to consume A. Note that the equilibrium constant value does not change. When A is increased, initially the equilibrium expression gives a low value. When the system adjusts itself, equilibrium position moves back to the value of the equilibrium constant (i.e. to the right).

If [A] is reduced, the equilibrium expression assumes a value higher than the equilibrium constant. To restore equilibrium, the reaction from right to left is temporarily favoured.

7.3.2 Effect of pressure change

This applies to gaseous reactions only. Only those reactions with differences in total moles of products and reactants are affected by changes in pressure.

$$\underbrace{\text{A(g)} + \text{2B(g)}}_{\text{3 moles}} \rightleftharpoons \underbrace{\text{C(g)} + \text{D(g)}}_{\text{2 moles}}$$

Effect of increasing pressure

Equilibrium position changes in such a way as to reduce pressure. Pressure is caused by gas molecules hitting walls of the container. The more molecules there are in the container, the higher the pressure.

The system reduces pressure by forming fewer number of molecules. Equilibrium position shifts towards the side with fewer number of molecules. This reduces the pressure.

Effect of decreasing pressure

This favours the direction where more molecules are formed in order to increase pressure. Position of equilibrium shifts to the left.

When the number of molecules is equal on both sides of the reaction, the position of equilibrium is not affected. No direction of the reaction will increase or reduce pressure.

7.3.3 Effect of changing temperature

To comment on effect of temperature, there is need to know whether heat is given out or taken in (absorbed) during the reaction.

$$A + 2B \rightleftharpoons C + D; \Delta H = -250kJmol^{-1}$$

The forward reaction is exothermic. It gives out 250kj of heat per mole of A used up or per mole of each of C and D formed. The reverse reaction is endothermic absorbing 250kj when C and D react.

Effect of increasing temperature

The position of equilibrium will shift such that temperature is reduced. For a system in equilibrium at 200°C, if the temperature is increased to 400^{0}C, the system will cool itself by absorbing heat added, the backward reaction is favoured. Position of equilibrium moves to the left. The yield of the reaction is lowered at equilibrium.

Effect of decreasing temperature

The direction which increases temperature will be favoured in this case the forward reaction since heat is given out. The yield at equilibrium, i.e the amounts of products will increase at equilibrium.

7.3.4 Le Chatelier's principle and catalysts

Le Chatelier's principle does not apply to catalysts. Catalysts affect the rate of both forward and backward reactions to the same extent. It enables equilibrium to be reached quickly.

7.3.5 The Haber process conditions

The following conditions are used in the Haber process for the manufacture of ammonia

Temperature - 400^{0}C - 500^{0}C

Pressure - 200 atm

Catalyst - iron

Explaining conditions

Temperature

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}; \Delta H = -92kJmol^{-1}$$

There is need to shift position of equilibrium to the right as far as possible to increase the yield of the reaction in the equilibrium mixture. The forward reaction is exothermic. It is favoured by lowering temperature. To increase yield, the temperature must be lowered as much as possible. The temperature used in the process is not very low. If a low temperature is used, a high yield is achieved, but the reaction is slowed down. The high yield will be achieved after a very long time. The temperature of 400- 500^{0}C is set to give a reasonable yield in a short time. Recall that reaction rates usually increase with temperature exponentially.

Pressure

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

There are 4 molecules on the reactants side and 2 on the products. Increasing pressure on such a system will favour the formation of ammonia, since fewer molecules are formed, thus reducing pressure.

Increasing pressure improves the yield of reaction. 200atm is not very high. The reason is that very high pressure conditions are very expensive to produce. Thick pipes and vessels, are required to withstand the high pressures. The cost of equipment increases. Maintenance costs are high. The process would become unprofitable at higher pressure.

Catalyst

The catalyst does not affect the position of equilibrium. This function is to ensure that equilibrium is established quickly.

Activity

State and explain the conditions employed in the Contact process for the manufacture of sulphuric acid.

7.4 Acids and bases

7.4.1 Bronsted- Lowry theory of acids and bases

According to the theory, an acid is a proton (H$^+$) donor, and a base is a proton acceptor.

When gaseous hydrogen chloride dissolves in water, it donates a proton to a water molecule

$$HCI + H_2O \rightarrow H_3O^+ + Cl^-$$

HCl donates a proton to water (H_2O). It is an acid. H_2O accepts a proton from HCl. It is a base.

$$NH_3 + HCl \rightleftharpoons NH_4Cl$$

NH_3 accepts a proton. It is the base and HCl is an acid.

7.4.2 Acid strength

The strength of an acid depends on the extent to which it dissociates into ions.

$$HA_{(aq)} + H_2O_{(\ell)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{aq}$$

The equilibrium position of a strong acid lies far to the right. In fact the dissociation can be regarded as complete e.g.

The equilibrium of a weak acid lies far to the left

$$CH_3COOH_{(aq)} + H_2O_{(\ell)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

The extent to which the weak acid dissociates is expressed as:

$$K_a = \frac{\left[CH_3COO^-\right]\left[H_3O^+\right]}{\left[CH_3COOH\right]}$$

K_a - acid dissociation constant

Organic acids are weak acids.

A strong base completely dissociates in water

$$NaOH_{(s)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

A weak base dissociates partially.

$$NH_3(aq) + H_2O(\ell) \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

The equilibrium expression is:

$$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_3\right]}$$

K_b- base dissociation constant. The strength of bases depends on the size of K_b. The higher the value of K_b the stronger the base.

7.4.3 Conjugate acids and bases

When a base dissociates it forms an a "Broonsted Lowry acid"

$$NH_{3(aq)}^{+} + H_2O_{(\ell)} \rightleftharpoons NH_{4\,(aq)}^{+} + OH_{(aq)}^{-}$$

base acid acid base

Ammonia accepts a proton from water. Therefore NH_3 is a base and water an acid. During the backward reaction, NH_4^+ donates a proton to OH^- hence NH_4^+ is an acid and OH^- is a base. NH_4^+ is called the conjugate acid of NH_3 while OH^- is the conjugate base of H_2O.

Activity

Write the conjugate acids or bases of the following substances. Indicate whether species you suggest is an acid or base.

(i) CH_3NH_2

(ii) CH_3CH_2COOH

7.4.4 The Ionic product of water

Water dissociates partially to form H^+ and OH^-

$$H_2O_{(\ell)} \rightleftharpoons H_{(aq)}^{+} + OH_{(aq)}^{-}$$

The equilibrium expression is:

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

Water is a pure liquid hence its activity is 1 or its concentration is constant since the extent of dissociation is very slight.

$$\therefore K[H_2O] = [H^+][OH^-]$$

This is so when all sides are multiplied by $[H_2O]$. Since both K and $[H_2O]$ are constants, their product i.e. K x $[H_2O]$ gives a new constant K_w.

$$\therefore K_w = [H^+][OH^-]$$

K_w is the ionic product of water.

At 25^{0}C the value of K_w was determined to be 1 x 10^{-14} mo1^2 dm^{-6}. If the value of K_w is substituted in the expression,

$$\therefore K_w = [H^+][OH^-]$$

then the concentrations of H^+ and OH^- at 25^{0}C can be deduced.

$$1x10^{-14} mol^2 dm^{-6} = [H^+][OH^-]$$

Whenever 1 mole of H^+ ions are produced, an equal number of OH^- ions are produced so that $[H^+] = [OH^-]$. Therefore $[OH^-]$ can be replaced with $[H^+]$ in the expression above.

$$1x10^{-14} = \left[H^+\right]\left[H^+\right]$$

$$1x10^{-14} mol^2 dm^{-6} = \left[H^+\right]^2$$
$$\therefore \left[H^+\right] = 1x10^{-7} moldm^{-3}$$

Since $\left[H^+\right] = \left[OH^-\right]$
The concentration of OH^- in pure water = $1x10^{-7} moldm^{-3}$ at 25°C.

7.4.5 P. Functions

The p- function is a convenient way of expressing small numbers such as H^+ ion concentration in solution to any other quantities e.g. K_a and K_b. The p- function is a logarithmic scale based on base 10.

Since $[H^+]$ in an aqueous solution is usually small, it can be expressed as pH

Where $pH = -\log_{10}\left[H^+\right]$

The acidity of a solution can therefore be expressed in terms of pH
∴ e.g an acid with a concentration of 0.1 moldm^{-3} would have a pH of:
$$pH = -\log\left[H^+\right]$$
$$pH = -\log(0.1)$$
$$= 1$$
It is convenient to deal with a whole number such as 1 in place of 0.1. In this calculation it is assumed that $[H^+]$ concentration is 0.1 mol dm^{-3} since HC1 dissociates completely.

Acid dissociation constants K_a and base dissociation constants K_b are usually small and can be expressed as p functions in which case they become pK_a and pK_b respectively.

7.4.6 Calculation of the pH of strong acid solutions

pH can be calculated directly by inserting the concentration of H^+ ions in the expression.
pH= -log $[H^+]$

7.4.7 Calculation of the pH of weak acid solutions

Weak acids set up equilibria in solution. Therefore the actual $[H^+]$ in solution should be determined before pH can be calculated. The acid dissociation constant K_a should be known, usually the value of K_a is provided in a question or can be found in a data booklet.

e.g. to calculate the pH of $0.1MCH_3COOH$
$K_a = 1.7 \times 10^{-5}$ moldm^{-3}

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$K_a = \frac{\left[CH_3COO^-\right]\left[H_3O^+\right]}{CH_3COOH}$$

To get the concentration of H_30^+ at equilibrium, there is need to consider the stoichiometry of the reaction. From the reaction equation $\left[CH_3COO^-\right] = \left[H_3O^+\right]$ when x mo1 per dm^{-3} of CH_3COOH dissociate, an equal number of moles of CH_3COO^- and H_3O^+ are formed.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H_3O^+$$

Initially concentrations ($moldm^{-3}$)	0.1	0	0
Equilibrium concentration ($moldm^{-3}$)	$(0.1-x)$	x	x

At equilibrium (0.1-x) moles per litre remain undissociated. The equilibrium expression can be re-written as:

$$K_a = \frac{x.x}{0.1-x}$$

$$\therefore \quad K_a = \frac{x^2}{0.1-x}$$

To avoid the complicated quadratic equation, an assumption is made about the value of $(0.1-x)$. Since the dissociation constant is very small, (1.7×10^{-5} $moldm^{-3}$) the amount of x is very small compared to 0.1 such that essentially the term $(0.1-x)$ is approximately equal to 0.1. The denominator therefore is taken as 0.1.

Hence $K_a = \frac{x^2}{0.1}$

Substituting the value of K_a into the equation above:

$1.7 \times 10^{-5} \times 0.1 = x^2$

$1.7 \times 10^{-6} = x^2$

$x = \sqrt{1.7 \times 10^{-6}}$

$x = 1.3838 \times 10^{-3}$ $moldm^{-3}$

$\therefore$ pH = -log x

= 3- log- 1.3838

= <u>2.86</u>

For a weak base e.g. NH_3

K_b is used and it has a value of 1.8×10^{-5} mol dm^{-3}.

To calculate the pH of 0.1 $moldm^{-3}$ ammonia, $[OH^-]$ is calculated first. $[NH_4^+] = [OH^-]$

$$NH_{3(aq)} + H_2O_{(\ell)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

Initial concentration	0.1	0	0
Equilibrium concentration	$0.1-[OH^-]$	$[OH^-]$	$[OH^-]$

$$K_b = \frac{[NH_4^+]\ [OH^-]}{[NH_3]}$$

$$K_b = \frac{[0H^-]^2}{0.1 - [0H^-]}$$

Since $[OH^-]$ is very small compared to 0.1

$$K_b = \frac{[OH^-]^2}{0.1}$$

Substituting for the value of K_b

$$1.8 \times 10^{-5} = \frac{[OH^-]^2}{0.1}$$

On rearrangement,
$1.8 \times 10^{-5} \times 0.1 = [OH^-]^2$
$\sqrt{1.8 \times 10^{-5} \times 0.1} = [OH^-]$

1.34×10^{-3} moldm^{-3} = $[OH^-]$
The ionic product of water is
$K_w = [OH^-]\ [H^+]$
$K_w = 1 \times 10^{-14}$ mo1^2 dm^{-6}
$[OH^-] = 1.\ 34 \times 10^{-3}$ moldm^{-3}

The ionic product of water is
$K_w = [OH^-]\ [H^+]$

$K_w = 1 \times 10^{-14}$ mo1^2 dm^{-6}
$[OH^-] = 1.34 \times 10^{-3}$ moldm^{-3}

Substituting these values into K_w expression

$$[H^+] = \frac{1.\ X\ 10^{-14}\ \text{mo1}^2\ \text{dm}^{-6}}{1.3 \times 10^{-3}\ \text{mo1 dm}^{-3}}$$

$= 7.46 \times 10^{-12}$ mol dm^{-3}

pH = $-\log [H^+]$
= $-\log (7.46 \times 10^{-12})$
= $\underline{11.1}$

Activity
Calculate pH of
(i) 0.1 mol dm^{-3} NaOH
(ii) 0.01 moldm^{-3} NH_3
(iii) 0.1 moldm^{-3} $CH_3\ COOH$

($K_b = 1.8 \times 10^{-5}$) for NH_3
$K_a = 1.75 \times 10^{-5}$) for CH_3C00H

7.4.8 Acid base titrations

A titration is an analytical procedure for determining the volume of a known solution that is required to react with a fixed volume of another solution whose concentration is to be determined. The solutions involved may be acids and bases.

The solution whose concentration is called a standard solution. The second solution is the sample. Its identity is known but not its concentration. The concentration of the sample can be calculated if the volume of the standard solution that reacts completely with a fixed volume of a sample is determined.

pH measurement provides a means of determining the volume of the standard solution required for complete reaction. For the reaction between HCl (aq) and NaOH (aq) the equation is

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(\ell)$$

If HCl is the sample, then its concentration is unknown. The standard is NaOH and its concentration is known.

Procedure

The standard solution is put in a burette, and is added to a fixed volume of HCl in a beaker with a magnetic stirrer. A pH meter is used to measure the pH of the sample solution as reaction occurs. The standard is added in small regular portions and pH is measured after the addition of each portion. Data of volume and pH is recorded. The values of pH are then plotted against volume of standard solution. A curve like the one below is obtained.

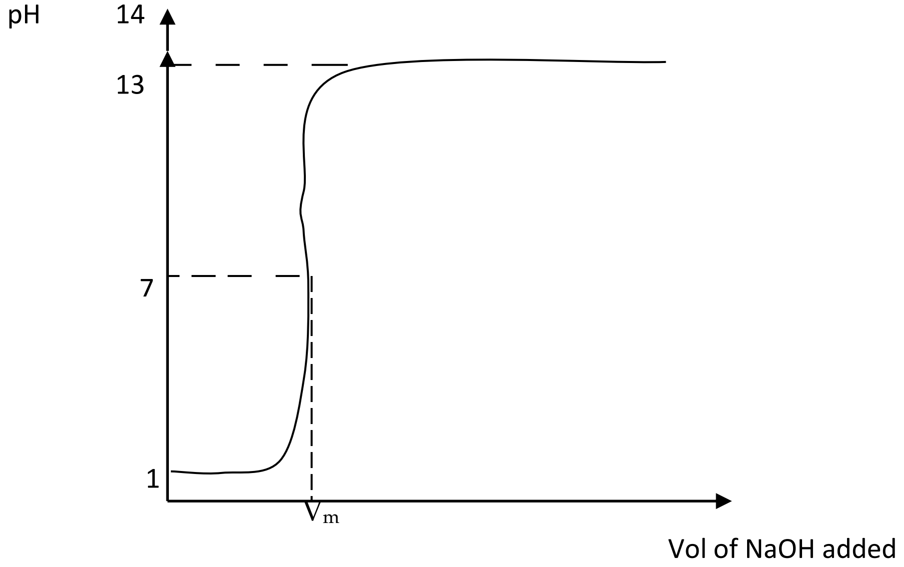


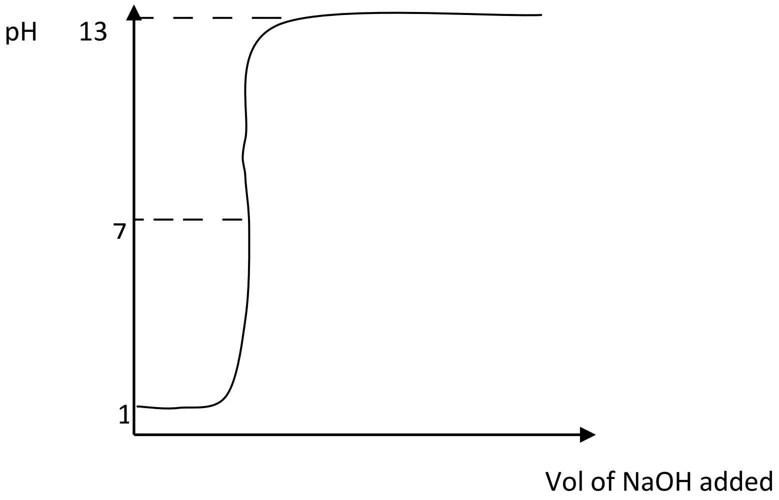
Fig 7.4.1 Titration curve

Initially pH has a low value since the solution in the beaker is a strong acid. As the base is added, the concentration of H^+ ions decreases and pH starts to rise slowly. As more base is added, a point is reached when all the H^+ have just been used up. Complete neutralization takes place. The two solutions would have reacted exactly according to the stoichiometry of the reaction. This point is called the equivalence point. In the diagram, the point lies on the vertical part of the curve. At that point addition of a drop of the standard solution causes the solution in the beaker to change from being acidic to being basic. There is rapid change in pH as shown by the vertical part. Complete neutralisation will occur at a specific value of pH depending on the strengths of the acids and bases involved. In the diagram above assuming that neutralisation occurs at a pH of 7 the volume required for neutralisation is determined by drawing a horizontal dotted line at pH 7 up to the curve. The two meet at the vertical part. Another dotted line is drawn form where the two meet down to the horizontal axis. The volume of standard solution required to react with the sample solution is read off form the horizontal axis. On the diagram above it is V_m.

Acid-base titration types

1. **Strong base Vs strong acid**

$$HCI_{(aq)} + NaOH(aq) \rightarrow NaCI(aq) + H_2O$$

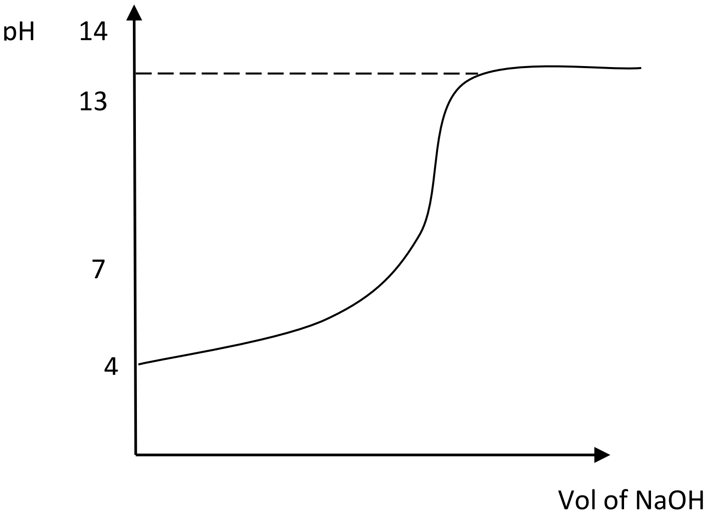


- Curve starts at low pH due to strong acid
- It levels off at a pH above 12 (alkali presence)
- At equivalence point pH of solution is due to presence of NaCl (aq) which is neutral
- Vertical part is relatively long

Figure 7.4.2 Titration of strong acid with strong base.

2. **Strong base Vs Weak acid**

$$NaOH(aq) + CH_3OOH \square\ \square\square\ CH_3COO^-Na^+_{(aq)} + H_2O(\ell) =$$



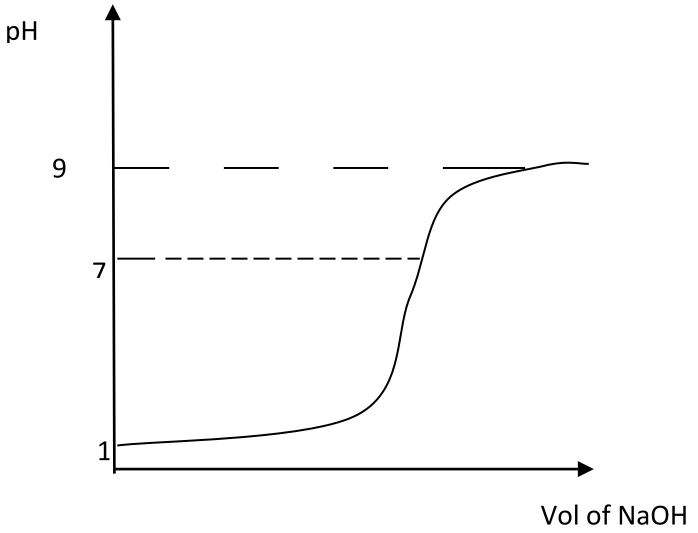
- Curve starts at fairly high pH; weak acid has relatively high pH
- Curve levels off at pH indicating strong alkali/base
- At equivalence point pH is basic since CH_3C00H produces conjugate base i.e. CH_3C00^- which hydrolyses. Thus $CH_3COO^- + H_2O \rightarrow CH_3COOH + OH^-$

Vertical part shorter than the previous curve in 1.

Figure 7.4.3 Titration of weak acid with strong base

3. **Weak base Vs strong acid**

$NH_3(aq) + HClaq \rightleftharpoons NH_4Cl_{aq}$



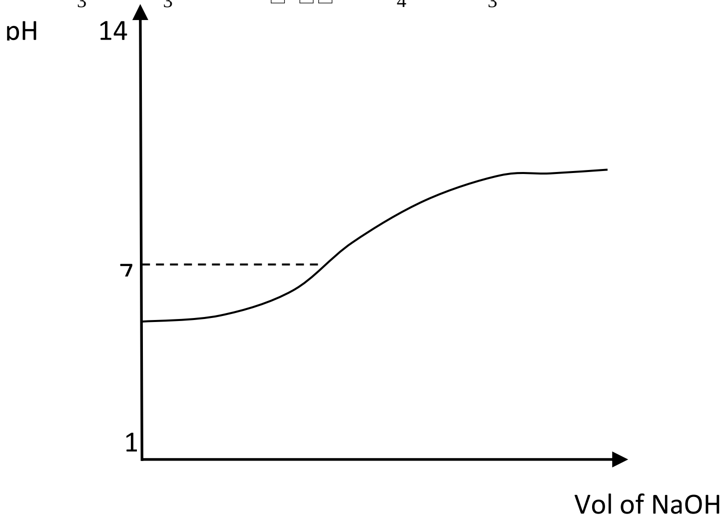
- Curve starts at low pH due to strong acid.
- Curve levels at a pH of about 10 because ammonia is a weak base
- At equivalence point the solution present is acidic due to presence of the conjugate acid (NH_4^+) which hydrolyses thus:

  $NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$

Figure 7.4.4 Titration of strong acid with weak base.

4. **Weak base Vs weak acid**

$NH_3 + CH_3COOH \rightleftharpoons NH_4^+ + CH_3COO^-$



- Curve starts at fairly high acidic pH due to presence of weak acid
- Curve levels off at pH of about pH 10 due to weak base

after equivalence point. Solution can be acidic, neutral or basic. Both the cationic and anionic parts of the salt are hydrolyzed.

Figure 7.4.5 Titration of weak acid with weak base.

7.5 Indicators (acid- base)

are weak acids and the following equilibrium is set up.

$HIn(aq) \rightleftharpoons H^+_{(aq)} + In^-_{(aq)}$

Change in H+ concentration and hence pH causes a shift of the equilibrium position and hence a change of colour.

Bromothymol blue is yellow in the form HIn and is blue in the form In^-

$$Hin \rightleftharpoons H^+ + In^-$$

Yellow Blue

Adding OH- ions
Causes position of equilibrium to shift to the right. At a certain ratio of In- and HIn when In- dominates, the solution turns blue.

On adding acid the following reaction occurs: $In^- + H_30^+ \longrightarrow HIn + H_20$

Blue yellow

The change in colour can be used to indicate the end of an acid- base reaction. If base is used to titrate an acid, at the end of reaction the acid is used up and the next drop of base causes the equilibrium of the indicator to shift to the right and colour changes form yellow to blue. Titration is stopped on addition of one drop of base that causes permanent colour change. This is the end point. It is slightly higher than the equivalence point but the difference is insignificant.

End-point indication
The end point of an acid- base reaction occurs when reactants have reacted exactly. An ideal indicator should be in the middle of its colour change at the pH of the equivalence point. The equilibrium constant for the dissociation of the indicator K_{In} is:

$$K_{In} = \frac{[H^+][In^-]}{[HIn]}$$

When the indicator is in the middle of changing colour $[HIn] = [In^-]$. The above expression becomes.

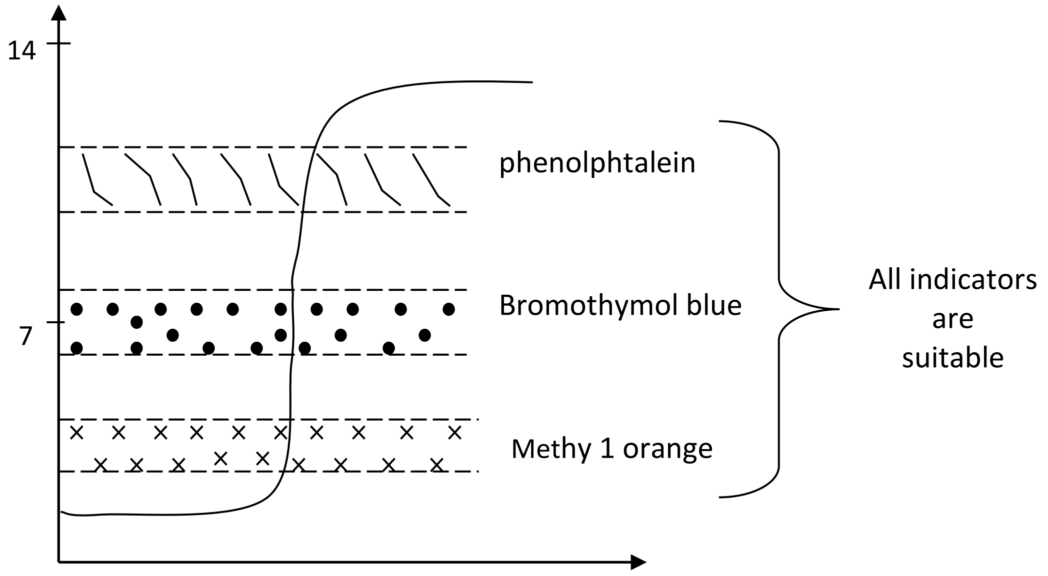
$$Kin = [H+]$$
$$\text{Since pH} = -\log[H^+]$$
$$pH = -\log K_{In}$$
$$\underline{pH = Pk_{In}}$$

For an ideal indicator pK_{in} ,should coincide with pH at the equivalence point.

7.5.1 Choosing indicators

An ideal indicator changes colour at the equivalence point. Practically any indicator that changes colour at a pH which is within the vertical part of a titration curves is suitable. It serves the purpose.

The diagram below illustrates indicators that can be used for strong base Vs strong acid titration.



- Bromothymol blue is the ideal indicator

Figure 7.5.1 Choice of indicators

7.6 Buffer solutions

A buffer solution resists changes in pH when small amounts of acid or base are added. There are two types of buffers: Acidic buffers and Basic buffers.

An acid buffer consists of a weak acid and its conjugate base. The latter is supplied by a suitable salt so that essentially an acid buffer is a mixture of a weak acid and the salt of its conjugate base. e.g.

$CH_3COOH \text{ and } CH_3COO^-Na^+$

A basic buffer is therefore a mixture of a weak base and the salt of its conjugate acid e.g

$NH_3 and NH_4^+CI^-$

For an acid buffer, the equilibrium involved is:

$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$

The salt is highly soluble and dissociates completely.

$MA_{(s)} \rightarrow M^+_{(aq)} + A^-_{(aq)}$

The salt increases the concentration of A$^-$ in the mixture. This causes the position of equilibrium system above to shift to the left forming undissociated acid HA. The buffer system has therefore a large reservoir of HA and of A$^-$.

7.6.1 How a buffer resists changes in pH

When H$^+$ ions are added, acidity increases. A$^-$ reacts with added H$^+$ thereby removing the protons from the solution according to equation $H^+ + A^- \rightarrow HA$

When OH^- ions are added

OH^- ions removed by reaction with HA thus $HA + OH^- \rightarrow H_2O + A^-$

7.6.2 The pH of a buffer

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Rearranging to get $[H^+]$

$$[H^+] = K_a \frac{[HA]}{[A^-]}$$

K_a is very small. The amount of HA at equilibrium is essentially the same as the initial concentration of the acid. The amount of A^- is almost the same as was contributed by the salt therefore $[A^-]$'s taken as equal to [salt].

$$[H^+] = K_a \frac{[ACID]}{[SALT]}$$

:- pH will depend on the ratio of acid to salt, and dilution will not affect it.

Example

A buffer solution is made by adding 2.05g $CH_3COO^-Na^+$ to 1 dm^3 of 0.09 $moldm^{-3}$ ethanoic acid. What is the pH of the buffer solution?

$$K_a(CH_3COOH) = 1.7 \times 10^{-5}\ moldm^{-3}$$

$$H^+ = K_a \frac{[Acid]}{[Anion]}$$

$$[CH3C00^-] = \left(\frac{2{,}05g}{82g}\right) mol\ dm^{-3}$$

$$= 0{,}025 moldm^{-3}$$

$$[H^+] = \frac{1.7 \times 10^{-5} \times 0.09}{0{,}0.25}$$

$$= 6.12 \times 10^{-5}\ moldm^{-3}$$

$$pH = -\log_{10}(6.12 \times 10^{-5})$$

$$= \underline{4.21}$$

Activity

Explain in terms of the equilibrium formed how a buffer functions.

7.7 Solubility equilibria

Some solids are partially soluble. The solid exists in equilibrium with its ions.

$$MX_{(S)} \rightleftharpoons M^+(aq) + X^-(aq)$$

The equilibrium expression is

$$K = \frac{[M^+][X^-]}{[MX]}$$

[MX] is the concentration of a pure solid, it is a constant. Multiplying both sides by [MX] gives

$K [MX] = [M^+]\ [X^-]$
$K[MX] = Constant = Ksp$
$K_{sp} = [M+]\ [X^-]$
K_{sp} is called the solubility product

Activity
Write K_{sp} expressions for (a) $AgCl$, (b) Mg $(0H)_2$ (c) $CaSO_4$

6.71 **Solubility**
The solubility of a substance is the amount of solid needed to make a saturated solution. Solubility can be calculated from K_{sp} data.

K_{sp} for $Mg(OH)_2$ is 2.0×10^{-11} mol^3dm^{-9} at 25°C.

$$Mg(OH)_{2(S)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^-(aq)$$

:- $Ksp = [Mg^{2+}][0H^-]^2$

If the solubility of $Mg(0H)_2$ is x $moldm^{-3}$

At equilibrium $[Mg^{2+}] = x$
$[0H^-] \quad = 2x$

Substituting into the Ksp expression

$\therefore Ksp = x\ (2x)^2$
$= 4x^3$
Since $K_{sp} = 2 \times 10^{-11}$,

$$x = \sqrt[3]{\frac{2x10^{-11}}{4}}$$

$x = 1.71 \times 10^{-4}$ mol dm^{-3}

K_{sp} can be calculated from solubility data

Example
Calculate the Ksp value for bismulth sulphide (Bi_2S_3) which has a solubility of 1×10^{-15} mol dm^{-3} at 25^0C

Solution
$Bi_2S_3(s) \rightleftharpoons 2Bi^{3+}(aq) + 3S^{2-}(aq)$

$K_{sp} = [Bi^{3+}{}_{(aq)}]^2 [S^{2-}{}_{(aq)}]^3$
Solubility= 1×10^{-15} mol dm^{-3}

At equilibrium, stoichiometry shows that
$[Bi^{3+}] = 2 \times 1 \times 10^{-15} = 2 \times 10^{-15}$ mol dm^{-3}

$[S^{2-}] = 3 \times 1 \times 10^{-15}$ mold m^{-3}= 3×10^{-15}mol dm^{-3}

$K_{sp} = [2 \times 10^{-15}]^2 [3 \times 10^{-15}]^3$

$= 1.1 \times 10^{-73}$ mol^5 dm^{-15}

7.7.2 Common ion effect

The solubility of $Mg(OH)_2$ at 25°C was given as 2.0×10^{-11} $moldm^{-3}$. This is its solubility in water. If it were to be dissolved in a solution containing 0.1$moldm^{-3}$ sodium hydroxide, what is its solubility?

$Ksp = 2 \times 10^{-11}$ mol^3dm^{-9}

$Ksp= [Mg^{2+}] [0H^-]^2$
Let solubility be s
then at equilibrium $[Mg^{2+}]$= S mol dm^{-3}
$\left[OH^- = 2s\right]$ + 0.1 $moldm^{-3}$ $0H^-$ from NaOH
Total $[0H^-]$= 0.1 + 2s

:- $Ksp = S (0.1 + 2s)^2$
The contribution of the solid is much smaller than $[0H^-]$
From NaOH
:- $0.1 + 2s \approx 0.1$
$Ksp = s (0.1)^2$
$\underline{2 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9} = s}$
$(0.1 \text{ moldm}^{-3})^2$

$S = 2 \times 10^{-9}$ mol dm^{-3} < 1.71×10^{-4} mol dm^3

The solubility of $Mg(OH)_2$ is lower in sodium hydroxide than in pure water.
Explanation: the equilibrium is:

$Mg(0H)_{2(s)} \rightleftharpoons Mg^{2+}{}_{(aq)} + 20H^-{}_{(aq)}$
the presence of a common ion in solution i.e $0H^-$, causes a stress on the equilibrium. As the $[0H^-]$ increases, the system responds by shifting in the backward direction thus reducing solubility of $Mg(0H)_2$

7.8 Summary

1. Reversible reaction - is a reaction with a forward reaction and a backward reaction which occur at the same time.
2. Dynamic equilibrium is achieved when the rate of forward reaction equals the rate of backward reaction.
3. The position of equilibrium is determined by external variables such as temperature.
4. Equilibrium constant K- ratio of products to reactants at equilibrium. For a reaction of the form aA +bB $\longrightarrow$ cC +dD.

$$K=\frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

The units of K depend on the stoichiometry of the reaction.

5. K_c is used for reaction in aqueous solutions.
   K_p is used for gaseous systems.

6. Homogeneous equilibrium involves components of a reaction whose phase or state is the same e.g. all components being in the aqueous (aq) phase.
7. Heterogeneous equilibria has components of the reaction in different phases
   e.g. $CaCO_{3(s)} + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g)$

\- Solid and pure liquid components are absent in the K expression

8. Le Chartelier's principle states that if a change in conditions is imposed on a system at equilibrium, the equilibrium will shift in a direction that tends to lessen the effects of the change imposed. The principle is used to predict the change to an equilibrium system when variables change.

- The temperature used in the Haber process is a compromise between yield and speed.
- The pressure used in the Haber process is not very high (yield promoted by high pressure) because it is expensive to maintain high pressure.
- According to the Bronsted-Lowry theory of acids and bases, an acid is a proton (H^+) donor and a base is a proton acceptor.
- Strong acids and bases dissociate completely in solution. Weak acids and bases dissociates partially in solution.
- A conjugate acid is a species derived from a weak base.
- A conjugate base is derived from a weak acid.
- The ionic product of water is $K_w= [OH^-]\,[H^+]$ at $25^0C = 10^{-14}$ mo1^2 dm^{-6}. Used to find $[OH^-]$ or $[H^+]$ when calculating pH or pH.
- The shape of a titration curve and its other characteristics are determined by the strengths of acids and bases used in the titration. When weak acids or bases are involved with strong bases or acids they tend not to produce neutral solutions at the equivalence point.
- The colour of an acid-base indicator depends on pH.
- An ideal indicator is one that changes colour at the equivalence point of a reaction.
- Solubility refers to the amount of solid that dissolves in a solvent to form a saturated solution. Solubility product (K_{sp}) is the product of ions in concentrations of ions in solution raised to their stoichiometric coefficients.
- Buffers are solution mixtures of (i) weak acids and salts of their conjugate bases (ii) weak bases and salts of their conjugate acids.
- Common ions reduce the solubility of a solid.

Examination Type Questions

1 State Le Chatelier's principle. [2]

b) Discuss the factors which affect the position of the equilibrium.

$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g);\Delta H - negative$

in the Haber process for the manufacture of ammonia. [8]

c) Explain the choice of operating conditions in industrial production of ammonia. [10]

2(a) Explain how and why the presence of a catalyst affects the rate of a chemical reaction [5]

(b) State and explain how the rate constants k_1 and k_{-1} of the forward and reverse reactions and the equilibrium constant K_c for the reaction $H_2(g)+I_2(g) \rightleftharpoons 2HI(g)\Delta H - positive$ would change, if at all.

(i) In the presence of a catalyst. [4]

(ii) With an increase in temperature. [5]

(c) Use examples to illustrate homogeneous and heterogeneous catalysis. [6]

3. Define pH.

Calculate the pH of,

(i) 0.1 mo1 dm^{-3} aqueous ethanoic acid. [3]

(ii) A mixture of equal volumes of 0.10 $moldm^{-3}$ aqueous ethanoic acid and 0,100$moldm^{-3}$ aqueous sodium ethanoate.

What is the name given to the mixture in (ii)? What can such mixtures be used for? [3]

$K_a(CH_3COOH)=1.75x10^{-5}moldm^{-3}$

4. The solubility of barium hydroxide, Ba $(OH)_2$ at 25^0C is 0.24g dm^{-3}.

a) (i) Calculate the molar concentration of the saturated aqueous solution.

(ii) Calculate the hydroxide ion concentration of the solution.

(b) (i) Write the K_{sp} expression for Ba $(OH)_2$.

(ii) Using values obtained in (a) calculate the value of the solubility product stating the units.

CHAPTER 8

REACTION KINETICS

The commercial application of a reaction depends upon a thorough knowledge of many of its characteristics. Reaction kinetics which is about the rates at which reactions proceed among many other aspects is one of the important characteristics. While thermodynamics may predict the spontaneity of a reaction, the reaction may not take place at all or it may occur at a very slow rate. To be useful, reactions must occur at reasonable rates. The other goal of studying reaction kinetics is to establish and understand the mechanisms of reactions, that is, the steps involved in the reaction. With an understanding of the mechanism it is possible to come up with means to facilitate the reaction eg use of high temperatures and catalysts to speed up reaction.

This chapter will focus on important ideas of reaction kinetics: reaction rates, rate laws, reaction mechanism, collision theory and catalysis.

Content

8.1 Reaction rates

8.2 Rate laws and orders of reactions

8.3 First order rate laws and half life concept

8.4 Reaction mechanisms

8.5 Collision theory

8.6 Mechanisms of catalysis

8.7 Enzymes

8.8 Summary

Learning outcomes

On completing this chapter the student should be able to:

- explain the term ‘reaction rate’ in terms of concentration and time.
- identify the factors which affect the rate of reaction
- write rate laws
- deduce the orders of reactions with respect to reactants using the graphical method and the initial rates method
- calculate the overall order of a reaction

- calculate the rate constant from experimental data
- derive the integrated rate law for first order reactions
- define the term half life
- determine by calculation the half life of a reaction
- determine graphically the half life of a reaction
- deduce the order of a reaction using the half life concept.
- explain what is meant by the term reaction mechanism
- propose mechanisms of given reactions that are consistent with observed kinetics
- describe the molecularity of a reaction
- outline the collision theory and use it to explain how concentration, temperature and catalysts affect the rate of reactions
- differentiate between heterogeneous and homogeneous catalysis.
- describe the nature of enzymes.

8.1 Reaction rates

8.1.1 Measuring rates

The rate of a reaction is the rate of removal of reactant or the rate of formation of product. It is the change in concentration or amount divided by the time taken for that change.

$$\text{Rate} = \frac{change\ in\ amount\ or\ concentration}{time\ taken\ for\ change\ to\ occur}$$

For a reactant removal

$$\text{Rate} = -\frac{change\ in\ concentration\ (dc)}{time\ taken\ (dt)}$$

$$= \frac{-dc}{dt}$$

For formation of product;

$$Rate = \frac{dc}{dt}$$

Experimental results can be obtained in many ways depending on the type or nature of reaction such as;

1. Collecting a gaseous product in a gas syringe or inverted burette where gas is produced.
2. Titrating an acid or alkali if one is produced.

For a reactant, if concentration data is plotted against time, a graph of the type indicated below is obtained.

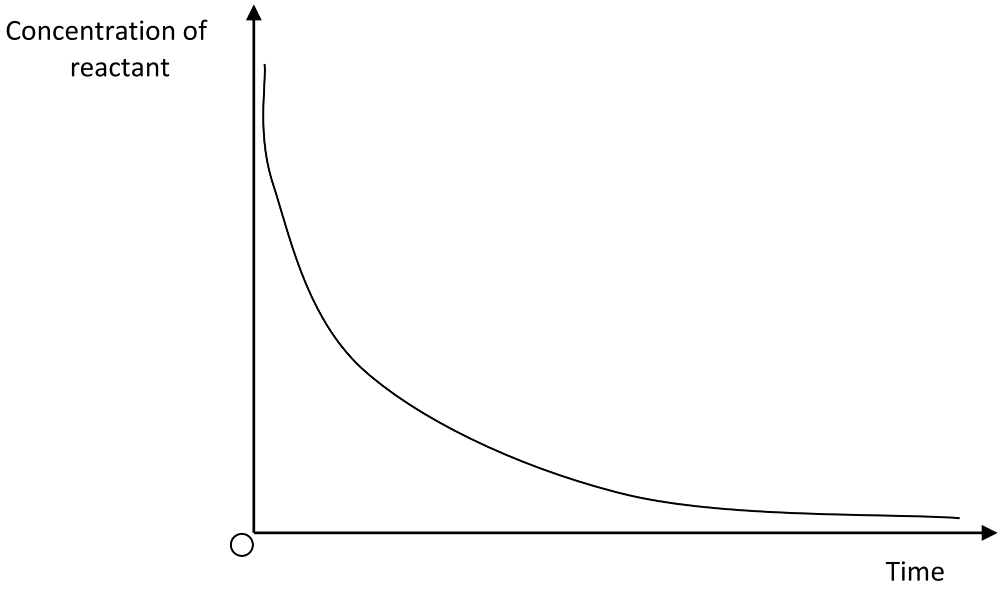


Fig 8.1 **Change in concentration of a reactant with time.**

The rate of a reaction at a particular time can be determined by drawing a tangent to the curve at a point that corresponds to the particular time and finding its gradient. The gradient is taken as the rate of reaction

Thus, Rate = $= \frac{-dc}{dt}$

8.1.2 Factors affecting the rate of reaction

1. Chemical nature of reactants

This is about the reactivity of elements. Some elements are more reactive than others. Some elements easily lose electrons i.e. they are good reducing agents and others are good acceptors of electrons. Such elements will react quite fast compared to others

2. The state of the reactants

The state of subdivision of reactants determines the extent of contact between reactants. Solid lumps are less reactive compared to powders which have greater surface area. Liquids are more reactive than solids.

3. Concentration of reactants

Most reactions are affected by concentration. The higher the concentration the higher the rate of reaction. There are many particles per unit volume, collision rate increases hence rate also increases.

4. Temperature

High temperature increases the rate of most reactions. It increases the fraction of particles with activation energy or more. Particles gain energy. Frequency of collision increases so does reaction rate.

5. Catalysts

A catalyst alters the rate of a reaction but is itself not used up during the reaction. It increases the speed of reactions.

8.2 Factors affecting the rate of reaction

From experimental results, it is necessary to know how the rate of a reaction varies with respect to the concentration of individual reactants. A rate expression can then be derived which summarizes what controls the speed of a particular reaction in terms of the relevant reactants. Not necessarily all reactants may affect the rate of a reaction. For a reaction with 3 reactants, Aa + Bb + cC→. . .

The rate expression has the form.

Rate = $k\,[A]^a\,[B]^b\,[C]^c$

(Also called rate equation or rate law)

k is the rate constant; it is constant at a given temperature

a, b and c are the orders of reaction with respect to individual reactants, the orders specify the dependence of rate on a particular reactant, e.g. if a = 1 then the rate varies directly as the concentration of A .

The overall order of the reaction is the sum of the individuals orders i.e. a+b+c. orders of reaction are determined experimentally and not from stoichiometry.

8.2.1 Determination of order of reaction

8.2.1 Graphic method

The rate law has the form

$R = k[x]^n$

for a specific component or reactant. In this method R is plotted against $\left[x\right]$ and then order with respect to x is deduced from the shape of the resulting graph.

Zero order

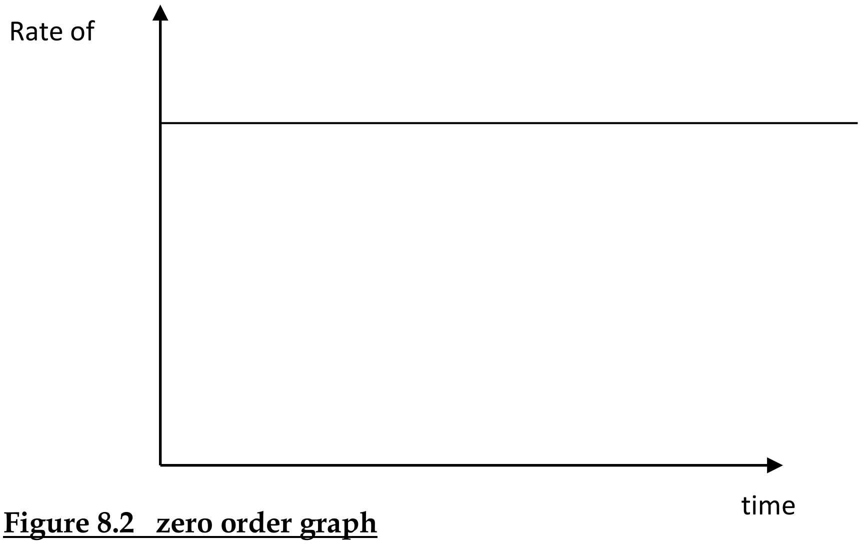


Figure 8.2 zero order graph

The rate of reaction is not affected by change in $[x]$. The rate is constant and is equal to K.

First order

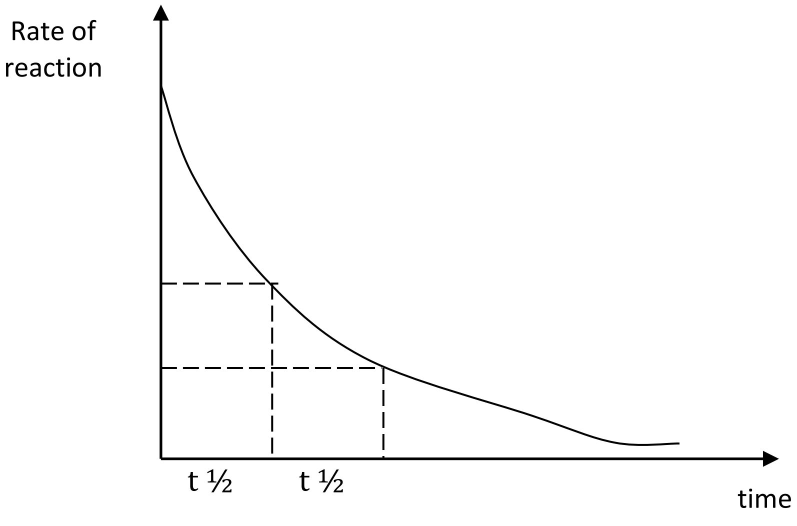


Figure 8.3 : first order graph

The rate increases as $[x]$ increases. Linear relationships exist between the two.

Half-life is constant.

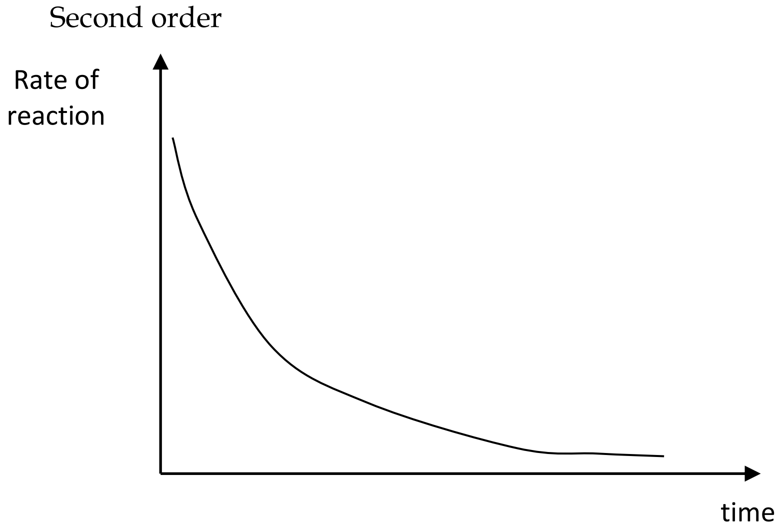


Figure 8.4 Second order graph

If a plot of R against $[x]$ shows an exponential relationship then reaction order with respect to x is 2 but half life is not constant.

7.2.2 The initial rates method

In this method initial rate of reaction is measured before and after varying the concentration of the reactant whose order is to be determined. Concentrations of the other reactant (s) is/are maintained constant. This is done in turn for all reactants. Appropriate equations are formed and solved using the rate law.

Example: The following data was obtained at 25°C for the reaction $A+2B\rightarrow C$

Exp. No	$[A]/moldm^{-3}$	$[B]/moldm^{-3}$	**Rate of Formation of C moldm^{-3} sec^{-1}**
1	0,10	0.05	$0.02\text{x}10^2$
2	0,10	0.10	$0.04\text{x}10^2$
3	0,05	0.10	$0.01\text{x}10^2$
4	0,10	0,20	$0.08\text{x}10^2$

(a) Deduce order with respect to A.

Exp 2 and 3 $[A]$ is changed $[B]$ is constant R = k $[A]^a [B]^b$

Substituting values for exp . 2 (1) $0.04\text{x } 10^2 = k\,[0.10]^a\,[0.10]^b$

Substituting for exp 3 (2) $0.01 \text{ x } 10^2 = k\,[0.05]^a\,[0.10]^b$

Dividing equation (1) by equation (2)

$$4 = 2^a$$

$$\therefore a = 2$$

(b) Deduce order with respect to B.

Exp 4 $0.08 \times 10^2 = k\,[0.10]^a\,[0.20]^b$ (3)

Exp 2 $0.04 \times 10^2 = k\,[0.10]^a\,[0.10]^b$ (4)

Dividing equation 3 by equation 4

$$2 = 2^b$$

$$\therefore b = 1$$

Rate law = R = k $[A]^2\,[B]$

(c) Calculate the value of k and state its units.

Take any one experiment; substitute its values in the rate law.

R = k $[A]^2\,[B]^b$

Using exp 4;

Exp 4 0.08×10^2 moldm^{-3-15} = $K\left[0.10\right]^2\left[0.20\right] mol^3 dm^{-9}$

$$K = \frac{0.08 \times 10^2\, moldm^{-3}s^{-1}}{\left(0.10\right)^2\left(0.20\right) mol^3 dm^{-9}}$$

$$= 4 \times 10^3\, mol^{-2} dm^6 s^{-1}$$

Activity

The reaction of bromate and bromide ions in acidic aqeous solution was studied.

$$BrO^-_{3(aq)} + 5Br^-_{(aq)} + 6H^+_{(aq)} \rightarrow 3Br_{2(l)} + 3H_2O_{(l)}$$

The results of four experiments are given below in the table.

Table 8,2 . Results for $BrO^-_{3\,(aq)} + 5Br^-{}_{(aq)} + 6H^+{}_{(aq)} \rightarrow 3Br_{2(aq)} + 3H_2O_{(l)}$

Exp	Initial conc $BrO_3^- moldm^{-3}$	Initial conc $Br^- moldm^{-3}$	Initial conc $H^+ moldm^{-3}$	Measured initial rate $moldm^{-3}s^{-1}$
1	0.10	0.10	0.10	8.00×10^{-4}
2	0.20	0.10	0.10	1.60×10^{-3}
3	0.20	0.20	0.10	3.20×10^{-3}
4	0.10	0.10	0.20	3.20×10^{-3}

Using the information above,

(a) determine the orders for all reactants

(b) the overall order

(c) the value of the rate constant

8.3 First order Rate laws and half life concept

8.3.1 Integral rate law

For a reaction of the form $aA \rightarrow products$

The differential rate law is

$$R = \frac{d[A]}{dt} = k[A]$$

The integrated first order law is

In[A] = -kt + l [A]$_o$

$\left[A\right]_o$ = Initial concentration

$\left[A\right]$ = Concentration at time t.

1. The law shows how the concentration of A depends on time. If $\left[A\right]_o$ and k are known, $\left[A\right]$ at any time can be determined.
2. The equation is of the form y = mx + c. Plot of y against x gives a straight line.

   $\therefore$ Plot of [A] against t gives a straight line. This is used to test whether a reaction is first order.

8.3.2 Half life ($t_{½}$)

It is the time taken for the concentration of a reactant to fall by half

For a reaction $aA \rightarrow products$

$$In\left(\frac{[AY_0]}{A}\right) = kt$$

At t = $t_{½}$, $\left[A\right] = {}^{1}\!/_{2}\left[A\right]_o$

$$\therefore \ln\left(\frac{\left[A_0\right]}{\left[\frac{1}{2}A_0\right]}\right) = kt_{\frac{1}{2}}$$

$$\ln 2 = Kt_{\frac{1}{2}}$$

$$t_{\frac{1}{2}} = \frac{0,693}{K}$$

$t_{½}$ can be calculated if k is known.

The half life of first order reaction is constant. The half life can also be determined graphically. Concentration is plotted against time.

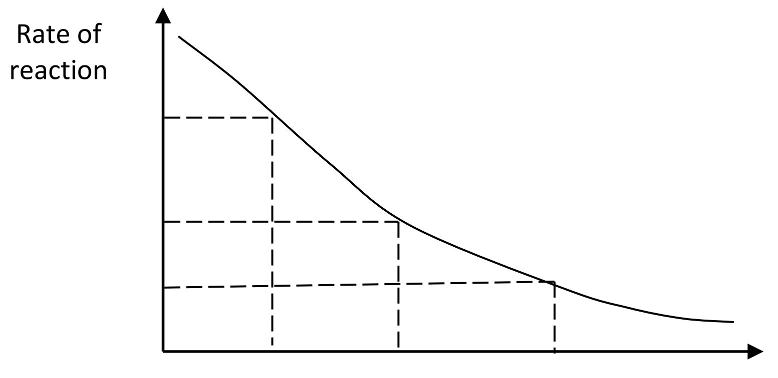


Figure 7.5 half life determination.

t_1, t_2 and t_3 are compared . If they are equal , then each of them is equal to $t_{1/2}$ and reaction is first order with respect to the reactant.

Activity

Decomposition of N_2O_5 was studied at constant temperature .

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

The following results were obtained.

$[N_2O_5]\,moldm^{-3}$	$Time(s)$
0.1000	0
0.0707	50
0.0500	100
0.0250	200
0.0125	300
0.00625	400

Verify that the reaction is first order with respect to in $[N_2O_5]$

8.4 Reaction mechanisms

One of the objectives of determining the order of a reaction is to establish the mechanisms by which the reactions occur. The rate equation is a summary of what actually happens during a reaction. The series of steps leading to the formation of the products makes up the reaction mechanism. It is a detailed account of how the reaction takes place. Having obtained the rate law, one should be able to propose a mechanism for the reaction that is consistent with the observed kinetics according to the rate law.

The reaction of NO_2 and CO is summarized below

$$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$$

The rate law, determined through experiment is

$$Rate = K\left[NO_2\right]^2$$

The reaction above occurs by a series of steps and one of the steps is slow compared with the other steps. It is the slow step that determines the rate of the reaction, therefore only terms in the slow step should be in the rate law.

Proposed mechanism for the reaction above is a two step process suggested as follows:

$$NO_{2(g)} + NO_{2(g)} \xrightarrow{k_1} NO_{3(g)} + NO_{(g)} \quad \text{slow}$$

$$NO_{3(g)} + CO_{(g)} \underset{\rightarrow}{k2} NO_{2(g)} + CO_{2(g)} \quad \text{fast}$$

K_1 and K_2 are not rate constants for the individual steps

NO_3 does not appear in the overall reaction. It is an intermediate. It is formed and consumed during the reaction.

Each of the steps is referred to as an elementary step. The elementary step is a reaction whose rate law can be written from its molecularity. The molecularity of a reaction is the number of species that must collide to produce the reaction indicated by the reaction step.

A reaction step involving one species is said to be unimolecular. A step involving collision between two species is bimolecular. A step with three colliding species is termolecular.

The reaction mechanism must satisfy two conditions:

(i) The sum of elementary steps should simplify to the overall balanced equation.

(ii) The mechanism must be consistent with the experimentally determined rate law.

$$\therefore \text{Step 1 } NO_{2(g)} + NO_{2(g)} \rightarrow NO_{3(g)} + NO_{(g)}$$

$$\therefore \text{Step 2 } NO_{3(g)} + CO_{(g)} \rightarrow NO_{2(g)} + CO_{2(g)}$$

Adding the reactants and products

Step 1 + step 2

$$NO_{2(g)} + \cancel{NO_{2(g)}} + \cancel{NO_{3(g)}} + CO_{(g)} \rightarrow \cancel{NO_{3(g)}} + NO_{(g)} + \cancel{NO_{2(g)}} + CO_{2(g)}$$

$$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$$

- The first condition is satisfied.
- The first step is proposed as slow. Analysis of the rate law shows that it contains species in the slow step. Since the first step is the rate determining step the second condition is satisfied. The mechanism is therefore valid or acceptable.

Activity

The reaction between $NO_{2(g)}$ and flourine is given by

$$2NO_{2(g)} + F_{2(g)} \rightarrow 2NO_2F_{(g)}$$

The experimentally determined rate law is

$$Rate = K\left[NO_2\right]\left[F_2\right]$$

(a) Suggest a mechanism for this reaction

(b) What is its molecularity.

8.5 Collision theory

It is important to understand how concentration and temperature affect the rate of a reaction hence it is necessary to know what happens to molecules during reaction. The collision theory states that for a reaction between two particles to take place, an effective collision must occur. An effective collision is one that results in a reaction.

The rate of reaction measures the frequency of effective collisions. The rate of reaction will be improved by any factor that increases the frequency of collisions.

8.5.1 Concentration:

Increased concentration will lead to a situation whereby there are many particles present in the same volume. The frequency of collision is high and the probability of effective collisions increases.

Effective collision requires that molecules be correctly oriented, otherwise no reaction takes place. It also requires that molecules / particles have sufficient kinetic energy. The minimum kinetic energy necessary for reaction is called activation energy (E_A). Slow moving particles will not form the product. The particles must collide with sufficient energy to break reactant bonds so that new ones are formed.

8.5.2 Temperature

The distribution of kinetic energy in a reaction system at temperature T_1 can be represented using Boltzman's distribution curve.

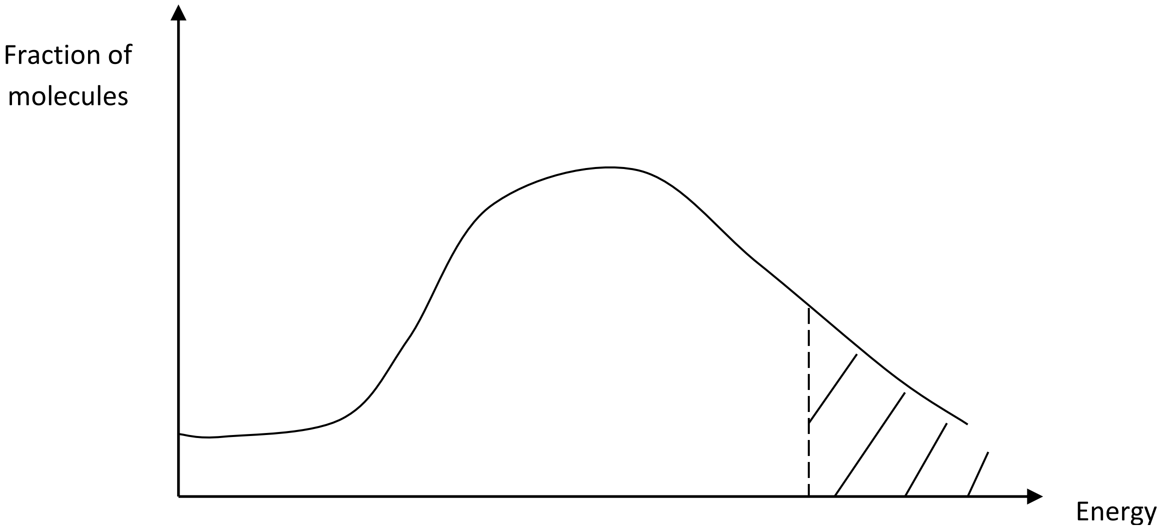


Figure 8.6 Boltzman distribution of kinetic energy

The shaded part represents particles with activation energy or more. These are the particles, with the potential to react. If the temperature is increased the proportion of particles with activation energy increases. Then there are more particles with enough energy to react.

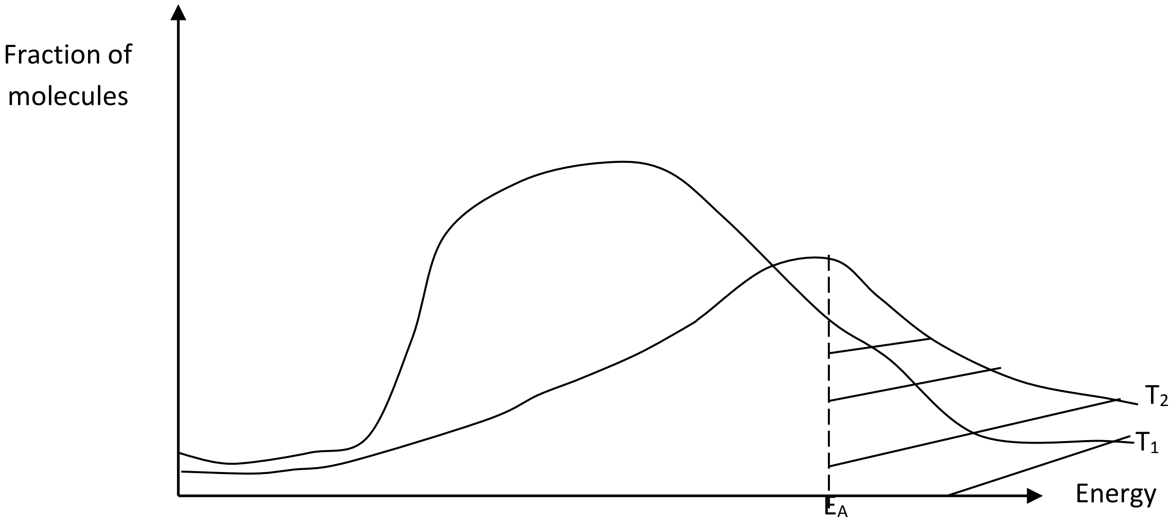


Figure 8.7 Effect of changing temperature
Temperature $T_2 > T_1$

8.5.3 The effect of a catalyst

A catalyst speeds up a reaction and it works by lowering the activation energy of a reaction. It provides an alternative reaction pathway for a reaction. The effect of a catalyst is illustrated using the Boltzman distribution below.

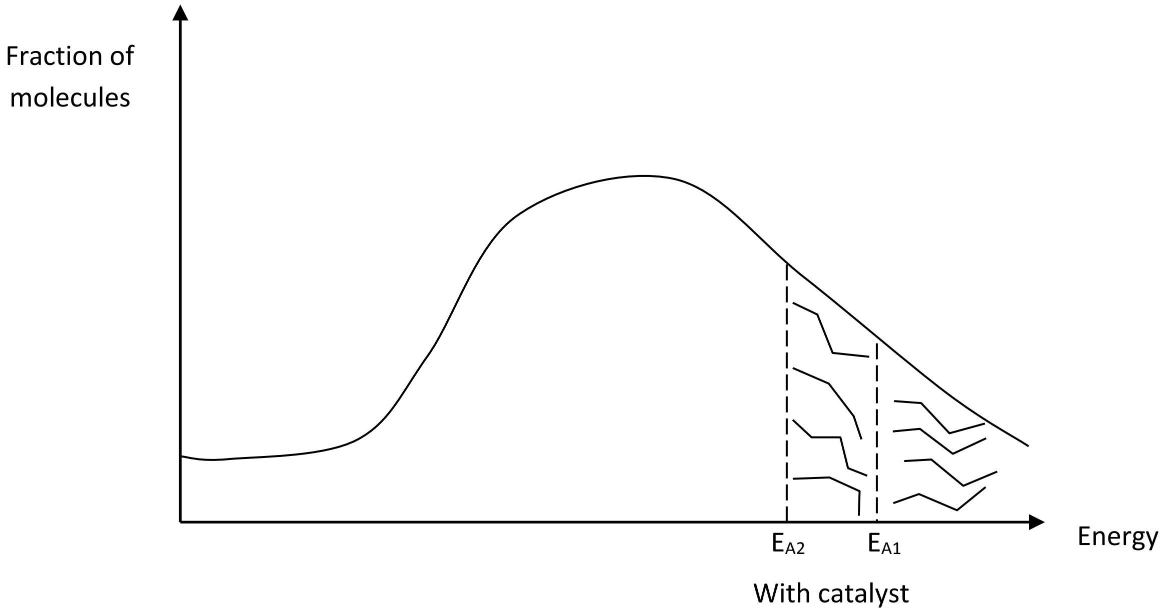
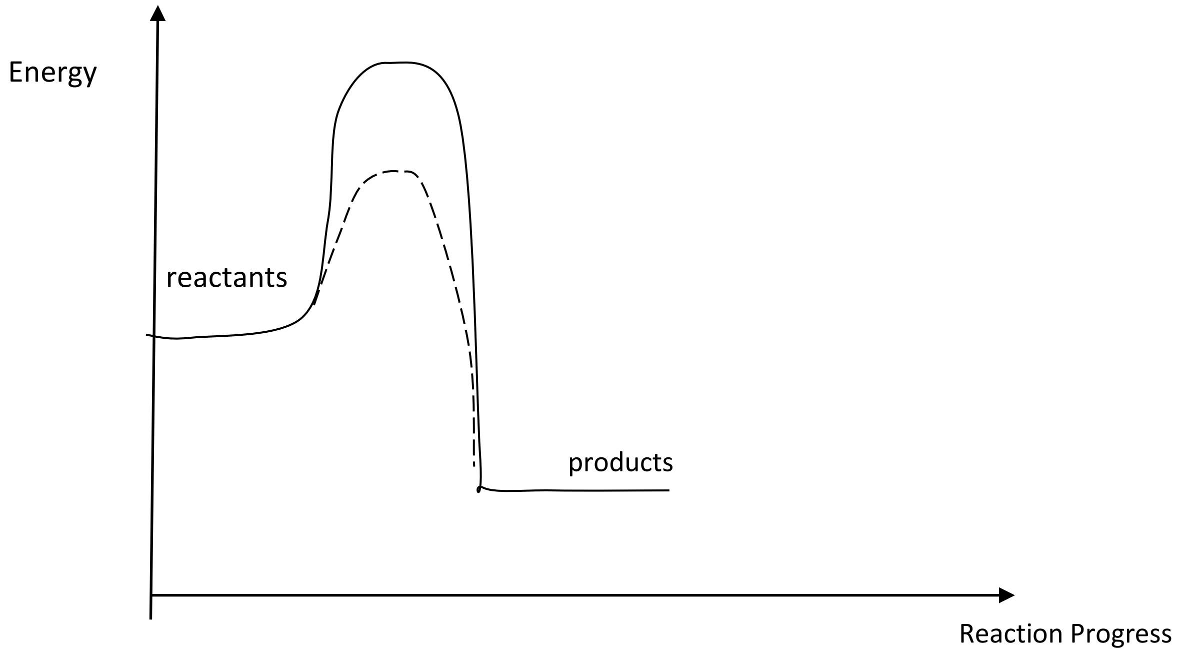


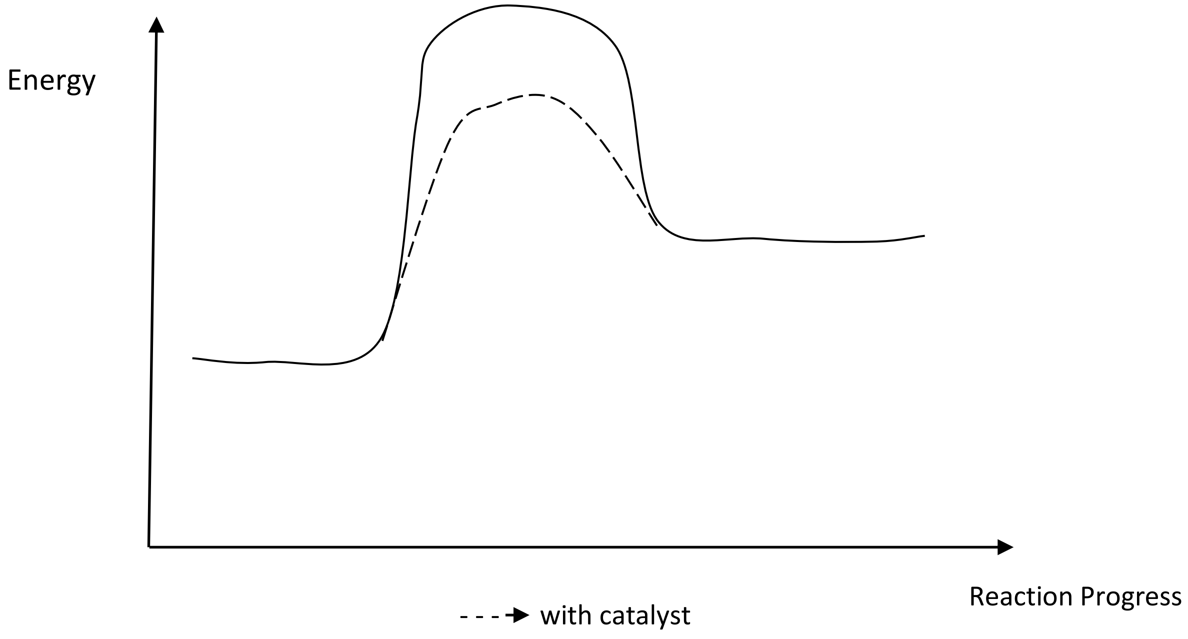
Figure 7.8 Effect of a catalyst.

E_{A_1} is the number of molecules with activation energy or more, (for the small fraction of particles has enough energy to react). The rate of reaction is low since the probability of the particles colliding is low.
E_{A2} is the number of molecules with activation energy or more for the catalysed reaction . is E_{A2} is lower than E_{A_1} . A greater proportion of particles (shaded part) have enough energy to react at the same temperature.

Effect of catalyst on exothermic and endothermic reactions also shown on diagrams below

Exorthermic Reaction





8.6 MECHANISMS OF CATALYSIS

8.6.1 Heterogeneous catalysis.

The catalyst and reactants are in different physical states, or phases. In most instances, the catalyst is solid and the reactants can be liquid or gaseous. The reaction takes place on the surface of the catalyst which may be a transition metal or one of its compounds.

The reactants must be adsorbed on to the catalyst surface at the active sites. The reactants can be physically adsorbed or could be weakly bonded chemically to the catalysts surface. This has the effect of bringing close together the reactants to allow a high probability of effective collision. Product is desorbed.

Examples of heterogeneous catalysis

Pt , Rh and Pd are used in catalytic converters to remove oxides of nitrogen from the exhaust of cars.
Iron is used in the Haber process for the manufacture of ammonia

$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$$

The catalyst catalyses the combination of nitrogen and hydrogen.

8.6.2 Homogeneous catalysis

The catalysts and reactants are in the same phase usually in solution. The catalytic action takes place within bulk of the reaction medium. Catalysis can be due to temporary changes in the oxidation state and ligands of a transition metal ion resulting in catalytic cycle. The catalyst reacts but is regenerated.

Catalysis involving Fe^{2+} / Fe^{3+}

The reaction involved is

$$S_2O_8^{2-}{}_{(aq)} + 2I^-{}_{(aq)} \rightarrow I_{2(aq)} + 2SO_4^{2-}{}_{(aq)}$$

The uncatalysed reaction involves collision between two negative ions hence very high activation energy E_{A_1} is required.

The collision between Fe^{3+} and I^- is favourable since the ions have opposite charge.

Mechanism

First step

$$2Fe^{3+}{}_{(aq)} + 2I^-{}_{(aq)} \rightarrow 2Fe^{2+}{}_{(aq)} + I_{2(aq)}$$

Second step

$$2Fe^{2+}{}_{(aq)} + S_2O_8^{2-}{}_{(aq)} \rightarrow 2SO_4^{2-} + 2Fe^{3+}{}_{(aq)}$$

The Fe^{3+} is regenerated and is therefore involved in a catalytic cycle.

Addition of the two steps gives the desired reaction

$$S_2O_{8(aq)}^{2-} + 2I^-{}_{(aq)} \rightarrow 2SO_{4(aq)}^{2-} + I_{2(aq)}$$

Fe^{2+} is an intermediate.

8.7 Enzymes

They are biological molecules that function in a similar way to inorganic catalysts. They are globular proteins. They have active sites in three dimensional structure. They are specific and will catalyse a particular type of reaction. Enzyme activity is affected by temperature. Above certain temperatures the enzymes are denatured. They are less affected by pH. Different enzymes work best at different optimum pH values.

Summary

The rate of a reaction = $\frac{change\ in\ concentration}{time\ taken\ for\ change}$

- The factors that affect the rate of a reaction are; the state of subdivision of reactants, concentrations of reactions, temperature and the presence of a catalyst.
- The rate law has the form
- $Rate = K[A]^a[B]^b$

  Where K = rate constant
- The rate law is experimentally determined
- The orders of reaction can be deduced using the graphical or the initial rates method.
- The integrated rate law has the form

  $\ln[A] = -kt + \ln[A]_o$
- The integrated law can be used to verify that a reaction is first order.
- Half–life is the time taken for the concentration of a reactant to fall by half.
- The half-life of a first order reaction is constant.
- A reaction mechanism is the series of steps in a reaction.
- Only terms in the rate determining step appear in the rate law.
- The rate determining step is the slowest step.
- Molecules react if they collide with sufficient energy E_{A_1} and if they are properly oriented.
- A catalyst provides an alternative pathway for a reaction with lower activation energy.
- Heterogeneous catalysis involves a solid catalyst but reactants may be liquid or gaseous.
- In homogeneous catalysis all reactants and catalyst are in the same phase.
- Enzymes are biological catalysts.

Examination Type Questions

1. (a) What is meant by the rate of reaction? (1)
   (b) Two substances X and Y react in an inert solvent according to the following equation

$$X + 2Y \rightarrow XY_2$$

To determine the order of the reaction between X and Y , the following results were obtained for experiments 1 – 4.

Exp. No	**Initial conc** $X\ /\ moldm^{-3}$	**Initial conc** $Y\ /\ moldm^{-3}$	**Initial rate of fomartion of** $XY_2\ /\ moldm^{-3}\ \text{min}^{-1}$
1	0.10	0.10	0.0010
2	0.10	0.20	0.0040
3	0.10	0.30	0.0090
4	0.15	0.10	0.0010
5	0.20	0.20	

(i) Predict the initial rate of formation of XY_2 in experiment 5 and complete the box above.

(ii) What is the order of reaction with respect to each of X and Y ? [4]

(iii) Write a rate equation / law for the reaction which includes the rate constant K. [1]

(iv) Calculate the numerical value of K , stating the units. [3]

(v) Suggest a possible mechanism for the reaction between X and Y which is consistent with the observed kinetics. [2]

INORGANIC CHEMISTRY

CHAPTER 9

INORGANIC CHEMISTRY

Periodicity and the Periodic Table

Objectives

By the end of this chapter you should be able to:

1) describe qualitatively (and indicate the periodicity) in the variations in atomic radius, ionic radius, melting point and electrical conductivity of the elements sodium to argon.
2) explain qualitatively the variation in atomic radius and ionic radius for the elements sodium to argon.
3) interpret the variation in melting point and electrical conductivity in terms of the presence of simple molecular, giant molecular or metallic bonding in the elements sodium to argon.
4) explain variation in the first ionization energy of the elements sodium to argon.
5) describe the reactions if any, of the elements $Na-Ar$ with oxygen (to give $Na_2O, MgO, A1_2O_3, P_4O_6, P_4O_{10}, SO_2, SO_3$) with chlorine to give $NaCl, MgCl_2, Al_2Cl_6, SiCl_4, PCl_3, PCl_5$ and with water for Na and Mg.
6) state and explain the variation in oxidation number of the oxides and chlorides for $Na-Ar$.
7) describe the reactions of oxides with water.
8) describe and explain the acid/base behavior of oxides and hydroxides including amphoteric behaviour in reaction with $NaOH$ and acids.
9) describe and explain reaction of the chlorides with water.
10) interpret the variations and trends in 6,7,8, 9 and above in terms of bonding and electro-negativity.
11) suggest the types of chemical bonding present in chlorides and oxides from observations of their chemical and physical properties.
12) predict the characteristic properties of an element in a given group by using knowledge of chemical periodicity.
13) deduce the nature, possible position in the periodic table and identity of unknown elements from given information of physical and chemical properties.

Introduction

Mastery of the structure of the Periodic Table is critical in the understanding of trends in both chemical and physical properties across periods and within groups of elements. You will find it necessary to refer to some topics in physical chemistry for a thorough grasp of periodicity of the properties of selected groups of elements.

The Periodic Table

The Periodic Table is said to be the backbone of chemistry. Indeed it would be extremely difficult to find any order in all the 103 known elements. The modern Version of the Periodic Table is shown.

The Periodic Table

Group								
I	II		III	IV	V	VI	VII	O

In addition to groups and periods, the table has 4 blocks labelled s,p,d and f. These represent the sub-shells occupied by the outermost electron in the atom of the elements in each block. The table below shows the electronic configurations of selected elements in each of blocks s,p and d of ground state.

Group	Element	Electron configuration
S	Na Mg	$1s^2 2s^2 2p^6 3s^1$ $1s^2 2s^2 2p^6 3s^2$
P	Si P	$1s^2 2s^2 2p^6 3s^2 3p^2$ $1s^2 2s^2 2p^6 3s^2 3p^3$
d	V Cr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$

Periodicity of Physical Properties

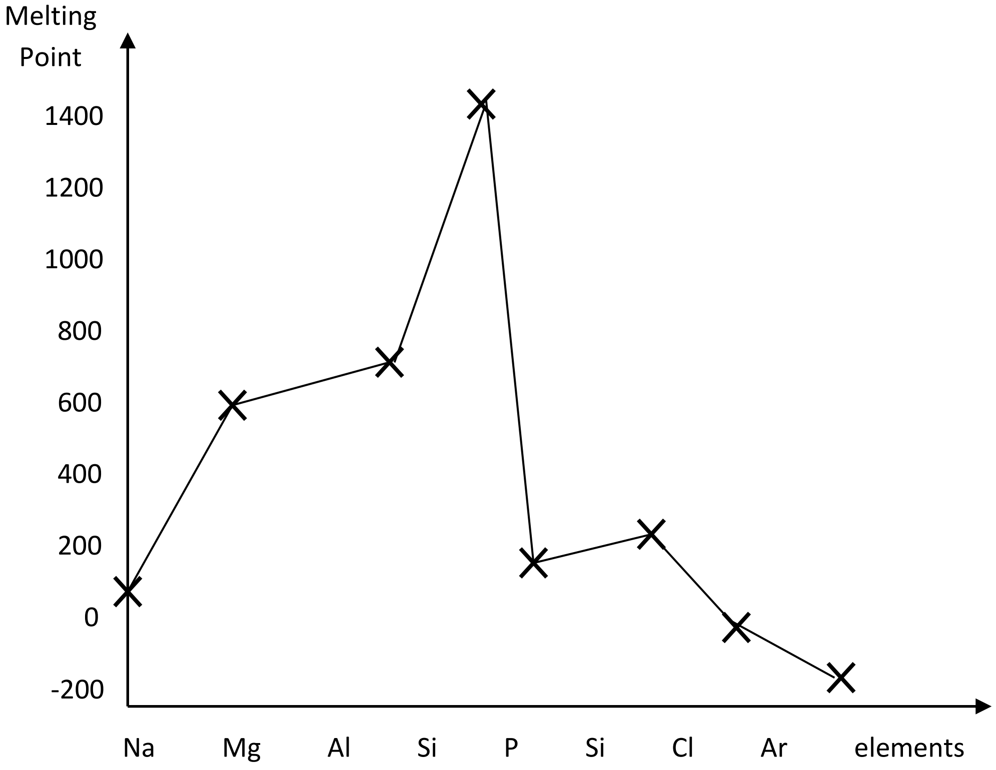
In this section only selected physical properties will be considered. In order to meet syllabus demands reference will only be made to period 3 (Sodium- Argon).

Trends in melting points (Na- Ar)

The table below shows variations of melting points across period 3.

Element	Melting point/^{0}C
Na	98
Mg	650
AI	660
Si	1410
P (white)	44
S	119
Cl	-101
Ar	-189

A sketch graph of melting points shows the trend more clearly

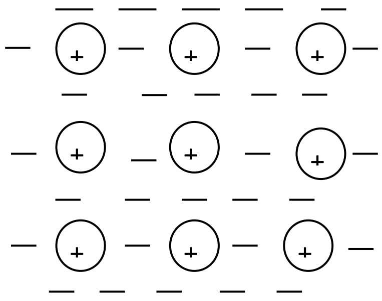


Proton 11 12 13 14 15 16 17 18

Figure
How can you describe the trend in melting points across the period from sodium to Ar?

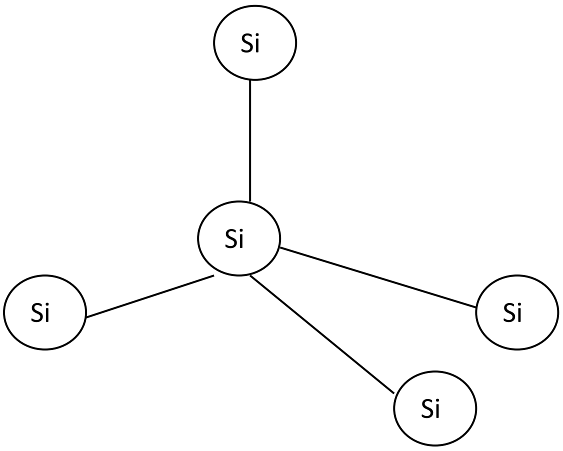
Looking at the sketch graph you notice an increase in melting points in metals Na- Al. Silicon has a very high melting point. There is a large drop from silicon to phosphorus, a slight increase to sulphur and another big drop to chlorine and argon.

In order to explain this trend in melting points we need to consider the crystal structures of these elements as we traverse the period Na- Ar. The metals Na, Mg, Al have a giant metallic structure in which the positive metallic cores are immersed in a "sea" of delocalized mobile electrons within the crystal lattice.



Within the crystal lattice there are strong electrostatic forces of attraction between the metallic cores and delocalized electrons. Hence a lot of energy is required to pull the cores away from the sea of electrons. This accounts for the high melting points in metals. As the number of outer electrons increases from Na- Al more energy has to be expended to release the "cores". This causes the melting points to increase from Na- A1. The strong metallic bonding from Na- Al means a very close packing of metal atoms making it difficult to separate them.

Silicon has a giant molecular structure in which each atom is strongly bonded covalently to four others in a tetrahedral structure. The four strong covalent bonds hold atoms in a lattice to form a giant molecule. The covalent bonds holding each atom are difficult to break.



Hence the element has a very high melting point.

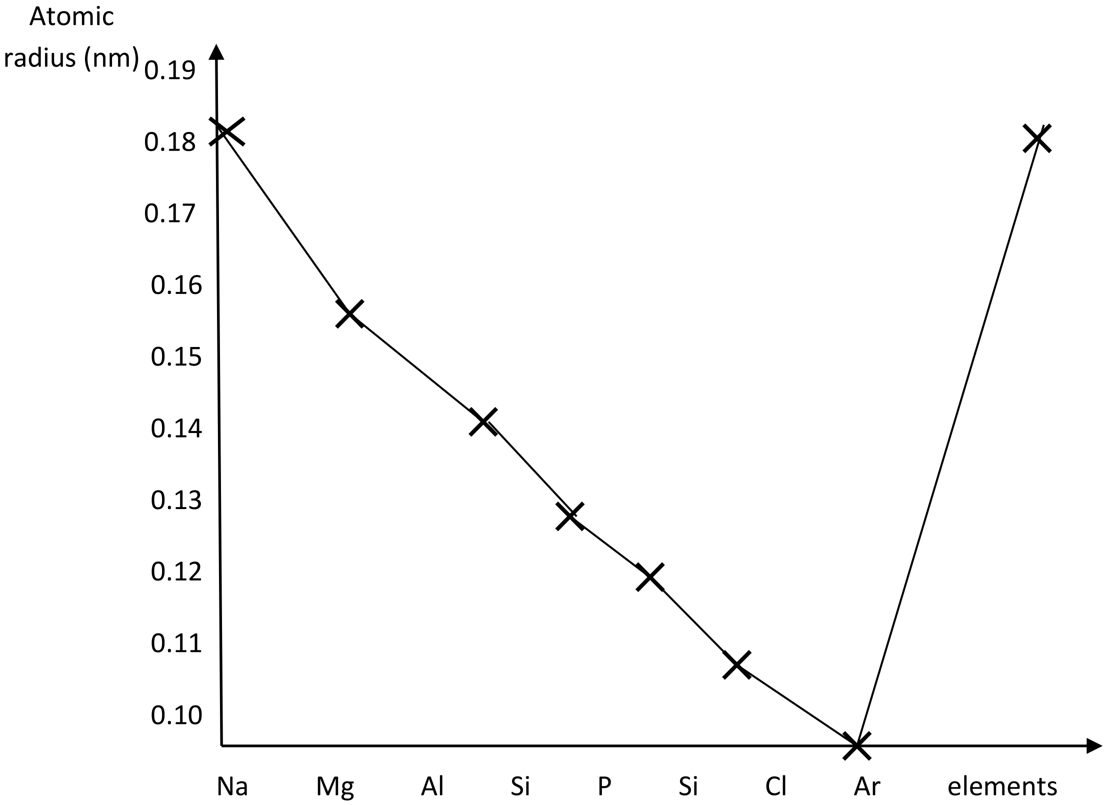
The sudden drop in melting point from silicon to phosphorus is due to simple molecular structure. The elements phosphorus to argon have small separate molecules or atoms. Though there are strong interatomic covalent bonds in the molecules, there are weak inter-molecular forces of attraction. Hence their low melting points.

Trends in atomic and ionic radii

The atomic radius is the distance between the nucleus of the atom and the boundary of the closest identical atom. Effectively this is the distance of the outermost electrons or shell from the nucleus. The table below shows atomic radii across period 3 (Na- Ar) measured in nanometres.

Element	atomic/covalent radii (nm)
Na	0,186
Mg	0,160
A1	0,143
Si	0,117
P	0,110
S	0,104
Cl	0,099
Ar	0,192

A graph of atomic radius for elements Na- Ar shows the trend.



Can you describe the trend in atomic radii from Na-Ar? Try to explain this trend.

There is a significant decrease in atomic radii from Sodium to Silicon and suddenly there is an increase for argon. The decrease from Na- Ar is attributed to an increase in nuclear attraction for the outer electrons. As electrons are added to the same shell coupled with an increase in the number of protons, there is an increase in the net positive charge which attracts the outer electrons causing the atom to shrink. The net positive charge increases from Na- Ar.

How does one explain the sudden jump in argon? As we increase the number electrons they start to repel each other causing the atom to increase in size/radius or volume. The slight decrease results from poor shielding of the outer 3p electrons from nuclear attraction by the inner 3s electrons. Shielding becomes less effective for Ar hence an slight increase in its atomic radius.

Trends in ionic radii (Na- Nr)

This table show ionic radii for Na- Ar

Ion	ionic radius (nm)
Na^+	0,095
Mg^{2+}	0,065
$A1^{3+}$	0,050
Si^{4+}	0,040
$P3^-$	0,213
S^{2-}	0,184
Cl^-	0,181

Ar does not form ions due to electronic stability.

What differences and similarities do you notice between the graph for atomic radii and ionic radii for the elements $Na-Cl$? Can you account for these differences and or similaries?

The trend as observed from the graph is the same. However ionic radii cations are smaller than those of corresponding atoms. This is to be expected as removal of outer electrons results in greater nuclear attraction for the remaining electrons hence shrinking the atom. Nuclear attraction increases with the increase in the cation charge.

Compared to atomic radii, ionic radii of the elements P- Cl are larger. This is due to electron-electron repulsion and reduced nuclear attraction due to increased number of electrons.

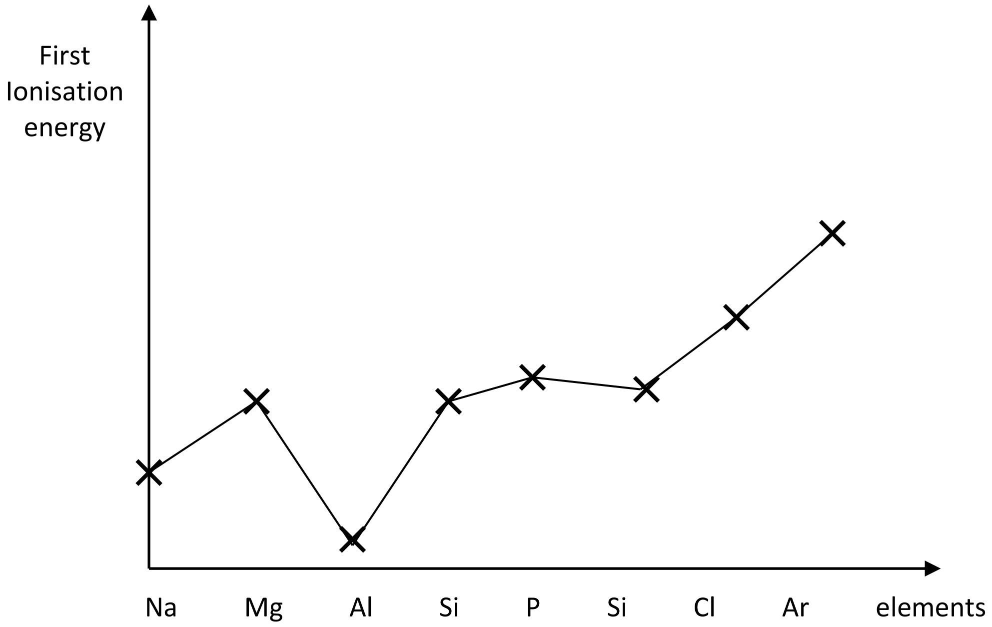
Can you account for the decrease in ionic radii from $P \rightarrow S \rightarrow Cl$?

Trends in Ionisation Energy

Ionisation energy of an element is the energy (ΔH) required to remove one mole of outermost electrons completely from atoms in the gaseous state. The first ionization energies for elements $Na \rightarrow Ar$ are shown below.

Element	First Ionisation Energy (kJ/mol)	Electron Configuration
Na	494	$1s^2 2s^2 2p^6 3s^1$
Mg	736	$1s^2 2s^2 2p^6 3s^2$
Al	577	$1s^2 2s^2 2p^6 3s^2 3p^1$
Si	786	$1s^2 2s^2 2p^6 3s^2 3p^2$
P	1060	$1s^2 2s^2 2p^6 3s^2 3p^3$
S	1000	$1s^2 2s^2 2p^6 3s^2 3p^4$
Cl	1260	$1s^2 2s^2 2p^6 3s^2 3p^5$
Ar	1520	$1s^2 2s^2 2p^6 3s^2 3p^6$

What is the trend in ionization energy $Na \rightarrow Ar$? Again, a sketch graph shows the pattern more clearly.



You will notice that as we move across the period from sodium to Argon there is a general increase in ionisation energy. This is due to the increase in nuclear attraction for outer electrons from $Na - Ar$ As we have seen earlier, electrons are added to the same shell across the period. This is accompanied by a corresponding increase in proton number which increases the nuclear charge. The nuclear charge holds the outer electrons more firmly, making it difficult to remove them from the atom. The ionisation energy of aluminum is lower than that of magnesium. Why is this so? Magnesium has a full $3s^2$ sub-shell. The $3p^1$ electron is easier to remove than one in $3s^2$. The ionization energy for phosphorus is higher than that of sulphur. Looking at the electron configurations that of sulphur is $1s^2 2s^2 2p^6 3s^2 3p^4$ while that of phosphorus is $1s^2 2s^2 2p^6 3s^2 3p^3$. The half-filled sub-level $3p^3$ for phosphorus is more stable than the $3p^4$ sublevel in sulphur. It is therefore more difficult to remove an electron from the $3p^3$ in phosphorus hence phosphorus has a greater ionization energy than sulphur.

Generally the ionization energy of an element depends on the distance of the outer electrons from the nucleus, the screening effect of outer electrons by the inner ones and the strength of the positive nuclear charge.

Electrical Conductivity

This is the ability of elements to allow passage of an electric current by movement of charge. The table below shows electrical conductivities of elements $Na - Cl$.

Element	Conductivity $(x10^{-8}\Omega^{-1}m^{-1})$ At $25^{o}C$	Electron Configuration
Na	0,218	$1s^2 2s^2 2p^6 3s^1$
Mg	0,224	$1s^2 2s^2 2p^6 3s^2$
Al	0,382	$1s^2 2s^2 2p^6 3s^2 p^1$
Si	0,017	$1s^2 2s^2 2p^6 3s^2 3p^2$
P	0,0023	$1s^2 2s^2 2p^6 3s^2 3p^3$
S	10^{-23}	$1s^2 2s^2 2p^6 3s^2 3p^4$
Cl	gas at 25°C	

The table shows an increase in conductivity from sodium to aluminum then a decrease from $Al \rightarrow Si$ and a phenomenal decrease from $Si \rightarrow P \rightarrow Cl$.
We explain this trend. We need to consider the role of electrons in electrical conductivity. When an electric current is passed through a material the electrons in the material are excited into what is known as the conduction band. The more the electrons in this band, the greater the electrical conductivity. Remember, in a metal crystal lattice, there are delocalized electrons which are mobile. When a current is passed through the metal these electrons readily occupy the conduction band, hence the high conductivities of metals Na, Mg and Al. The number of delocalized mobile electrons increases from sodium to aluminum. Electrical conductivity also increases as shown in the table… Silicon atoms are held together by strong covalent bonds and there are no free mobile electrons. However under a potential difference, some of the electrons are free to move. This makes silicon a partial or semi-conductor.

In phosphorus and sulfur the atoms that form molecules are held together by strong covalent bonds. Molecules are held together by weak Van der Waals forces and there are virtually no free electrons to conduct an electric current. This makes their electrical conductivities very small as shown in the table. This trend shows a decrease in conductivity from metals (Na, Mg, Al) through metalloids (Si) to non metals (P, S, Cl).

Periodicity of Chemical Properties

In our study of chemical periodicity, we will confine our focus to the period 3 elements (Sodium to Argon). This study will include the following:-

- Reactions of the elements with oxygen
- Reactions of the elements with chlorine
- Reactions of the elements with water
- Variation in oxidation states of oxides and chlorides
- Reactions of oxides with water
- Acid/base behaviour of oxides and hydroxides
- Reactions of the chlorides with water
- types of chemical bonding in chlorides and oxides

Perhaps in order to help you understand the trends in chemical properties of the elements in period 3, we will need to revisit the concept of electro-negativity. Electronegativity is the measure of the tendency to an atom to attract electrons. This tendency varies across the period as shown below.

Element	Electronegativity	Electron Configuration
Na	$0,9$	$1s^2 2s^5 p^6 3s^1$
Mg	$1,2$	$1s^2 2s^2 2p^6 2s^2$
Al	$1,5$	$1s^2 2s^2 2p^6 3s^2 3p^1$
Si	$1,8$	$1s^2 2s^2 p^6 3s^2 3p^2$
P	$2,1$	$1s^2 2s^2 2p^6 3s^2 3p^3$
S	$2,5$	$1s^2 2s^2 2p^6 3s^2 3p^4$
Cl	3.0	$1s^2 2s^2 2p^6 3s^2 3p^5$

It is clear from the table that electro-negativities increase from the left to the right across the period. This trend can be explained in terms of atomic radii which generally decrease across the period. As the effective nuclear charge increases $Na \rightarrow Cl$ so does the tendency of atoms to attract electrons from other atoms.

Reactions of elements with oxygen

The reactions of the elements $Na, Mg, Al, PandS$ with oxygen are summarized below.

Element	Reactivity	formula of oxide	Bonding	Structure
Sodium	Reacts slowly at room temperature; vigorously when heated; yellow flame	Na_2O	ionic	giant ionic
Magnesium	Reacts slowly at room temperature but vigorously when heated Bright white flame.	MgO	ionic	giant ionic
Aluminum	Reacts slowly ;Coated with oxide at room temperature	Al_2O_3	Covalent	giant ionic
Phosphorus	Reacts readily and vigorously at room temperature; catches fire. Bright yellow flame	P_4O_{10}	Covalent	simple Covalent
Sulphur	Reacts when heated in oxygen; Blue flame	SO_2 SO_3	Covalent	simple molecular

As seen above the reactivity decreases from sodium to aluminum because of increased nuclear charge and therefore a reduced tendency to donate electrons to oxygen. For phosphorus and sulphur the reactivity is increased in order for these atoms to attain a stable electron configuration in the 3p sub-shell.

Reaction with Chlorine

Element	**Reactivity**	**Formula of chloride**	**Bonding**
Sodium	reacts vigorously at room temperature	$NaCl$	ionic
Magnesium	reacts when heated in chlorine	$MgCl_2$	ionic
Aluminum	Reacts when heated strongly	$AlCl_3$ Al_2Cl_6	Covalent
Silicon	Reacts when heated strongly	$SiCl_4$	Covalent
Phosphorous	Reacts readily at room temperature	PCl_5 PCl_3	Covalent

Reaction of sodium and magnesium with water

Sodium reacts vigorously with cold water, the reaction is very exothermic and sodium catches fire. Hydrogen is displaced from the water because sodium is high in the reactivity series.

$$2Na_{(s)} + 2H_2O_{(\ell)} \rightarrow 2NaOH_{(aq)} + H_{2(g)}$$

The resulting solution is strongly alkaline about pH-13.
Magnesium reacts very slowly with cold water but reacts vigorously when heated in steam

$$Mg_{(s)} + H_2O_{(g)} \rightarrow MgO_{(s)} + H_{2(g)}$$

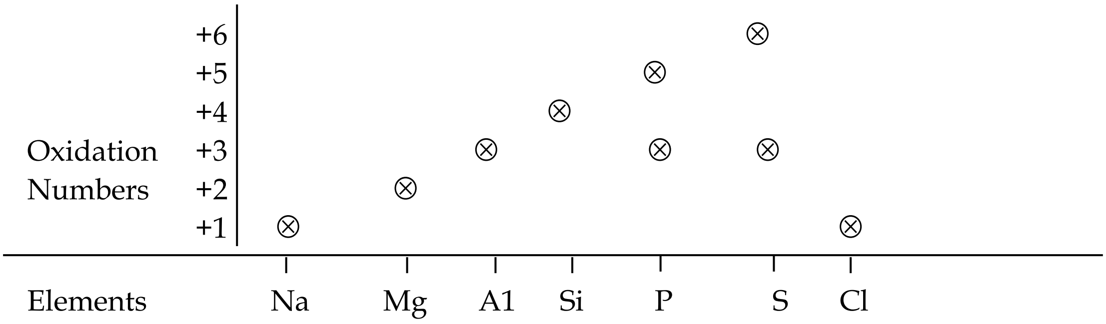
Magnesium oxide is weakly basic forming a solution of $pH \approx 10$

Variation in oxidation number of oxides

The variations across the period are shown below.

Element	**Formula of oxide**	**Oxidation Number of Period 3 element**
Sodium	Na_2O	+1
Magnesium	MgO	+2
Aluminium	Al_2O_3	+3
Silicon	SiO_2	+4
Phosphorus	P_4O_6	+3
	P_4O_{10}	+5
Sulfur	SO_2	+4
	SO_3	+6
Chlorine	Cl_2O	+1

The oxidation numbers in oxides are positive and increase across the period. This is caused by the large electro-negativity of oxygen (3,5). This enables the oxygen to pull the bond electrons leaving a partial positive charge on the atoms of silicon, phosphorus and sulfur. The more the number of bonded oxygen atoms the greater the oxidation number. Notice that the largest oxidation number is the same as the group numbers of the atoms. The graph below shows the trend in oxidation states across the period.



The oxidation numbers of sodium (+1), magnesium (+2) and aluminium (+3) are due to electron donation to oxygen by elements.

Variation in Oxidation numbers of chlorides.

The trend across the period is shown below

Element	Formula of chloride	oxidation Number of element
Sodium	$NaCl$	+1
Magnesium	$MgCl_2$	+2
Aluminium	Al_2Cl_6	+3
Silicon	$SiCl_4$	+4
Phosphorus	PCl_3	+3
	PCl_5	+5
Sulfur	SCl_2	+2
	S_2Cl_2	+1

As observed for the oxides the oxidation number of chlorides increases across the period. As in oxides the oxidation numbers are all positive. The increase in the oxidation number is also due to the high electro-negativity of chorine which pulls the electrons in order to complete its octet of electrons.

Reaction of Oxides with water

The vigour of reactions with water decreases from Na_2O to $A1_2O_3$. Sodium oxide reacts readily with water to form a strongly basic solution. Sodium oxide, being ionic, releases oxide ion (O^{2-}) in an aqueous solution which combines with water molecule to form hydroxyl ions.

$$O^{2-}_{aq} + H_2O_{(\ell)} \rightarrow 2OH^-_{(aq)}$$

The overall equation is $Na_2O_{(s)} + 2H_{(2)}O_{(l)} \rightarrow 2NaOH_{(aq)}$

On the other hand MgO reacts slowly with water to form a weakly basic solution

$$MgO_{(s)} + H_2O_{(\ell)} \rightarrow Mg(OH)_{2(aq)}$$

Due to its increased nuclear charge the magnesium in MgO does not release its oxygen readily hence there are few OH^- ions formed in water.

$A1_2O_3$ does not react with water because the oxygen is tightly held by the small aluminum ion which carries a large nuclear charge.

SiO_2 does not react with water due to the strong $Si-O$ bond, but forms a weakly acidic solution in water. Oxides form solutions with water as shown.

$$P_4O_{6(s)} + 6H_2O_{(\ell)} \rightarrow 4H_3PO_{3(aq)}$$

$$P_4O_{10(s)} + 6H_2O_{(\ell)} \rightarrow 4H_3PO_{4(aq)}$$

$$SO_{2(g)} + H_2O_{(\ell)} \rightarrow H_2SO_{3(aq)}$$

$$SO_{3(g)} + H_2O_{(\ell)} \rightarrow H_2SO_{4(aq)}$$

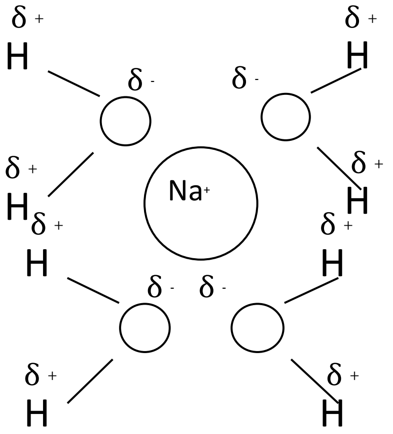
Thus the basicity of the metallic oxides decreases from $Na_2O \rightarrow MgO \rightarrow Al_2O_3$. The acidity increases from $SiO_2 to SO_3$. Aluminum oxide is amphoteric. It reacts with sodium hydroxide (base) and acids to form slats.

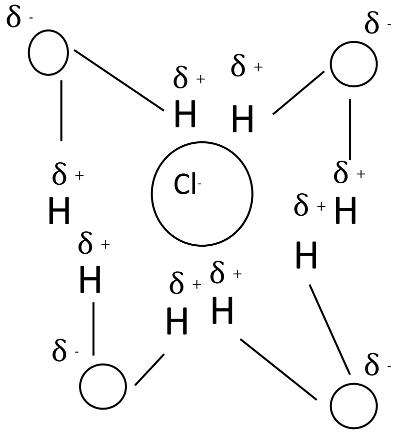
$$A1_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(\ell)} \rightarrow \underset{\text{Aluminate}}{2Al\left(OH\right)_4^- aq}$$

$$A1_2O_{3(s)} + 6H^+_{aq} \rightarrow 2A1^{3+}_{(aq)} + 3H_2O_{(\ell)}$$

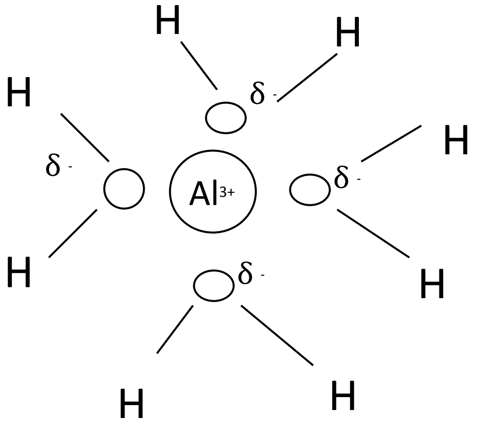
Reaction of chlorides with water

Chlorides of $Na, MgandAl$ are ionic. They dissolve in water due to the attraction between the ions and water molecules. For example the sodium ions and chloride ions are hydrated and this breaks the $Na^{+}-Cl^{-}$ ionic bond.





Aluminum chloride is acidic in aqueous solution because the small but highly charged aluminum ion (Al^{3+}) attracts electrons from surrounding water molecules releasing $H^{+}_{(aq)}$ in the process.



$$\rightarrow Al(H_2O)_5OH + H^{+}_{(aq)}$$

Chlorides of $Si, PandS$ react with water to form acidic solutions.

$$SiCl_{4(\ell)} + 2H_2O_{(\ell)} \rightarrow SiO_{2(s)} + 4HCl_{(aq)}$$

$$PCl_{3(\ell)} + 3H_2O_{(\ell)} \rightarrow H_3PO_{3(aq)} + 3HCl_{(aq)}$$

Summary

1. In the period, from $Na-Al$ the melting points increase with number of valence electrons. Low melting points from P_4-Cl_2 are due to weak intermolecular forces.
2. Atomic radii decrease from $Na-Ar$ due to increased attraction for electrons by the nuclear charge.

3. The ionisation energy generally increases from $Na-Ar$ due to in increase in nuclear charge.
4. Electrical conductivity increases from $Na-Al$ due to increase in the number of delocalised mobile electrons.
5. Electronegativity of elements increases from $Na-Cl$.
6. Reactivity of elements with oxygen decreases $Na \rightarrow Al$ but increases for non metals P and S. Increased nuclear charge reduces reactivity with metals.
7. Reactivity with chlorine decreases from Na to P.
8. The oxidation numbers increase from $Na-S$ and are all positive for oxides and chlorides
9. The reactivity of oxides with water decreases from $Na-Al$ for metals forming basic solutions with oxides of P and S forming acidic solutions.
10. Metallic chlorides dissolve in water due to hydration of ions. Chlorides of $Si, PandS$ react with water to form acidic solutions.

Study Questions

1. Describe and explain the variation in atomic radius of the elements across the period $Na-Ar$.
2. The table shows variation of electrical conductivity of elements across the period $Na-Ar$

Element	Na	Mg	Al	Si	P	S
Conductivity	good	good	Vgood	poor	nil	nil

a) Why is aluminium a better conductor than Na?
b) Why are P and S poor electrical conductors?
3a) What is the nature of bonds in the chlorides formed when Na, Mg and S react with excess chlorine?
b) How do the chlorides react with water?
c) Sodium chloride is a high melting point solid, which changes into a gas at 1800°C and phosphorus trichloride a volatile liquid. Explain this observation in terms of the nature of chemical bonding in these chlorides.
4. Some of the properties of elements X and Y are given below.
(i) Soft and malleable
(ii) Floats in water
(iii) Has a melting point of 100°C

(iv) Forms a chloride of formula XCl
Element Y
(i) Has a melting point of 1120°C
(ii) Forms oxides of formulas $YO_{2,}YO_3$
(iii) Has oxidation numbers of +4 and +6
(iv) Forms simple molecular compounds in its highest oxidation state
a) State the deductions you can make about X and Y from the above information
b) To which blocks s, p, or d do X and Y belong in the periodic table.
c) Identify X and Y.

5. Explain the following
a) The atomic radii decrease from $Na-Cl$.

b) The ions $Na^{+}, Mg^{2+} and Al^{3+}$ have radii which are less than their atomic radii while the radii of $Cl^{-} and S^{2-}$ are greater than the radii of their atoms.

c) The first ionization energy of Al is less than that of Mg.

d) The first ionization energy of P is greater than that of S.

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CHAPTER 10

Group II Chemistry

Objectives

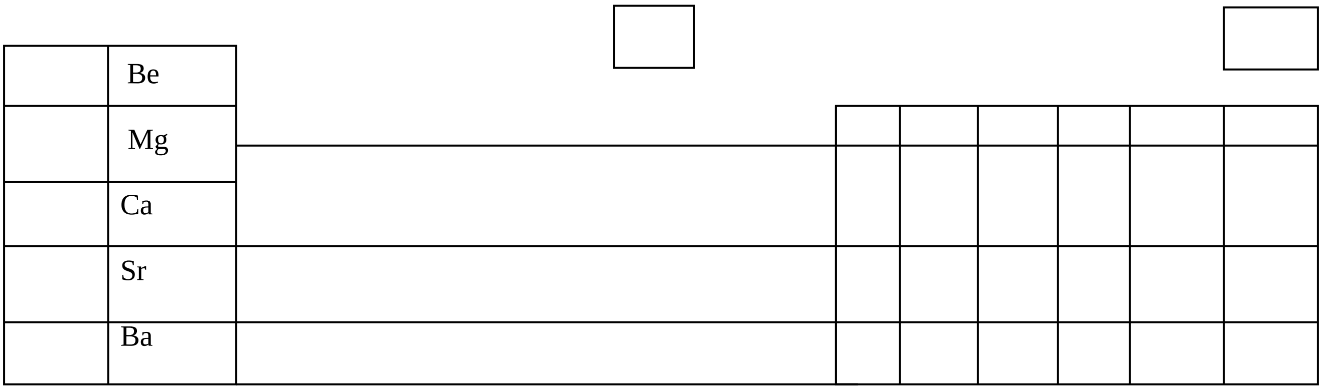
By the end of this chapter you should be able to:

1. describe the reactions of the elements with oxygen and water.
2. describe the behaviour of the oxides with water.
3. describe the thermal decomposition of the nitrates and carbonates.
4. interpret and make predictions from, the trends in physical and chemical properties of the properties of the elements and their compounds.
5. explain the use of magnesium oxide as a refractory lining material and carbonates as building material.
6. describe the use of lime in agriculture.
7. interpret and explain qualitatively the trend in the thermal stability of the nitrates and carbonates in terms of the charge density of the cation and the polazisability of the large anion.
8. interpret and explain qualitatively the variation in solubility of the sulphates in terms of relative magnitudes of the enthalpy change of hydration and corresponding lattice energy.

Introduction

Group II elements are found in the s-block of the periodic table. They are generally known as alkaline earth metals. In the study of this group reference will be made to:

- similarities between the elements.
- differences between members of the group.
- trend in chemical and physical properties of the elements and their compounds.
- reactivity of the elements with oxygen, water and chlorine.
- stability and solubility of nitrates and carbonates.
- solubility of sulphates.
- structure and bonding of compounds.
- uses of some of their compounds.
- The study will be confined to $Be \rightarrow Ba$.
- The sketch of the periodic table shows the position of this group of elements in relation to the rest of the elements.



Their position shows that they are typical metals.

Trends in physical properties

Electronic	**Configuration**
Beryllium	$1s^2 2s^2$
Magnesium	$1s^2 2s^2 2p^6 3s^2$
Calcium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Strontium	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$
Barium	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$

You will notice that the last sub-shell is occupied by 2 electrons reflecting the group number.

Melting points

The table below shows the melting points of the elements

Elements	Melting Point (°C)
Beryllium	1280
Magnesium	650
Calcium	840
Strontium	768
Barium	714

There is a general decrease in melting points down the group. You will also notice that the melting points of these elements are generally lower than those expected for metals. As shown by the electron configuration, the size of the atoms increases down the group and so the electrostatic forces between atoms get weaker. Hence atoms can be separated at relatively low temperatures. Beryllium is an exception. Due to its small size the nuclear attraction is strong and this holds the atoms firmly together. A high temperature is therefore required to separate the atoms. Hence its high melting point.

Atomic Radii

Element	Atomic Radius (nm)
Beryllium	0,112
Magnesium	0,160
Calcium	0,197
Strontium	0,215
Barnium	0,217

It is clear from the information above that the atomic radii increase down the group. As shown by the electron configuration, the number of shells increases down the group. This means that the outermost electrons get further from the nucleus. This leads to the attraction by the nucleus of outer electrons getting weaker and weaker allowing these electrons to spread out. This increases the atomic radii of the atoms.

Ionic Radii (M^{2+})

Element	Ionic Radius (nm)
Beryllium	0,031
Magnesium	0,065
Calcium	0,099
Strontium	0,113
Barium	0,135

As expected, the trend in ionic radii is the same as for atomic radii. Looking at the atomic and ionic radii how do the values compare? Can you think of the reasons for the differences? When the elements ionise they release two electrons $M \rightarrow M^{2+} + 2e^-$. Each ion then carries an extra charge in its nucleus. This will increase the nuclear attraction for the remaining electrons effectively shrinking the ion. This accounts for the lower values of ionic radii. The reduction in the atom of beryllium is greater due to its small size resulting in a greater attraction for the remaining electrons.

Element	**Oxidation Numbers**
Be	+2
Mg	+2
Ca	+2
Si	+2
Ba	+2

The oxidation numbers are the same down the group as the atoms lose two s electrons during chemical reactions.

Crystal structure

The elements are typical metals and their crystal structure is giant metallic. This structure as you will remember consists of positive ion cores in a "sea" of delocalized electrons. The crystal is held together by the attraction between the ionic cores and the delocalized electrons. The atoms can only release two s electrons into the delocalized zone of the crystal and this renders forces of attraction between electrons and positive cores weak. This is why the melting points of these elements are relatively low.

Ionisation Energy **First ionisation energy:** $M_{(g)} \rightarrow M^+{}_{(g)} + e^-$

Second ionization energy $M^+{}_{(g)} \rightarrow M^{2+}_{(g)} + 2e^-$

Element	**Sum of 1st and 2nd Ionisation Energies** (KJ / Mol^{-1})
Be	2660
Mg	2486
Ca	1740
Sr	1608
Ba	1468

For the purposes of this group the second ionization energy values have been quoted because atoms of these elements lose two electrons to form stable M^{2+} ions. The values above show a decrease down the group. This is not surprising considering the increase in atomic size down the group. The force holding on the outer electrons is reduced as the atomic size increases. The energy required is reduced as is reflected by the ionisation energy values

Electronegativity

This is a measure of the tendency to gain electrons.

$M +_{(g)} 2e^{-} \rightarrow M^{2-}_{(g)}$

Table

Element	Electronegativity
Be	1.5
Mg	1.2
Ca	1.0
Sr	1.0
Ba	0.9

As you can see from the table the electro-negativity values are low and decrease down the group. The converse of electro-negativity is electro-positivity which is measure of the tendency to lose electrons.

$$M_{(g)} \rightarrow M_{(g)}{}^{2+} + 2e$$

The electro-positivity in this group is large and increases down the group. This is not surprising because as the size of the atoms increases down the group, the attraction of the nucleus for the outermost electrons gets less and less. The tendency to lose electrons therefore increases down the group.

Standard Electrode Potential E$^{\theta}$

This is a measure of the reactivity of the elements compared to hydrogen. Electrode potentials (also known as redox potentials measure the tendency to release electrons

M □ □□ $M^{2+}_{(aq)} + 2eE^{\theta}, V$

The E^{θ} values are quoted in negative volts for metals. The more negative the values the more reactive the element.

Element	$E^{\theta}_{/v}$
Be	-1.85
Mg	-2.37
Ca	-2.87
Si	-2.89
Ba	-2.90

The values become more negative down the group. This means the reactivity of the elements increases down the group as the element releases electrons more and more readily from $Be \rightarrow Ba.$ Due to the readiness with which they release electrons they are strong reducing agents.

Trends in chemical properties

Reactions with water

The general equation for the reaction of the elements with water is given by

$$M_{(s)} + 2H_2O_{(\ell)} \rightarrow M(OH)_{2(aq)} + H_{2(g)}$$

Beryllium does not react with water directly due to its reluctance to release its 2s electrons. The nuclear attraction for these electrons is large due to the small size of the atom.

Magnesium reacts slowly with cold water forming magnesium hydroxide but rapidly when heated in steam forming magnesium oxide and hydrogen.

$$Mg_{(s)} + 2HO_{2(g)} \rightarrow Mg\ O_{(s)} + H_{2(g)}$$

The reactivity with water increases in vigour from $Ca \rightarrow Ba$. This is due to the readiness with which these elements release electrons and the readiness increases down the group. Why does the vigour of the reactions increases down the group?

Equations for the reactions are:

$$Ca_{(s)} + 2H_2O_{(\ell)} \rightarrow Ca(OH)_{2(aq)} + H_{2(g)}$$
$$Sr_{(s)} + 2H_2O_{(\ell)} \rightarrow Sr(OH)_{2(aq)} + H_{2(g)}$$
$$Ba_{(s)} + 2H_2O_{(\ell)} \rightarrow Ba(OH)_{2(aq)} + H_{2(g)}$$

Reaction with oxygen

The general equation is:

$$M_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow M^{2+} + O^{2-}$$

Stables ionic oxides are formed when the elements are heated in oxygen

$$2Be_{(s)} + O_{2(g)} \rightarrow +2Be^{2+} + 2O^{2-}$$
$$2Mg_{(s)} + O_{2(g)} \rightarrow 2Mg^{2+} + 2O^{2-}$$
$$2Ca_{(s)} + O_{2(g)} \rightarrow 2Ca^{2+} + 2O^{2-}$$
$$2Sr_{(s)} + O_{2(g)} \rightarrow 2Sr^{2+} + 2O^{2-}$$
$$2Ba_{(s)} + O_{2(g)} \rightarrow 2Ba^{2+} + 2O^{2-}$$

The oxides are basic and react with water to give weakly alkaline solutions. The basicity increases down the group.

$$BeO_{(s)} + H_2O_{(\ell)} \rightarrow Be(OH)_{2(aq)}$$
$$MgO_{(s)} + H_2O_{(\ell)} \rightarrow Mg(OH)_{2(aq)}$$
$$CaO_{(s)} + H_2O_{(\ell)} \rightarrow Ca(OH)_{2(aq)}$$

$$SrO_{(s)} + H_2O_{(\ell)} \rightarrow Sr(OH)_{2(aq)}$$
$$Ba_{(s)} + H_2O_{(\ell)} \rightarrow Ba(OH)_{2(aq)}$$

Due to their larger atomic radii atomic strontium and barium form peroxides represented by MO_2 and hence give H_2O_2 as well in solution with H_2O.
The oxide of beryllium (BeO) is amphoteric and displays both acidic and basic characteristicS in solution or in its reactions.

Reaction with chlorine

The elements react readily with chlorine and this increases down the group. The readiness of the reactions is due to the high electro-positivity of the group and the high electro-negativity of chlorine. The chlorides formed are ionic and have a giant ionic structure. Beryllium is an exception as its reactivity with chlorine is slow due to the reluctance of the beryllium atoms to release electrons.
Reactions:

$$Be_{(g)} + Cl_{2(g)} \rightarrow BeCl_{2(s)}$$
$$Mg_{(s)} + Cl_{s(g)} \rightarrow MgCl_{2(s)}$$
$$Sr_{(s)} + Cl_{2(g)} \rightarrow SrCl_{2(s)}$$
$$Ba_{(s)} + Cl_{2(g)} \rightarrow BaCl_{2(s)}$$

The chlorides are ionic solids, but $BeCl_2$ is covalent owing to its small size.
Ionic chlorides:

$$Mg^{2+} + 2Cl^-$$
$$Ca^{2+} + 2Cl^-$$
$$Sr^{2+} + 2Cl^-$$
$$Ba^{2+} + 2Cl^-$$

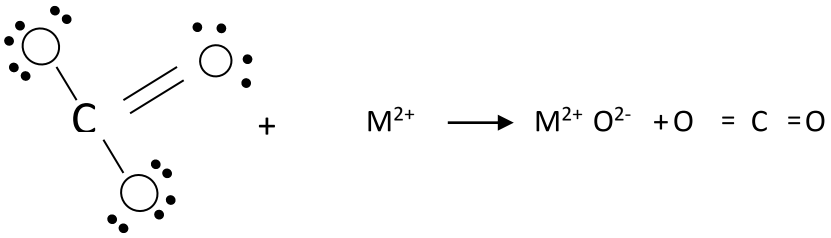
Thermal stability of Salts

A thermally stable compound does not decompose when heated to a high temperature. The following equations show how nitrates and carbonates of the elements respond to heating

Carbonates:

$$MgCO_{3(s)} \rightarrow MgO_{(s)} + CO_{2(g)}$$
$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$
$$SrCO_{3(s)} \rightarrow SrO_{(s)} + CO_{2(g)}$$
$$BaCO_{3(s)} \rightarrow BaO_{(s)} + CO_{2(g)}$$
$$Mg(NO_3)_2 \rightarrow MgO + 2NO_{2(g)} + \frac{1}{2}O_2(g)$$

The carbonates decompose to give a more stable and smaller oxide ion. The O^{2-} ion is much smaller than the CO_3^{2-} and gets closer to the cation M^{2+} than the bulky CO_3^{2-}. Thus the O^{2-} forms a much stronger bond with the cation. In terms of stability of the ionic crystal this is preferred. The thermal stability of CO_3^{2-} increases along series $Mg \rightarrow Ba$ as the cation charge density decreases down the group. The density of the cation tends to attract electron cloud of the oxygen in the CO_3^{2-} anion. This breaks the $O-C$ bond to give O^{2-} and CO_2. This can be illustrated generally as follows:



$$M^{2+}O^{2-} + CO_2$$

Cation $M^{2+}CO_3^{2-}$anion.

Nitrates

The general equation is

$$M^{2+}(NO_3)_2^- \rightarrow M^{2+} + O^{2-} + 2NO_{2(g)} + \frac{1}{2}O_{2(g)}$$

Decomposition of the nitrate gives a smaller O^{2-} ion

Like in carbonates the decomposition temperature increases down the group as the cation charge density decreases.

Solubility of Sulphates

$$\Delta H_{soln} = -\Delta H_{latt} + \Delta H_{hyd}$$

The table shows the solubilities in $mols/100g$ of water at 25°C for the sulphates $MgSO_4 \rightarrow BaSO_4$

Sulphate	Solubility $(x10^{-4})$
$MgSO_4$	3600
$CaSO_4$	11
$SrSO_4$	0,62
$BaSO_4$	0,009

The table shows that the group sulphate becomes more and more insoluble down the group. Magnesium sulphate is an exception as it is very soluble in water. This is due to the small size of Mg^{2+} which is able to attract water molecules (hydration) pulling the ions apart making the salt soluble. Hydration hardly affects the cation- anion bonding in the sulphates $CaSO_4 \rightarrow BaSO_4$. As the cation size increases the effect of hydration virtually disappears. This is why these sulphates are insoluble in water. In reaction occurring in aqueous solution, the sulphates appear as white precipitates.

Bonding and structure in the compounds the group II elements

Except for the compounds of Be which have a covalent character, compounds in this group are ionic forming giant ionic structures in their crystal laltices.

Uses of some Group II Compounds

Cement

Cement is an important building material. It is a fine mixture of alumino silicates (Clay) and calcium oxide.

The calcium oxide is obtained by decomposing calcium carbonate in kilns. The calcium carbonate is mined as limestone. When water is added to cement the calcium oxide reacts with water to form calcium hydroxide.

$$CaO_{(s)} + H_2O_{(\ell)} \rightarrow Ca(OH)_{2(aq)}$$

When the cement is allowed to set the calcium hydroxide reacts with the carbon dioxide in the air to reform calcium carbonate.

$$Ca(OH)_{2(aq)} + CO_{2(g)} \rightarrow CaCO_{3(s)} + H_2O_{(\ell)}$$

The calcium carbonate crystals "bond" with the alumino silicates from clay forming a structurally hard material. Other material congregates, like quarry stones, pit sand and river sand are mixed with cement to make structures with high tensile and compression strength.

Agricultural Lime

This is calcium oxide added to the soil to improve its texture and increase its pH. Lime is often added to acid soils to reduce their acidity. These soils contain hydrogen ions (H^+) either from addition of polluting industrial by- products, from activities of soil organisms or decomposition of inorganic compounds in the soil. The basic reaction in the soil is represented by .

$$CaO_{(s)} + H_2O \rightarrow Ca^{2+}_{(aq)} + 2(OH)^-_{(aq)}$$

$$OH^- + H^+ \text{ (from the soil)} \rightarrow H_2O_{(\ell)}$$

This reaction reduces the hydrogen ion concentration in the soil, rendering the soil suitable for plant growth.

Magnesium Oxide as 'refractory material'

As we have seen magnesium reacts with oxygen to produce magnesium oxide.

$$2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$$

This is an ionic compound and because of the small size of ions the ionic bond is extremely strong. The attractive forces within the crystal lattice are very strong and therefore one would need a very high temperature to separate the ions. Hence magnesium oxide has a very high melting point. For this reason the oxide is used for lining furnace surfaces which are exposed to high temperatures.

Summary

1. On descending the group, the following increase
    - ionic and atomic radii
    - electro positivity
    - standard electrode potentials become more negative
    - thermal stability of compound

-chemical reactivity.

whilst the following decrease:-

-solubility of sulphates

-Electronegativity

-ionisation energy

2.Reaction of group 2 elements with halogens; oxygen and water are represented by:-

$$M_{(s)} + Cl_{2(g)} \rightarrow M^{2+} + 2Cl^{-}$$

$$M_{(s)} + O_{2(g)} \rightarrow M^{2+}O^{2-}$$

$$M_{(g)} + 2H_2O_{(l)} \rightarrow M^{2+}_{(aq)} + (OH)^{-}_{2aq} + H_{2(g)}$$

3.Cement is made from CaO + clay. Cement sets according the equation

$$CaO_{(s)} + H_2O_{(\ell)} \rightarrow Ca(OH)_{2(aq)}$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3$$

4. Lime (CaO) is used to lower acidity in acid soils

$$CaO_{(s)} + H_2O_{(\ell)} \rightarrow Ca^{2+}{}_{(aq)} + 2OH^{-}{}_{(aq)}$$

$$2OH^{-}_{(aq)} + 2H^{+}_{(aq)} \rightarrow 2H_2O_{(\ell)}$$

Study Questions

1. How do the following vary on descending the group II elements

a) Atomic and ionic radii?

b) Ionisation Energy?

c) Reactivity with water and chlorine? Explain your answers to a, b and c.

2. Beryllium shows properties which are not typical of its group. Explain this observation with reference to:

a) Bonding.

b) Melting points

3. Draw a graph each using given values for variations in :- Group II elements or compound.

a) Melting points.

b) Solubility of sulphates.

c) 2nd Ionisation energy.

d) Standard electrode potentials.

In each case comment on the trend.

4. a) Magnesium sulphate is very soluble in water while barium sulphate is insoluble. Explain this.

b) The thermal decomposition of a group II carbonate is represented by the general equation.

$$MCO_{3(s)} \rightarrow M^{2+}O^{2-} + CO_2$$

Explain how this happens.

5.a) Describe with equations how cement is made and how this material hardens

b) Agricultural lime has an important role in the production of crops. Comment on this statement.

6. Comment on the following data giving explanations where appropriate. Discuss variation in atomic radii and density. Suggest a simple relationship you might expect between density and atomic radius.

Metal	atomic radius (nm)	density gcm^{-3}
Mg	0,160	1,74
Al	0,143	2.70
Ca	0,197	1,54

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CHAPTER 11

GROUP IV ELEMENTS

By the end of this chapter you should be able to:

(a) outline the variation in melting points and electrical conductivity of the elements and interpret them in terms of structure and bonding.

(b) describe and explain the bonding in, molecular shape and volatility of the tetrachlorides.

(c) describe and explain the reactions of the tetrachlorides with water in terms of structure and bonding

(d) describe and explain the bonding , acid – base nature and thermal stability of the oxides of oxidation states ii and iv

(e) describe and explain the relative stability of higher and lower oxidation states of the elements in their oxides and aqueous cations including where relevant - the E^{Φ} values

Introduction

The elements carbon, silicon, germanium, tin and lead are found in group IV of the periodic table. the outermost electrons in their atoms occupy the p- subshell , hence they are also referred to as p – block element.

The electron configurations below show that the last shells in their atoms are occupied by s^2p^2 electrons.

Elements	**Proton Number**	**Electron Configuration**
C	6	$Is^2 2s^2 2p^2$
Si	14	$[Ne]3s^2 3p^2$
Ge	32	$[Ar]3d^{10}4s^2 4p^2$
Sn	50	$[Kr]4d^{10}5s^2 5p^2$
Pb	82	$[Xe]4f^{14}5d^{10}6s^2 6p^2$

Your study of the group will focus on physical properties of the elements and properties of their compounds.

Physical Properties

Under this topic we will consider bonding, melting point and electrical conductivity of the elements.

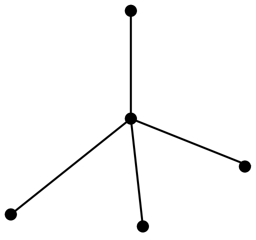
Bonding and structure

The table below shows the type and structure of the elements.

Elements	Type	Structure
C	Non- metal	Giant molecular
Si	non – metal	Giant molecular
Ge	Metalloid	Giant Molecular
Sn	Metal	Metallic
Pb	Metal	Metallic

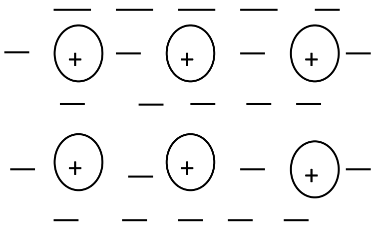
You will notice from the table that the metallic character increases down the group. The top members of the group (C and Si) are typical non – metals while the bottom elements (Sn and Pb) are metallic. However, germanium exhibits metallic and non- metallic properties. This element lies immediately to the left of the diagonal line dividing metals and non – metals. For this reason germanium is called a metalloid.

Bonding in the top three (C , Si, Ge) is to four others giving a giant molecular structure in the crystal lattice.



All the four s^2p^2 electrons of each atom bond to form a tetrahedral structure with strong atom – atom covalent bonds (diamond structure).

On the other hand bonding in Sn and Pb is metallic in which the lattice consists of metallic cations (positive cores) in an atmosphere of delocalized mobile electrons. It is the attraction between these ionic cores and delocalized mobile electrons which constitutes a metallic bond.



The bonding between ionic cores and delocalized electrons produces a giant metallic structure.

Melting points and bonding

The table shows the melting points and atomic radii of the elements.

Element	Atomic radius (nm)	Melting point / ^{o}C
C	0,077	3730
Si	0,118	1410
Ge	0,122	937
Sn	0,140	232
Pb	0,150	327

What trends do you see in the melting points and atomic radii in the elements as you go down the group the group? The figures show a definite decrease in melting points from C-Pb . However atomic radii increase down the group.

In order to explain the trend in melting points, we will consider the type of bonding in the elements. C, Si and Ge atoms form giant molecular crystal structures in which the atoms are held together by strong covalent bonds. These bonds are very strong and difficult to break. Hence they can only be broken by high temperature. The decrease in melting point from carbon (which sublimes) to germanium can be explained in terms of atomic radii. Carbon has a small atomic radius which enables the atoms to be packed close together by the strong covalent bonds. In the small atom the nuclear charge holds the nucleus and electrons together. However as you descend the group, the atomic radii (C- Pb) increase. This reduces the effect of the nuclear charge on the bond electrons and the effect is weakening of the covalent bond . Hence the bond will be broken at a lower temperature. The bond dissociation energy of these three elements shows that the bonds (C – Ge) get weaker down the group .

Element	**Bond**	**Bond dissociation Energy (kJ mol $^{-1}$)**
C	$C-C$	347
Si	$Si-Si$	226
Ge	$Ge-Ge$	167

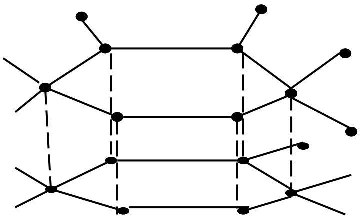
The data above shows a marked decrease in melting points from $Ge-Pb$ which is accompanied by an increase in metallic character. We already know that the bonding in metals is giant metallic in which there is attraction between positive ionic cores and delocalised mobile electrons. Due to the increase in size of the atoms (Sn and Pb) the attraction between the cores and the electrons will be less leading to a weak bond. This bond will be broken at a low temperature, hence low melting points for Sn and Pb . Sn still retains some non-metallic characteristics and as such, its metallic bonding is not well developed.

Electrical conductivity of elements (C - Pb)

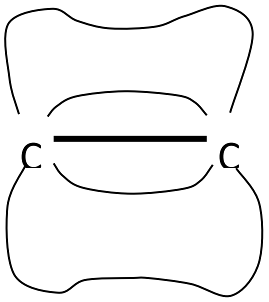
The flow of an electric current through a substance is due to the movement of free electrons . In order to conduct the current the electrons occupy what is called a conduction band. In this topic we will examine electrical conductivity of elements C – Pb. The table below shows the values for the elements.

Element	**Crystal**	**Electrical Conductivity $\Omega^{-1}m^{-1}$ x10^{8}**
$C(graphite)$	Giant molecular	7
Si	Giant molecular	1
Ge	Giant molecular	0,2
Sn	Giant metallic	880
Pb	Giant metallic	890

Conductivity ranges from fairly good (C) graphite through semi conductors (Si and Ge) to good Sn (and Pb) Diamond the other allotope of carbon, is a non conductor because all the outer s^2p^2 electrons are bonded and not available for conduction. The crystal structure of graphite and bonding are different from that of diamond and this accounts for the fairly good electrical conductivity of graphite. Graphite has a layered structure in which three sp electrons in each atom are bonded to form a plane hexagonal structure.



The fourth electron in each atom is unbonded and forms a charge cloud above and below each plane.



It is this electron charge cloud which conducts an electric current. In Si and Ge the crystal lattice has some unbonded electrons (spare electrons) which make these elements partial or semi conductors.

Tin and lead have a lot of delocalised mobile valence electrons which make the metals good electrical conductors. The electrons readily move to the conduction band.

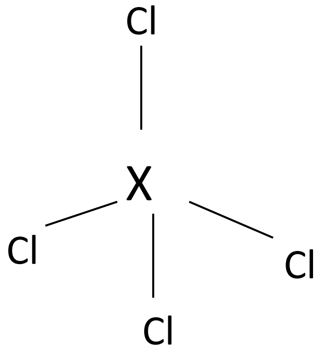
<u>Trends in chemical properties</u>

<u>Tetra-chlorides</u> XCl_4 (where X represents elements C – Pb). Generally the elements C – Pb are not very reactive .However, they react with a chlorine directly due to its high electro-negativity, forming tetrachlorides XCl_4 The table below will assist you to understand the chemistry of chlorides in this group.

Element	**Electronegativity**
C	2,5
Si	1,8
Ge	1,8
Sn	1,8
Pb	1.8

Bonding in tetrachlorides XCl_4

Except for C, the elements react directly with chlorine forming the more stable XCl_4 . All the four s^2p^2 electrons are bonded to chlorine for elements C – Ge , forming a simple molecular tetrahedral structure.



As the size of the atoms increases (C – Pb) down the group, the halides progressively assume an ionic character . This is because of their lower electro-negativity compared to that of chlorine

Stability of tetrachlorides $(CCl_4 - PbCl_4)$

As the atomic size increases down the group, the X – Cl bonds become longer and weaker . This makes the X – Cl bond in the tetrachlorides less stable . You will find that the tetrachlorides CCl_4 , $SiCl_4$ and $GeCl_4$ are quite stable compared to those of the lower members (Sn , Pb) , the tetrachlorides of Sn and Pb decompose readily on heating to give more stable dichloride.

$$SnCl_4 \rightarrow SnCl_2 + Cl_2$$

$$PbCl_4 \rightarrow PbCl_2 + Cl_2$$

This means that the +2 oxidation state becomes more stable than the +4 oxidation state.

Why is the +2 oxidation state more stable than the +4 oxidation state for Sn and Pb? You will notice that the s^2 sub- shell is full and would rather not take part in a reaction. These s electrons are referred to as the 'inert pair' due to their reluctance to take part in a chemical reaction.

Volatility of tetrachlorides

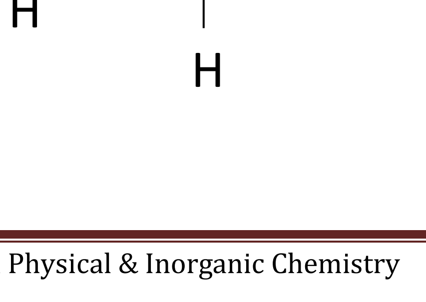
Due to weak intermolecular forces the XCl_4 have low melting and boiling points. As a result they are liquids which readily change to gases even at room temperature. Volatility decreases down the group with increase in number of electrons per molecule and hence increase in strength of van der Waals forces.

Reaction of tetrachlorides with water (hydrolysis)

Except for CCl_4, all the other tetrachlorides ($SiCl_4$ $GeCl_4$ $SnCl_4$, $PbCl_4$) are hydrolysed by water to form hydrogen chloride and hydroxides.

$$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$$
$$or SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$$
$$GeCl_4 + 4H_2O \rightarrow Ge(OH)_4 + 4HCl$$
$$SnCl_4 + 4H_2O \rightarrow Sn(OH)_4 + 4HCl$$
$$PbCl_4 + 4H_2O \rightarrow Pb(OH)_4 + 4HCl$$

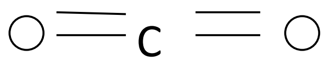
In order to explain this difference in the reactions of the tetrachlorides (Si - Pb) , we will consider the structure of the water molecule and outermost electron structure of the elements (Si – Pb) Generally , the outermost electrons in these atoms (Si - Pb) can be expressed in the form ns^2np^2 (where n represents the outermost shell). (These subshells come immediately below the 3d sub-)shell which can accept electrons during a reaction. In a water molecule, the oxygen has lone pairs of electrons.

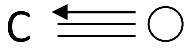


This one pair can be accommodated in the d sub shell to form a stronger X – O bond than the X – Cl bond. On the other hand CCl_4 is not hydrolysed by water because in the carbon atom the 3d sub shell is too far above the 2p sub- shell to accept the lone pair from the oxygen in the water molecule.

Oxides of Elements C – Pb

Here you will find that carbon is unique in the formation of oxides. It is not surprising as the element is the first member of the group with a higher electro-negativity due to its small atomic radius, Carbon forms two oxides CO_2 and CO which is less stable and easily forms the more stable dioxide. Carbon dioxide is a linear molecule with two double bonds

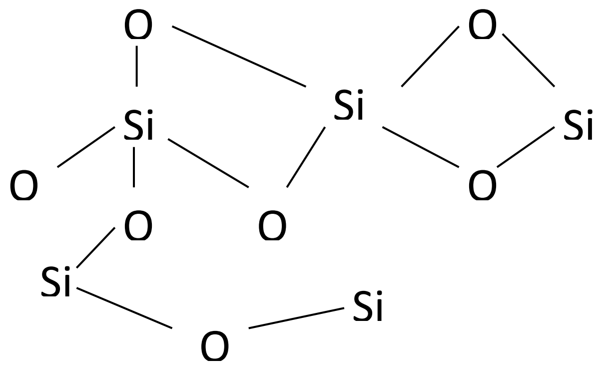




Can you work out how the double bonds are formed? In CO there are two unbonded electrons (DIAG) between the carbon and oxygen.

This makes the molecule unstable and it readily reacts with oxygen to form the more stable CO_2. Due to the small size of the carbon atom and its resulting high electro-negativity the +2 oxidation state is unusual.

Silicon on the other hand forms stable Si - O bonds in which each silicon atom is bonded to four oxygen atoms to form a giant tetrahedral structure like that of diamond.



You will notice from the diagram that each oxygen is shared between two silicon atoms. The resulting Si – O is much stronger than the C – O as shown by the bond formation enthalpies (energies given out) in CO_2 and SiO_2 . $CO_2 \Delta H_F = -394 kJMol^{-1}$

$$SiO_2 \Delta H_F = -859 kJMol^{-1}$$

Thus SiO_2 (quartz) is a hard substance with a high boiling point (2590 °C) compared to $CO_2 (-78^o C)$. Oxides of Ge (GeO_2), Sn(SnO_2) and Pb (PbO_2) all have giant structures , however SnO_2 and PbO_2 have a marked ionic character due to the larger atomic radii of Sn and Pb . The +4 oxidation state in SnO_2 will be more stable than the +4 oxidation state in

PbO_2 . Can you give a reason for this difference ? (Remember the +2 oxidation state is more stable than the +4 oxidation state in Pb)

REACTION OF DIOXIDES (XO_2)

The trend here is from acidic to amphoteric oxides. Carbon dioxide reacts with water to form a weakly acidic solution, carbonic acid.

$$CO_{2(g)} + H_2O_{(l)} \rightarrow H_2CO_3(aq)$$

On the other hand SiO_2 does not react with water but silicilic acid can be obtained by reacting silicates SiO_3^{2-} with acids. Oxides GeO_2, SnO_2 and PbO_2 also do not react with acids to form salts. In their reactions with aqueous alkalis $CO_2 and$ SiO_2 form carbonates and silicates respectively.

$$CO_{2(g)} + 2OH^-{}_{(aq)} \rightarrow CO_3^{2-}{}_{(aq)} + H_2O_{(l)}$$
$$SiO_{2(s)} + 2OH^-{}_{(aq)} \rightarrow SiO_{3(aq)}^{2-} + H_2O_{(l)}$$

Dioxides of Ge, Sn and Pb also form salts

$$GeO_{2(s)} + 2OH^-{}_{(aq)} \rightarrow GeO_3^{2-}{}_{(aq)} + H_2O_{(l)}$$

Germannate (iv)

$$SnO_{2(s)} + 2OH^-{}_{(aq)} \rightarrow SnO_3^{2-} + H_2O$$

Stannate (iv)

$$PbO_{2(s)} + 2OH^-{}_{(aq)} \rightarrow H_2O_{(l)} + PbO_3^{2-}{}_{(aq)}$$

Plumbate (iv)

Dioxides of Sn and Pb also react with concentrated acids to form salts. This shows their amphoteric nature.

$$SnO_2 + 4H^+ \rightarrow Sn^{4+} + 2H_2O$$
$$PbO_2 + 4HCl \rightarrow PbCl_4 + 2H_2O$$

Thermal stability of tetrachlorides (XCl_4)

Thermal stability of the tetrachlorides depends on one critical factor, the atomic size. As you move down the group, the bond length X – Cl increases with atomic size. This makes the X – Cl bond progressively weaker. Hence the stability of (XCl_4) will be expected to decrease down the group. The chlorides (CCl_4), ($SiCl_4$), ($GeCl_4$) are quite stable even at high temperatures. However ($SnCl_4$) and ($PbCl_4$) decompose on heating to produce the more stable (XCl_2). Can you explain the reason for the instability of $(PbCl_4)$? $(SnCl_4)$ and $(PbCl_4)$ decompose according to the equations :

$$SnCl_4 \rightarrow SnCl_2 + Cl_2$$
$$PbCl_4 \rightarrow PbCl_2 + Cl_2$$

Thermal stability of dioxides $\left(XO_2\right)$

The oxides CO_2, SiO_2, GeO_2 and SnO_2 are quite stable. But PbO_2 decomposes on warming to give PbO. Notice the change in oxidation state of Pb from the less stable +4 state to the more stable +2 state. So generally, oxides of the top members of the group are more stable than the bottom members

The thermal stability of the top members is attributed to the strong covalent bonds. Their smaller atomic size enables the bond electrons to be held firmly together. However, as we descend the group, stability decreases due to increased atomic size. Thus PbO_2 decomposes on warming to give PbO $(2PbO_2 \rightarrow 2PbO + O_2)$ in which Pb reverts to the more stable +2 oxidation state.

Thermal stability of the monoxides $\left(XO\right)$

The monoxides $CO, SiO, GeOand\ \ SnO$ are unstable and in fact the monoxides of Si , Ge and Sn are readily oxidized in air to form the more stable $\left(XO_2\right)$. This reactivity of the monoxides is attributed to the delocalized electrons around the $\left(X = O\right)$ double bond, as we saw for carbon monoxide earlier . The delocalized electrons become available for additional bonding. As we have discussed earlier , PbO is quite stable . Can you explain this contrast in stability between the monoxide of C, Si , Ge and Sn and that of Pb?

Relative stability of $\underline{X_{aq}{}^{4+}}$ and $\underline{X_{aq}{}^{2+}}$

In our study of stabilities of aqueous cations in group IV we will make reference to Ge, Sn and Pb. We will also consider the standard electrode potential $\left(E^{\Phi}\right)$ values for the systems $X^{4+} + 2e^- \rightarrow X^{2+}$. The values for Ge, Sn and Pb are listed.

$$Ge^{4+} + 2e^- \rightarrow Ge^{2+} : E^{\theta} = -1,6V$$
$$Sn^{4+} + 2e^- \rightarrow Sn^{2+} : E^{\theta} = +0,15V$$
$$Pb^{4+} + 2e^- \rightarrow Pb^{2+} : E^{\theta} = +1,69V$$

We can make some observation from the above values.

(a) The E^{Φ} values become more positive down the group.

(b) The readiness with which the X^{4+} cations gain electrons increases down the group, in other words the ease with which the +4 state is reduced to the +2 state increases down the group.

The overall picture is that the stability of the +2 state increases down the group due to the inert pair effect. You should also remember that E^{Φ} values enable us to determine the feasibility of a reaction. The more positive the value the greater the feasibility. The above half – reactions then, tell us that the $X^{4+} + 2e^{-} \rightarrow X^{2+}$ becomes more feasible down the group giving the more stable state.

Ceramics

Ceramic means hardening by heat. The history of ceramics dates back to biblical times during which clay pots were fired to a high temperature to give them a glassy appearance. Essentially , clay which is a hydrated alumina- silicate was mixed with sand (silicon IV oxide) and fired to high (2000^{o}C) temperatures in special kilns.

During firing the hydrated alumino silicate molecules undergo complete dehydration to produce the extremely hard water resistant substance.

Everyday usages of ceramics include the familiar china cups, sewage pipes, bath tubs and basins. Ceramics are also poor conductors of heat and electricity. The silicon (IV) oxide forms strong covalent bonds and there are no free electrons. It is for this reason that ceramics find their use in tea pots, cups and as points linking high voltage electric cables.

In the car industry ceramics are used in parts of internal combustion engines like valves and caps which have to withstand high temperatures and engine wear. Engineers are working to develop ceramics for frictionless engines which will not require lubrication and cooling.

Summary

(a) The last shell in group IV elements has ns^2np^2 electrons.
(b) The metallic character increases down the group.
(c) The bonding is from giant molecular at the top to metallic at the bottom.
(d) As the atomic radii increase down the group the melting points of the elements decreases.
(e) Electrical conductivity increases down group.
(f) Bonding in tetrachlorides is simple molecular.
(g) Thermal stability of tetrachlorides decreases with increase in $X - Cl$ bond length down the group.
(h) Tetrachlorides except CCl_4 react with water to form hydroxides or oxides and hydrochloric acid. $(XCl_4 + 4H_2O \rightarrow X(OH)_4 + 4HCl)$
(i) Dioxides of C and Si are acidic while those of Ge - Pb are amphoteric.
(j) Stability of dioxides decreases down the group while monoxides become more stable.
(k) The +4 oxidation states in the cations $X^{4+}_{(aq)}$ become less stable than the $X^{2+}_{(aq)}$ cations.

Ceramics are hard, water resistant and usually oxide based materials.

Study Questions (Group IV)

1. Discuss with the aid of equations where possible the following

(a) Structure, bonding and thermal stability of tetrachlorides.

(b) Structure and thermal stability of dioxides

(c) Reactions of tetrachlorides with water.

(d) Acid / base characteristics of dioxide $\left(XO_2\right)$ of Group IV elements.

2. Explain the following, fully

The +4 oxidation state becomes less stable down the group while the +2 state becomes more stable in the oxides

The E^{Φ} values for Ge, Sn and Pb cations are shown.

$$Ge^{4+} + 2e^{-} \rightarrow Ge^{2+} : E^{\theta} = -1,6V$$
$$Sn^{4+} + 2e^{-} \rightarrow Sn^{2+} : E^{\theta} = +0,15V$$
$$Pb^{4+} + 2e^{-} \rightarrow Pb^{2+} : E^{\theta} = +1,69V$$

What does this tell you about the relative stabilities of the +4 oxidation states as you go up the group ? Explain your answer.

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CHAPTER 12

GROUP VII ELEMENTS

At the end of this chapter, you should be able to :

- (a) describe the trends in volatility, and colour of chlorine, bromine and iodine.
- (b) describe and explain the relative reactivity of elements in terms of Van der Waals forces.
- (c) describe and explain the relative reactivity of elements as oxidizing agents including their reaction with sodium thiosulphate and with reference to E^{Φ} values.
- (d) describe and explain the reactions of the elements with hydrogen.
- (e) describe and explain the relative stabilities of hydrides.
- (f) describe and explain the reactions of halide ions with:
  - (i) aqueous silver ions followed by aqueous ammonia.
  - (ii) concentrated sulphuric acid.
- (g) outline a method for the manufacture of chlorine from brine by a diaphragm cell.
- (h) describe and interpret in terms of changes of oxidation number the reaction of chlorine with cold and with hot aqueous sodium hydroxide.
- (i) explain the use of chlorine in water purification.
- (j) recognize the industrial importance and environmental significance of the halogens and their compounds (e.g. for bleaches , pvc , halogenated hydrocarbons as solvents , refrigerants and aerosols.

Introduction

Halogens $F, Cl, Br and I$ are found in the p-block of the periodic table . Their outermost electrons occupy the p sub-shell. The general outer electron configuration is of the form ns^2np^5. This form is one electron short of the inert gas configuration of ns^2np^6.

The electron configurations and other physical properties of the elements is shown.

Element	**State**	**Proton Number**	**Electron Configuration**
Fluorine	g	9	$1s^2 2s^2 2p^5$
Chlorine	g	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Bromine	l	35	$[Ar]3d^{10}4s^2 4p^5$
Iodine	s	53	$[Kr]4d^{10}5s^2 5p^5$

In this group we will examine both physical properties and chemical properties of the elements and their compounds.

PHYSICAL PROPERTIES

Among other physical properties we will discuss the following:

Trends in Volatility of the elements $F_2 - I_2$

Colour of the elements $F_2 - I_2$

Volatility

Study the data below carefully.

Element	melting point °C	Boiling points °C
F_2	-220	-188
Cl_2	-101	-34,7
Br_2	-7,2	58,8
I_2	114 (sublimes)	184

What can you conclude about melting and boiling points? Is there any trend in these properties? Perhaps you realise that the melting and boiling points are low. You may also have realized that both these physical properties increase down the group. Substances whose melting and boiling points are low are said to be volatile. In other words they change from solid state to the liquid state or from the liquid state to the gaseous state at a low temperature. Looking at the melting points and boiling points reveals that F_2 and Cl_2 are gases at room temperature , bromine a liquid and iodine a solid at this temperature . You probably notice also that the elements are non- metals. In the gaseous state they exist as diatomic molecules (X_2).

The next task is to explain the trends in melting points and boiling points of the elements. The molecules in these elements are held together by weak Van der Waals forces which are broken even at room temperature. However, these forces of attraction increase in strength as we move down the group with increase in number of electrons per molecule. Hence the change of state from gas through liquid to solid.

Colour of elements

The change in colour is as shown

Element	**Colour**
Fluorine	pale yellow
Chlorine	greenish- yellow
Bromine	red brown
Iodine	shiny black (gives a purple vapour on heating)

As you can notice , there is a definite colour change from a light colour (F) to a darker colour as we descend the group.

Chemical properties

The data below will be very useful in the explanation of the chemical properties of the elements.

Elements	atomic radius (nn)	Electronegativity
Fluorine	0,072	4,0
Chlorine	0,099	3,0
Bromine	0,114	2,8
Iodine	0,133	2,5
Astatine	0,140	2,2

Reactivity,

Generally, these elements are reactive and this is not surprising as this enables their atoms to attain the stable configuration of the next inert gas structure. The atoms require just one electron to achieve this structure $ns^2np^5 + e^- \rightarrow ns^2np^6$.

You will also find that the reactivity decreases down the group with fluorine the most reactive. Looking at the atomic radius values and electro-negativity values one would expect this trend. In the smallest atom (fluorine) the nuclear attraction for electrons is greatest, but decreases down the group as the atomic radius increases.

Elements as oxidising agents

The ease with which the element atoms attract electrons to form negative ions is a measure of their oxidising power. Due to their relatively high electro-negativity values, the elements are strong oxidising agents, but this tendency also decreases down the group as you would expect. Can you give the reason for this decrease? This means that fluorine is the strongest oxidizing agent and the strength decreases down the group $F_2 > Cl_2 > Br_2 > I_2$. Another way of comparing the strength of their oxidising power is to use the redox / standard electrode potentials $\left(E^{\Phi}\right)$ for the reaction.

$X_2 + 2e^- \rightarrow 2X^-$, Where X = halogen

The table shows the $\left(E^{\Phi}\right)$ values.

Element	Reaction	(E^{θ}/V)
F_2	$F_2 + 2e \rightarrow 2F^-$	+2.87
Cl_2	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
Br_2	$Br_2 + 2e \rightarrow 2Br^-$	+1,09
I_2	$I_2 + 2e^- \rightarrow 2I^-$	+0.54

The $\left(E^{\Phi}\right)$ values decrease down the group due to decrease in oxidizing power.

Reactions with sodium thiosulphate

The strengths of the halogens as oxidising agents can also be compared in their reactions with sodium thiosulphate $(Na_2S_2O_3)$. Chlorine oxidises the thiosulphate ion to the sulphate ion in aqueous solution.

$$2S_2O_3^{2-}{}_{(aq)} + 4Cl_{2(g)} + 5H_2O_{(l)} \rightarrow 2SO_{4(aq)}^{2-} + 10H^+{}_{(aq)} + 8Cl^-{}_{(aq)}$$

The equation tells us that the oxidation state of sulfur increases from +2 in the thiosulphate ion to +6 in the sulphate ion . Similar observation with bromine. Iodine also oxidizes the thiosulphate ion but to the tetrathionate ion $(S_4O_6^{2-})$:

$$2S_2O_3^{2-}{}_{(aq)} + I_{2(aq)} \rightarrow S_4O_6^{2-}{}_{(aq)} + 2I^-{}_{(aq)}$$

Notice that the oxidation state of sulfur only increases by 0,5 showing that iodine is a weaker oxidizing agent than chlorine.

Reactions with hydrogen

All the halogens react directly with hydrogen to produce hydrogen halides, $X_{2(g)} + H_{2(g)} \rightarrow 2XH_{(g)}$.

All the X – H bonds are covalent. You will find that the intensity of the reactions decreases down the group. Fluorine reacts violently with hydrogen even in the dark at temperatures well below 0°C Chlorine reacts explosively with hydrogen in bright sunlight while bromine reacts with hydrogen when the mixture is heated . Iodine reacts reversibly with hydrogen when heated in the presence of a suitable catalyst $I_{2g} + H_{2g} \rightleftharpoons 2HI_g$

In order to explain this trend in reactivity down the group we will make use of the energy given out when the H-hal bond is formed. We notice that as you go down the group the bond energy decreases making the overall enthalpy change of reaction less exothermic as evidenced by iodine which has to be heated in the presence of a catalyst for it to react.

Stability of Hydrides (XH)

The table shows the bond energies of the hydrides. NB (all are endothermic values)

Hydride	**Bond energy (KJmol^{-1})**
H – F	562
H-Cl	431
H – Br	366
H – I	299

The bond energies reflect bond strength. The higher the bond energy the more stable the bond. The table shows that the H – F bond is very stable and the H – I bond the least stable. Can you relate the stability of the hydrides to the atomic radii of the elements?

Reaction of Halide ions with aqueous silver ions (Ag^+_{aq}).

Halide ions react with ($Ag^+_{(aq)}$) to form coloured precipitates.

$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$ white precipitate....eqnX

$Ag^+_{(aq)} + Br^-_{(aq)} \rightarrow AgBr_{(s)}$ cream precipitate

$Ag^+_{(aq)} + I^-_{(aq)} \rightarrow AgI_{(s)}$ yellow precipitate

However in order to distinguish further between the precipitate of AgBr and AgI they are reacted with concentrated aqueous ammonia. Silver bromide dissolves in concentrated aqueous ammonia but silver iodide is insoluble. Since AgF is soluble it does not give a precipitate. However AgCl is soluble in dilute aqueous ammonia while Ag I and Ag Br are insoluble. The dissolution of AgCl is due to complex ion formation $AgCl_{(s)} + 2NH_{3(aq)} \rightarrow \left[Ag(NH_3)_{2(aq).}\right]^+ + Cl^-_{(aq)}$ shifts position of eqnX to the right i.e. AgCl decomposes. The halides AgCl and Ag Br are decomposed by exposure to light forming silver and the halide. AgI is not affected by light.

Reactions of Halide ions with concentrated sulphuric acid.

The general reaction between solid halide ions and concentrated sulphuric is

$X^-_{(s)} + H_2SO_{4(l)} \rightarrow HSO_4^- + HX_{(g)}$

The hydrogen halide produced is given off as a gas. In the case of HBr and HI , the concentrated sulphuric acid oxidizes the hydrogen halides to Br_2 and I_2

$2HBr + H_2SO_4 \rightarrow Br_2 + 2H_2O + SO_2$

A mixture of white and reddish brown fumes of HBr and Br_2 is given out respectively.

$2HI + H_2SO_4 \rightarrow I_2 + 2H_2O + SO_2$

Purple fumes of I_2 are formed.

HCl not oxidized to Cl_2. The larger the halide ion the more strongly reducing it is. Suggest a reagent (s) that can further oxidize HCl to Cl_2?

Reactions of chlorine with aqueous sodium hydroxide.

In these reactions temperature determines the nature of the products. The initial reaction of chlorine with cold NaOH is as shown.

$Cl_{2(g)} + 2NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + NaClO_{(aq)} + H_2O_{(l)}$

In this reaction, the oxidation state of chlorine changes from O to +1 and -1 . This means that chlorine is oxidized and reduced in the same reaction. This type of reaction is called disproportionation Chlorine also reacts with hot aqueous NaOH.

$$3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$$

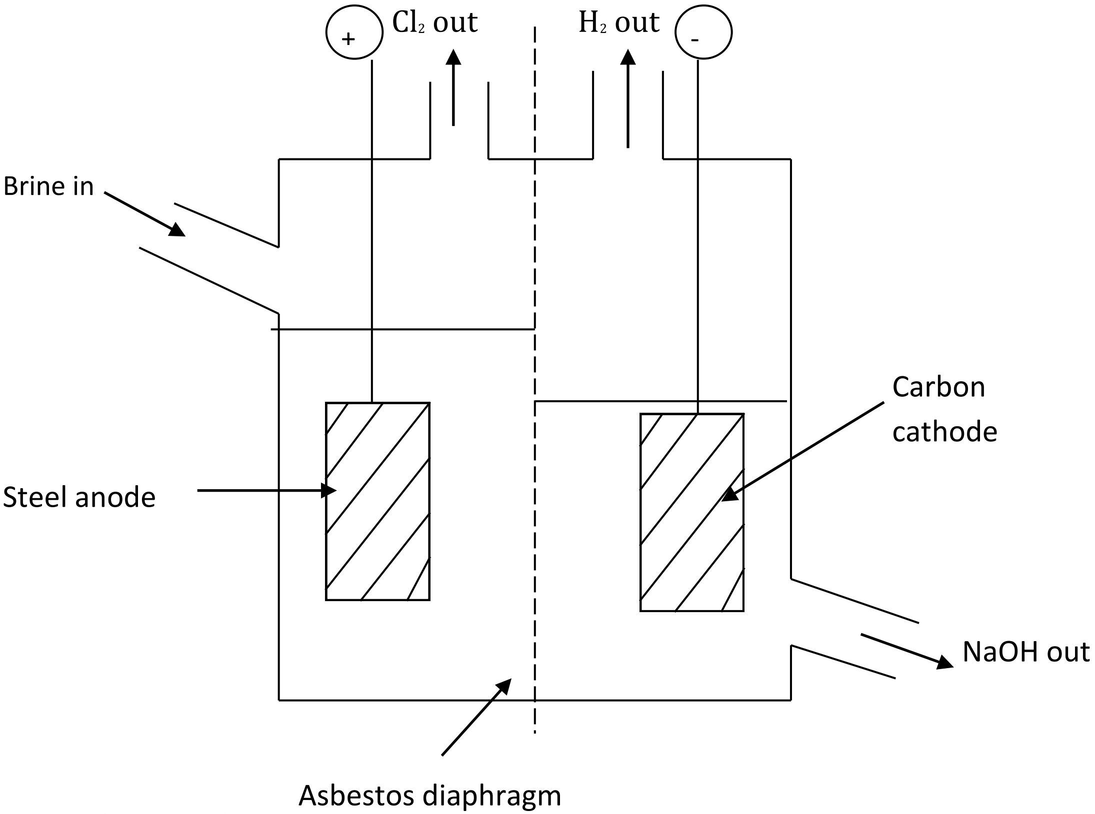
In this reaction the oxidation state of chlorine changes from 0 to +5 and -1 . Dispropotionation of the $OCl^-_{(aq)}$ ions also occurs after chlorine reacts with hot NaOH.

Species	Oxidation State
Cl^-	-1
ClO^-	+1
ClO^-_3	+5

The oxidation states of chlorine are as shown.

Manufacture of chlorine.

Chlorine is manufactured electrolytically from strong brine. The diagram shows the manufacture of chlorine by the diaphragm cell.



Diaphragm cell

Strong brine is introduced into the anode compartment where chlorine is produced

$$2Cl^{-}{}_{(aq)} \rightarrow Cl_{2(g)} + 2e^{-}$$

Hydrogen gas is produced in the cathode compartment $2H^{+}_{aq} + 2e \rightarrow H_{2g}$. Hydrogen is discharged at steel cathode in preference to Na^{+} because Na is more reactive than hydrogen and so remains in solution. Use E^{Φ} data to explain this. At the anode, chlorine is discharged in preference to oxygen because there are more chloride ions in strong brine than $OH^{-}_{(aq)}$ ions. The diaphragm allows the Na^{+} from the anode compartment to diffuse into the cathode compartment. Thus the cathode compartment contains a mixture of NaOH and NaCl. However there has been an improved version of the diaphragm in which a fluorocarbon membrane is used. This membrane is selectively permeable. It allows the cations (Na^{+}) through but not the anions (Cl^{-} and OH^{-}) . The H^{+} is discharged leaving NaOH to pass out.

Use of chlorine in water purification

The major use of chlorine is in the purification of drinking water. Chlorine dissolves and reacts with water to produce chloric (i) acid and hydrochloric acid.

$$Cl_{2(g)} + H_2O_{(l)} \rightarrow HClO + HCl$$

Chloric (i) acid

The chloric (i) acid is unstable and decomposes to hydrochloric acid and oxygen

$$2HClO_{(aq)} \rightarrow 2HCl_{(aq)} + O_2$$

Oxygen is toxic to pathogens and kills them rendering water safe to drink.

Industrial significance of Halogens.

Halogens and their compounds find a wide range of uses in industry, agriculture, medicine and in homes.

Halogen compounds in industry

Fluorine is incorporated into hydrocarbons to form fluorocarbons, a common example of which is polytetrafluorothene (PTFE) or Teflon. The substance is very unreactive, resisting corrosion. This property finds its use in valves and seals in the chemical industry. PTFE is also a water repellant and does not allow substances to stick on it. For this reason it is used to coat saucepan surfaces. PTFE is an insulator and is used as electric wire coats.

Chlorofluorocarbons (CFCs) are used as refrigerants , aerosol propellants and as solvents in the dry cleaning industry. However, these fluorocarbons have been found to deplete the ozone layer resulting in serious environmental consequences. In the presence of atmospheric radiation the CFCs split to form highly reactive free radicals which react readily with ozone molecules. Their use has raised serious environmental questions. Various forms of chlorocarbons are found in the plastics industry e.g. PVC, polyethene. These are non - biodegradable and pose pollution problems.

Halogen compounds in Agriculture

A wide range of chloroalkanes, DDT (dichlorodiphenly-trichloroethane) have been used extensively as pesticides. However these compounds have been found to pose a serious health hazard to humans. Their greatest disadvantage is that they are fat soluble and tend to accumulate in the animal lipids to toxic levels. They are then carried through the food chains. Due to their non-biodegradability they also accumulate in the soil only to be flushed on to water reservoirs. So their use has been restricted and they are completely forbidden in some countries.

Halogen compounds in the home

The compounds are used largely for disinfection, cleaning and bleaching. Calcium hypochlorite (chlorate (i)) is used as a disinfectant in swimming pools and sewage systems. Sodium chlorate (i) (hypochlorite; NaClO) is used as a domestic bleach , while sodium chlorate (v) is used as a weed killer.

Halogen compounds in medicines.

Tincture of iodine used in wound dressings is a solution of iodine in ethanol.

Summary

1. Halogens are the most reactive non- metals and are similar in their chemical properties.
2. Their reactivity decreases down the group (F – I) as the atomic radii increase.
3. Halogens are oxidising agents but the oxidising strength decreases down the group i.e.

   $F_2 > Cl_2 > Br_2 > I_2$.
4. They exhibit oxidation states of -1 , + 1 and +5 in the ions X^-, XO^-, XO^-_3 respectively.

5. The ions ClO^- and atoms Cl_2 undergo dispropotionation under alkaline conditions and in aqueous solutions.
6. Halide anions $Cl^-_{(aq)}, Br^-_{(aq)} and I^-_{(aq)}$ form coloured precipitates with silver ions, $Ag^+_{(aq)}$ and aqueous ammonia is used to distinguish between the anions.
7. Chlorine is used in water treatment plants to kill pathogens.
8. Halogen compounds are used in bleaches , pesticides , aerosols , refrigerants and disinfectants.
9. Chlorine is manufactured by electrolysis of strong brine.

Study Questions

1. (a) Describe and explain two specific physical properties and two specific chemical properties that show a regular gradation as one moves down the group from fluorine to iodine

   (b) Fluorides and fluorine show atypical properties in the group. Describe two physical properties for fluorine and two chemical properties for fluorides that show these differences.

2. The element X falls somewhere in group VII. Predict what happens in the following. Where possible write equations.
   (a) The vapour of X is heated with hydrogen.
   (b) Concentrated sulfuric acid is added to Na X .
   (c) Aqueous silver ions are added to the Na X solution.
   (d) X is added to aqueous thiosulphate ions.
3. Discuss the problems associated with the use of DDT, CFCs and PVC .

4. Chlorine is manufactured by the electrolysis of strong brine.
   (a) Write the anode and cathode equation.
   (b) How is the mixing of sodium chloride and sodium hydroxide minimized?
5. What problem would be encountered if weak $NaCl_{(aq)}$ were used in the diaphragm cell instead of strong sodium chloride ? Explain your answer.

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CHAPTER 13

Nitrogen and Sulfur

Objectives

By the end of this chapter you should be able to:

a) explain the lack of reactivity of nitrogen

b) describe
   i) the formation and structure of the ammonium ion.
   ii) the displacement of ammonia from its salts.

c) describe the Haber process for the manufacture of ammonia from its elements, giving essential operating conditions, and interpret these conditions qualitatively in terms of the principles of kinetics and equilibrium.

d) recognise the industrial importance of ammonia and nitrogen compounds derived from ammonia.

e) recognise the environmental consequences of uncontrolled use of nitrate fertilizers.

f) describe and explain the occurrence, and catalytic removal of oxides of nitrogen.

g) explain why atmospheric oxides of nitrogen are pollutants, including their catalytic role in the oxidation of atmospheric sulphur trioxide.

h) describe the formation of atmospheric sulphur dioxide from the combustion of sulphur contaminated carbonaceous fuels.

i) state the role of sulphur dioxide in the formation of acid-rain and describe the main environmental consequences of acid-rain.

j) state the main details of the Contact process for sulphuric acid production.

k) recognise the industrial importance of sulphuric acid.

l) describe the use of sulphur dioxide in food preservation.

Introduction

In this chapter we will study the chemistry of nitrogen and sulfur with emphasis on the formation and importance of some of their compounds. In some instances you will need to refer to some topics in physical chemistry in order to fully understand some chemical processes in this chapter.

Nitrogen Bonding and Reactivity

This element is the most abundant gas in the atmosphere constituting about 78% of the air. It is placed in group V of the periodic table and has the electron configuration of $1s^2 2s^2 2p^3$ Nitrogen exists as a diatomic molecule (N_2) in which atoms are joined together by a triple covalent bond. The bonding is shown overleaf.

$$N \equiv N$$

The strong triple bond makes the molecule very stable and hence the reluctance of nitrogen to react. It would require some 994kJmol^{-1} to break the triple bond in order to release nitrogen atoms for reactions. This high energy is not available under normal conditions. However, nitrogen does react with some elements under special conditions. For example when magnesium burns in air it forms a nitride. The high temperature of burning magnesium breaks the triple bond:

$3Mg_{(s)} + N_{2(g)} \rightarrow Mg_3N_{2(s)}$

Magnesium + Nitrogen ⟶ Magnesium nitride

Also, nitrogen combines with oxygen at high temperature to form nitrogen monoxide (NO). This happens during a lightning discharge or in the spark plugs of a car engine.

$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$

Nitrogen + oxygen = Nitrogen monoxide

Nitrogen can be made to combine with hydrogen at a high pressure in the presence of a catalyst.

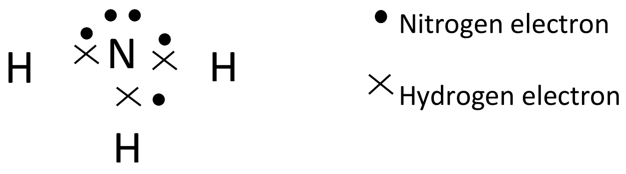
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

Microorganisms can convert nitrogen into nitrate in the soil.

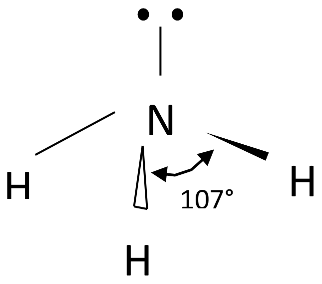
Compounds of Nitrogen

Ammonia

Nitrogen combines with hydrogen under special conditions as you have seen to form ammonia. How does this happen? You will recall the electron configuration of nitrogen as 1s^{2}2s^{2}2p^3 and hydrogen as 1s^1. In order to attain the stable electron configuration nitrogen requires three electrons. Hence its atom will combine covalently with three hydrogen atoms to achieve the stable structure.

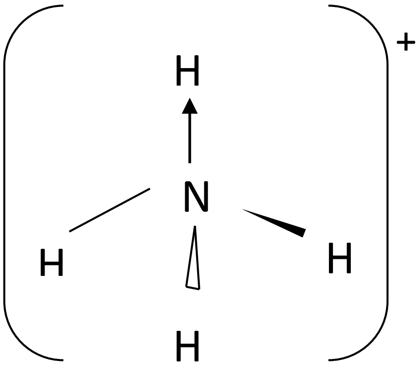


You will notice that a pair of nitrogen electrons remains unbonded. This is called a lone pair. The ammonia molecular structure is based on a tetrahedron with a bond angle of 109.5^0 but because of the repulsion between the lone pair and the N-H bond, the structure is 'pyramidal' with a H-N-H bond angle of 107^o.



Ammonium ion

Starting with the structure of ammonia, you saw that nitrogen has a pair of unbonded electrons. This pair can form a covalent bond with an electron deficient atom or ions in which the lone pair is shared with an ion. This kind of covalent bond is called a dative bond where the electron bond pair comes from one atom, nitrogen in this case.



In this example, the bond pair is shared with an electron deficient hydrogen ion to form an ammonium ion. The new N-H bond is represented by an arrow to show the origin of the bond pair. In the ammonium ion all the N-H bonds are the same, in strength and in length. The molecule carries an overall positive charge and is symmetrical about the nitrogen atom.

Displacement of ammonia from its compounds. When an ammonium salt is warmed with sodium hydroxide ammonia gas is released. This reaction can be represented as:

$$NH^+{}_4 + OH^- \rightarrow NH_{3(g)} + H_2O_{(l)}$$

In this equation, OH^- is a proton acceptor while the $NH^+{}_4$ ions acts as a proton donor. The reaction is used as a test for the presence of $NH^+{}_4$ ion in qualitative analysis

Manufacture of ammonia

Ammonia is produced on a large scale by the Haber process. As we have discussed earlier, nitrogen can be made to react with hydrogen under special conditions. We will now consider the role of these conditions.

The equation of this reaction is:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \Delta H = -92.4 kJmol^{-1}$$

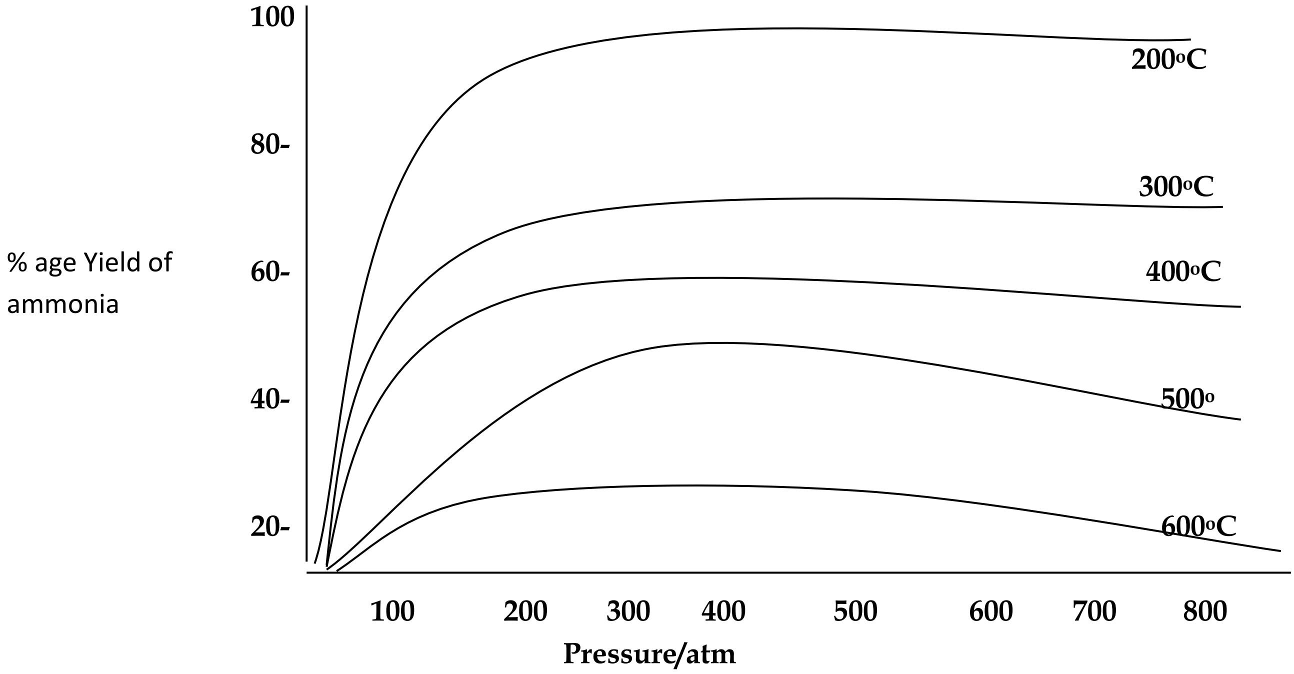
1 volume + 3 volumes → 2 volumes

We can tell from the equation that:
-one mole of nitrogen gas reacts with three moles of hydrogen gas to give 2 moles of ammonia gas or one volume of nitrogen gas reacts with three volumes of hydrogen gas to give 2 volumes of ammonia gas
-92.4kJ of heat are produced in this reaction per mole of ammonia formed.
- the reaction is reversible.
We can use Le Chateliers principle you learnt about in physical chemistry to deduce the effects of pressure and temperature on the reversible reaction. We can see from the equation that 4 volumes of gas on the left hand side of the equation give only 2 volumes of the gaseous product.

What more does this tell us about the reaction? Since the reaction is accompanied by a reduction in volume, it means, according to Le Chatelier's principle, that an increase in pressure will favour a decrease in pressure. (Le Chatelier's principle says if a condition is imposed on a system that is in equilibrium, position of the equilibrium will shift in such a way that the effect of the imposed condition is cancelled or nullified) In other words more ammonia will be produced at high pressure as the position of equilibrium is shifted to the right.

The effect of temperature can also be deduced from LeChatelier's principle. If the temperature is increased in this exothermic reaction, the position of equilibrium will shift to the left which means that ammonia will decompose to give back nitrogen and hydrogen. So a decrease in temperature will favour the formation of ammonia. However, at low temperature equilibrium will be reached very slowly. A catalyst in the form of finely divided iron is used to speed up the attainment of equilibrium.

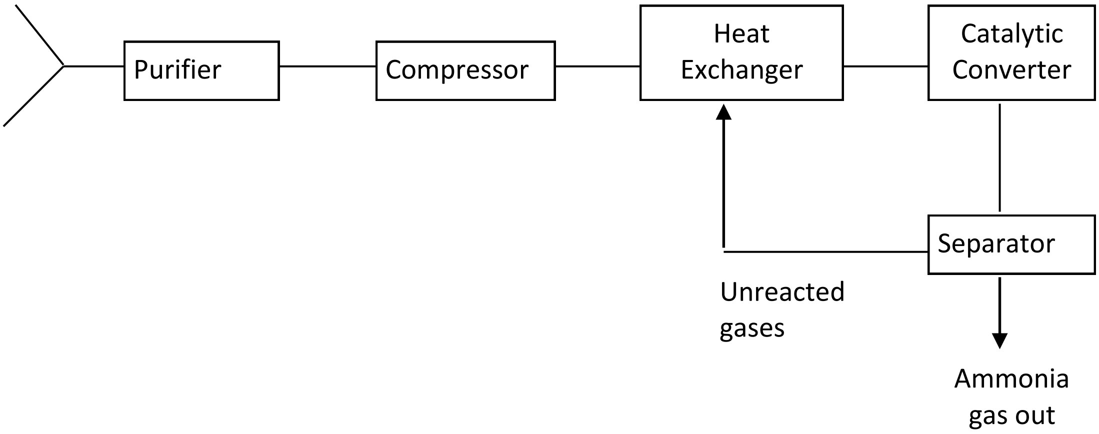
The graphs show the change in the yield of ammonia with changes in temperature and pressure when gases are mixed in the ratio of 1 part (nitrogen): 3 parts (hydrogen)



You will notice from the graphs the percentage yield of ammonia increases with decrease in temeperature. Theoretically a high pressure of about 800 atmospheres will produce a 100% yield. In practice, this would be expensive as equipment to withstand high pressure will be required. In the actual manufacture pressures around 250 atmospheres and temperatures of about 450°C are used.

As you have seen from the equation that the reaction is exothermic, once started there will be enough heat generated to maintain the reaction temperature.

A schematic diagram of the stages in the manufacture of ammonia is shown below:



Though there may be several sources of nitrogen and hydrogen, in Zimbabwe nitrogen is obtained from liquid air while hydrogen is a product of the electrolysis of water. Sable chemicals is however working on adoption of ‘coal gasification’ as a method of producing H_2 because of high electricity demands of electrolysis. Finally divided iron is used as a catalyst. As you may notice from the diagram above, unreacted gases (N_2,H_2) from the catalytic converter are recycled in the system.

Industrial Importance of Ammonia

The greatest percentage of ammonia is converted to nitric acid which is largely used to make inorganic fertilizers

Nitric acid production.

In the presence of platinum as a catalyst ammonia is converted to nitrogen oxide.

$$4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O$$

The nitrogen monoxide reacts with oxygen of the air forming nitrogen dioxide

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$$

Nitrogen dioxide is then reacted with water to produce nitric acid.

$$3NO_{2(g)} + H_2O_{(l)} \rightarrow 2HNO_{3(aq)} + NO_{(g)}$$

The $NO_{(g)}$ produced is allowed to react with oxygen to regenerate more NO_2 which is further reacter with water to form nitric acid.

Nitrate Fertilizer

The discovery of ammonia based fertilizers has improved agricultural output in many countries. As you may know nitrogen is an important component in plant tissues. The most common nitrogenous fertilizer is ammonium nitrate. It is preferable to other fertilizers because it contains the highest percentage of nitrogen. Can you calculate this percentage in NH_4NO_3, Ammonium nitrate readily dissolves in the soil and is used as "top dressing." However, this fact often presents storage problems. Manufacture of ammonium nitrate involves a direct neutralisation of nitric acid with ammonia.

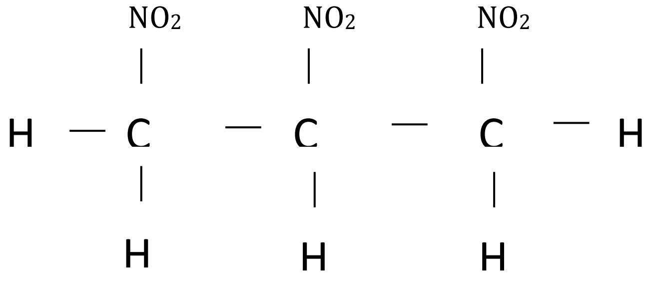
$$NH_{3(g)} + HNO_{3(l)} \rightarrow NH_4NO_{3(s)}$$

Though nitrate fertilizers are used to improve agricultural production, their excessive use can present serious environmental problems. Since they are soluble they can be carried into rivers and dams where they poison aquatic life. They can also encourage rapid growth of plants in rivers and dams (eutrophication). When the plants die, they decompose using the oxygen in the water and releasing carbon dioxide which is toxic to fish and other aquatic animals. Excessive use of the fertilsier will also lower the soil pH making the soil unsuitable for growth of some plants. Hence additional expense has to be met to neutralize the soil with lime

Explosives

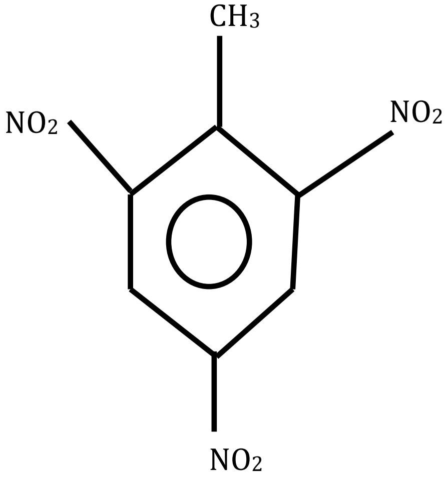
About 15% of nitric acid is used to make explosives like:

Nitrogycerine

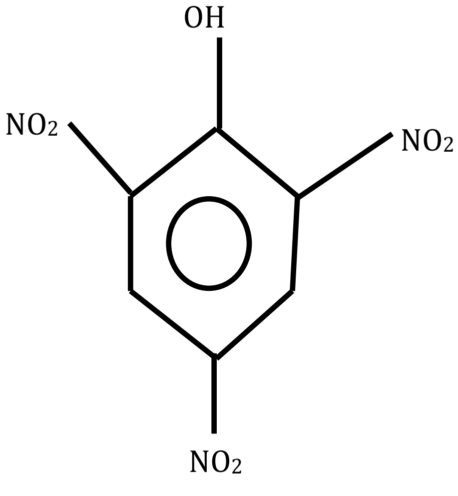


$$\begin{array}{ccccccc} & \mathrm{NO_2} & & \mathrm{NO_2} & & \mathrm{NO_2} & \\ & | & & | & & | & \\ \mathrm{H} - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - \mathrm{H} \\ & | & & | & & | & \\ & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \end{array}$$

Trinitrotoluene



Trinitrophenol



When these explosives are detonated an enormous amount of heat energy is released. This is accompanied by the sudden expansion of gaseous products. For example explosion of nitroglycerine can be represented by the equation:

$$4C_3\ H_5\ (NO_2)_3 + 5O_2 \quad \rightarrow \quad 10H_20\ + 6N_2\ +\ 12CO_2$$

This means that 4 moles of the explosive will produce 12 moles of CO_2, 10 moles of steam and 6 volume of nitrogen. The explosion also releases about 27 000kJ of heat energy.

Oxides of Nitrogen

As you have seen earlier, nitrogen though a relatively inert element does combine at high temperatures with oxygen. This reaction occurs mainly in internal combustion engines of cars which results in the formation of nitrogen monoxide.

$$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$$

Released into the air with other exhaust gases, nitrogen monoxide accounts for some of the air pollution. This is more pronounced in big cities with a large car population.

The NO (g) readily combines with atmospheric oxygen forming nitrogen dioxide.

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$$

When nitrogen dioxide reacts with rain water it forms nitric acid which comes down as "acid rain" The acid rain poses problems in the environment in that it:
-goes into the soil, lowers its pH making it unsuitable for the growth of some plants.
-flows into rivers and kills aquatic life.
-damages buildings by reacting with calcium carbonate in the structures.
-worsens the condition of people who have breathing problems.

Nitrogen oxides also catalyse through a series of reactions the conversion of sulphur dioxide to sulphur trioxide which dissolves in water in the atmosphere to form acid rain (sulphuric acid)

$$SO_{2(g)} + NO_{2(g)} \rightarrow SO_{3(g)} + NO_{(g)}$$

$$SO_{3(g)} + H_2O \rightarrow H_2SO_{4(aq)}$$

$$NO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow NO_{2(g),regenerated}$$

In order to reduce the amount of nitrogen oxides discharged into the air, modern car exhaust pipes are fitted with catalytic converters. The converter is basically a platinum gauze which catalyses the break- down of the nitrogen oxides and carbon monoxides to nitrogen and carbon dioxide which are relatively harmless gases.

$$2CO_{(g)} + 2NO_{(g)} \rightarrow 2CO_{2(g)} + N_{2(g)}$$

$$NO_2 \rightarrow \frac{1}{2}N_2 + O_2$$

Sulphur dioxide

This is an acidic gas produced by burning sulphurated coal. The basic equation is

$$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$$

In the presence of nitrogen oxides, the sulphur dioxide is oxidized to sulphur (VI) oxide as you have seen earlier. The sulphur trioxide then reacts with water in the atmosphere to produce sulphuric acid.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

It is this acid that causes acid droplets in the air and when the droplets condense they form "acid rain." This acidic atmosphere is common in industries that use sulphurated coal as a source of heat energy.

As you have observed with oxides of nitrogen, sulphur dioxide is also an atmospheric pollutant and in fact it is the major one. The effects of atmospheric sulpur dioxide stimulated research pertaining to health problems. The research showed that the gas was the main cause of complications in patients with lung conditions like bronchitis and emphysema.

In addition, it was found that the acid rain contributed to;
acidification of soils and river water
:rapid deterioration of buildings structures (Find out how this happens).
:formation of "acid food" in large industrial cities.

Manufacture of sulphuric acid
(Contact Process)

It has been said that the level of industrial development of a country is measured by its consumption of sulphuric acid. This shows the importance of this acid in the economic development of the country.

Sulphuric acid is manufactured by the Contact process. Basically, this process involves the oxidation of sulphur to sulphur (IV) oxide (SO_2), conversion of sulphur (IV) oxide to sulphur (VI) oxide (SO_3) and the reaction of ($SO_{3)}$ with water to form sulphuric acid.

The equations of the reactions taking place in the processes are summarised below.

$$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}; \Delta H^{\theta} = 297kJmol^{-1} ------(1)$$

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}; \Delta H^{\theta} = 197kJmol^{-1} ------(2)$$

$$SO_{3(g)} + H_2SO_{4(l)} \rightarrow H_2S_2O_{7(l)}; \Delta H^{\theta} = -907kJmol^{-1} -------(3)$$

$$H_2S_2O_{7(l)} + H_2O_{(l)} \rightarrow 2H_2SO_4$$

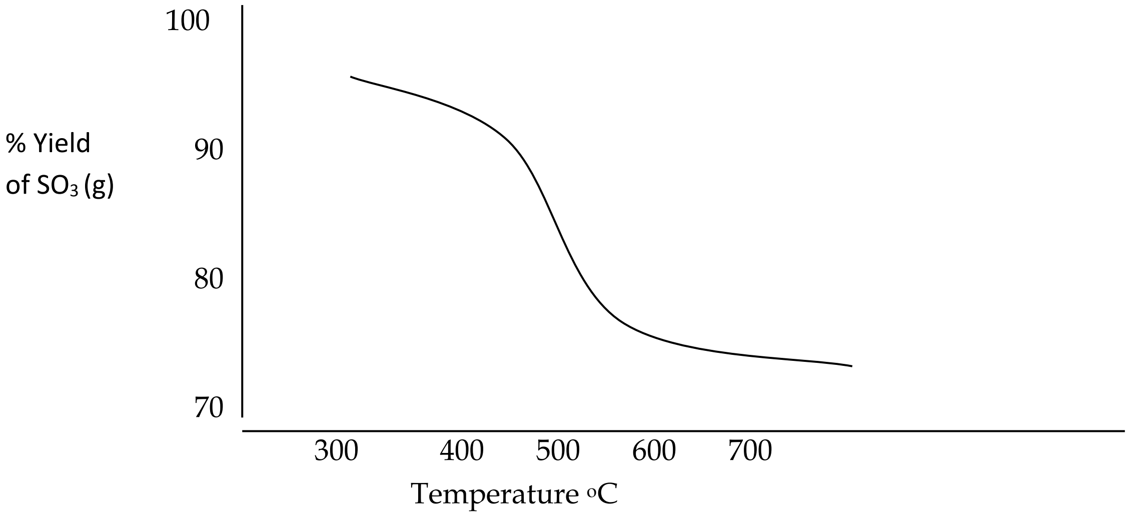
You will notice from the equations above that:

-in equation (2) the volume of the product (SO_3(g) is less than the total volume of the reactants

-all the reactions (1), (2) and (3) are exothermic

-conversion of SO_2(g) to SO_3 (g) is reversible.

applying Le Chatelier's principles in (2) we can deduce that the production of SO_3(g) will be favoured by low temperature. Also high pressure will shift the position of equilibrium towards the formation of more SO_3. An increase in the concentrations (or partial pressures) of SO_2(g) will increase the yield of SO_3(g) The above observations can also be illustrated in the graph below:

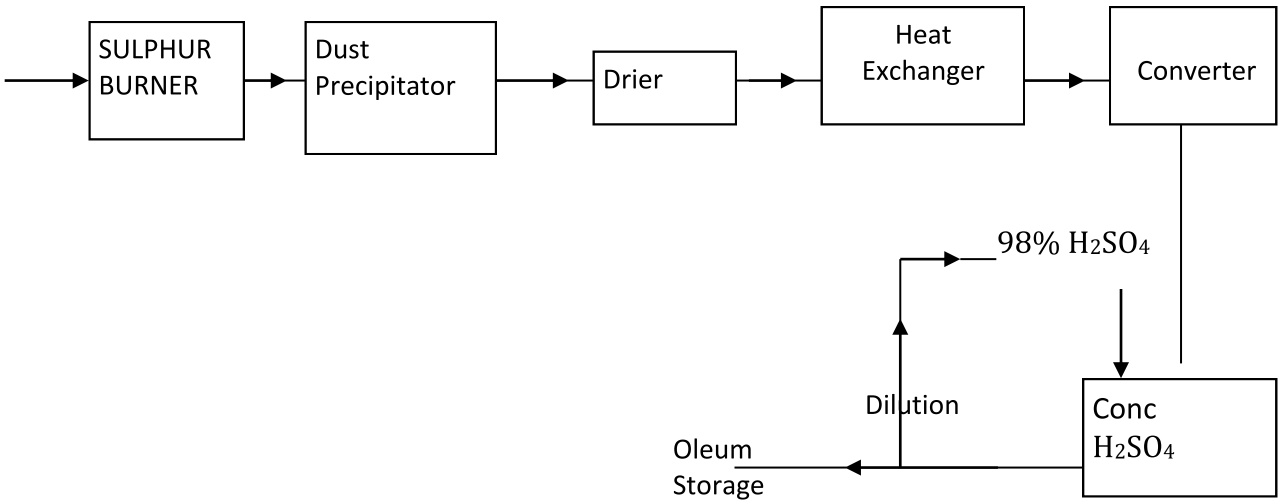


The graph shows us that the highest yield of SO_3(g) would be obtained at low temperatures. However, at low temperatures the reaction $SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ would be very slow. At high temperature the yield of SO_3(g) falls. A catalyst vanadium (v) oxide (V_2O_5) is used to speed up the attainment of equilibrium at fairly low temperatures. In practice a compromise temperature of 450°C is used.

Looking at the graph, you will also notice that the yield at 450°C is above 90% but falls at higher temperatures.

You may have noticed too that in equation (2) there is only a small decrease in volume during the formation of SO_3(g). So increase in pressure will not affect the position of equilibrium significantly.

The flow diagram illustrates the main stages of the Contact process.



Sulphur or a sulphide ore is roasted in burners in air to produce SO_2 (g). The SO_2 is mixed with air. Dust which contains substances which can poison the catalyst is removed from the mixture in the dust precipitator. From these the $SO_{2(g)}/O_{2(g)}$ mixture is dried and heated before entering the converter where SO_2 (g) and O_2(g) combine to form SO_3(g) in the presence of vanadium (v) oxide, a catalyst. The SO_3(g) from the converter is dissolved in 98% H_2SO_4 to form 100% $H_2S_2O_7$ (oleum) which is diluted to 98% for further absorption of SO_3(g). Direct reaction of SO_3(g) with water is avoided because the reaction is exothermic and forms acid spray mist.

Industrial Importance of H_2 SO_4

As indicated earlier, sulphuric acid is of critical importance in industry. Some of the major uses of the acid in the manufacturing industry are listed in the table.

Industry	**Products**
a) Fertilisers	-Phosphates -ammonium sulphate
b) Paints and Pigments	-paints
c)Fibres and Fabrics	-Synthetics (Viscose, rayon, paper Textiles, dyes
d) Soaps and detergents	-Synthetic detergents (soapless) like sulphonates soapy detergents

	like, oleates palmitates
e) Plastics	-Polythene, pVC Polystyrene
f) Mining	-purification of copper -cleaning metals
g) Car	-Lead acid accumulators
h) Other	-explosives -insecticides, Medicines perfumes.

Uses of sulphur –Dioxides

The uses of sulphur dioxide include the following:

a) manufacture of sulphuric acid

b) bleaching news-print, silk and straw

c) air fumigant to kill bacteria (disinfectant)

d) food preservation e.g drinks, canned fruit and fruit juices

e) making calcium hydrogen sulphate used in the pulp and paper industry to breakdown plant material

f) refining of petrol.

Summary

a) Nitrogen is unreactive because of the large energy required to break the N≡N bond.

b) The $NH^+{}_4$ion is formed by the formation of a dative bond between NH_3 and H^+.

c) Ammonia can be displaced from its ammonium salts by reaction with the OH^- ion which is a strong base.

d) Production of ammonia from nitrogen gas and hydrogen is favoured by a high pressure and a low temperature in the presence of an iron catalyst.

e) Ammonia is used to make fertilizers like ammonium nitrate.

f) Excessive use of nitrate fertilizers leads to acidic soils, poisoning of water sources and eutrophication of rivers.

g) Oxides of nitrogen NO,NO_2 are produced in car engines. They can be reduced by catalytic converters (Platinum) to harmless gases like N_2,CO_2 and H_2O.

h) Oxides of nitrogen dissolve in water in the atmosphere to form "acid rain" They also catalyse the formation of SO_3 from SO_2.

i) SO$_2$ is formed from burning coal containing sulphur. Sulphur dioxide forms "acid rain" in the atmosphere Acid rain makes the soils acidic and worsens the condition of patients suffering from lung diseases like emphysema and bronchitis.

f) Sulphuric acid is manufactured from sulphur (VI) oxide. In the reaction $SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

SO$_3$ formation is favoured by low temperature in the presence of V$_2$O$_5$ as a catalyst.

k) Sulphuric acid is used in the fertiliser, paint, soap, plastics, mining, and car industries.

Exam Type Questions

1a) Draw the electron configuration of a nitrogen atom and use this to show how the molecule N$_2$ is formed.

b) Nitrogen is normally an inert-element. However it does react with magnesium and oxygen under special conditions.

Explain how the above reactions occur. Give the equations for the reactions.

2a) Draw a displayed formula of an ammonia molecule and use this structure to show how an ammonium ion is formed.

b) Ammonia gas is formed when ammonium sulphate is heated gently with sodium hydroxide. Using the ammonium ion and the hydroxyl ions only show how ammonia is produced.

3a) The reaction in the manufacture of ammonia is represented by the equation

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \Delta H^{\theta} = -92,4kJmol^{-1}$$

State and explain three conditions that would promote the production of ammonia.

b) Explain how the following contribute to "acid rain"

i) Oxides of nitrogen

ii) Sulphur (iv) Oxide

c) Describe how the adverse effects of the oxides in b (i) and b (ii) on the environment can be minimized.

4 State the conditions that affect the production of SO$_3$ from SO$_2$. Explain how these conditions affect the production of SO$_3$

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CHAPTER 14

Transition Elements

By the end of this chapter you should be able to:

a) explain what is meant by a transition element in terms of a d-block element forming one or more stable ions with incomplete orbitals.
b) state the electronic configuration of a first row transition element and of its ions.
c) state that the atomic radii, ionic radii and first ionisation energies of the transition metals are relatively invariant.
d) contrast qualitatively the melting point, density, atomic radius, ionic radius, first ionisation energy and conductivity of the transition elements with those of calcium as a typical s block element.
e) describe the tendency of transition elements to have variable oxidation states.
f) predict from a given electronic configuration the likely oxidation states of a transition element.
g) describe and explain the use of $Fe^{3+}, Fe^{2+}; MnO_4^-, Mn^{2+}; Cr_2O_7^{2-}, Cr^{3+}$ as examples of redox systems.
h(i) explain the reaction of transition elements with ligands to form complexes including the complexes of copper (II) ions with water and ammonia.
(ii) describe the formation and state the colour of these complexes.
i) predict using E^{θ} values, the likelihood of redox reactions.
f) explain qualitatively that ligand exchange may occur, including CO, O_2 in haemoglobin.
k) State examples of catalysis by transition metals and/or their compounds.

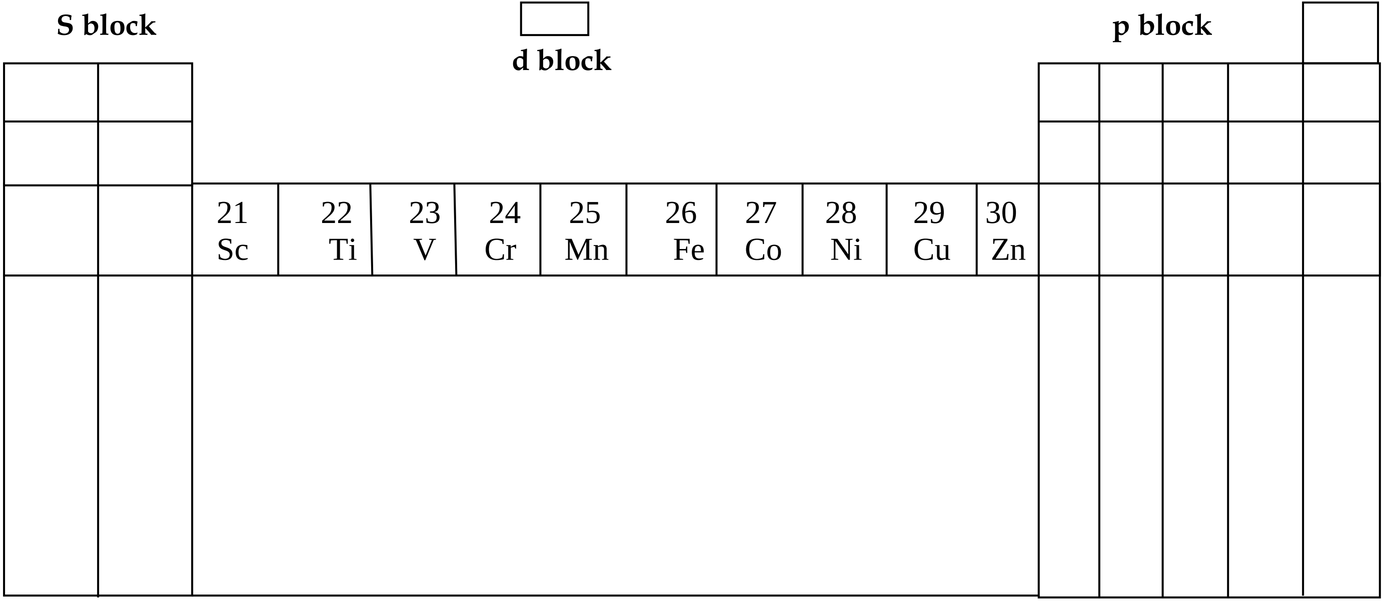
Introduction

Transition elements also known as d-block elements lie between the s and p blocks in the periodic table. They consist of the first series and the second series. The second series are sometimes called the inner transition series. Their electron configuration is characterized by the filling of the d and f sub-shell. However, in the first series it is the 3d sub-shell that is being filled. As the elements lie between the s and p blocks, they exhibit metallic and non-metallic properties either in their pure state or in their compounds. In this chapter we will confine our discussion to the first transition series, scandium to zinc. We will focus on the following:

a) Position in the periodic table
b) Electron configuration
c) Atomic radii
d) Ionic radii
e) Ionisation energy
f) Melting points, density, electrical conductivity compared with calcium.
g) Oxidation states and electron configuration.
h) Redox systems and E^{θ} values.
i) Ligand formation.
f) Colour formation.
k) Ligand exchange.

Catalytic properties.

Position in the Periodic Table



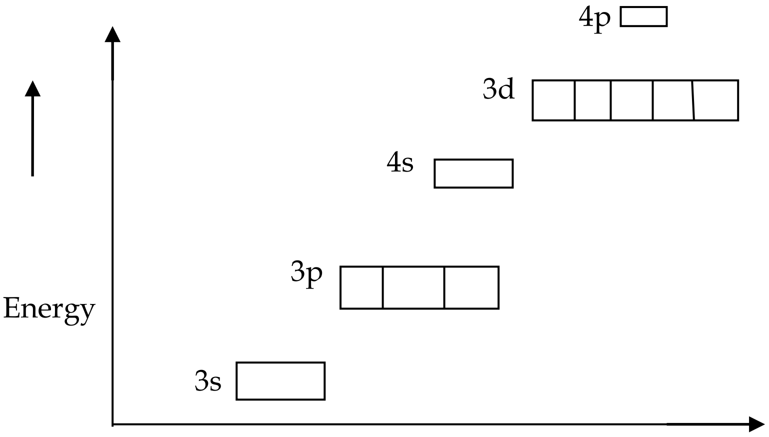
As you can see from the sketch of the periodic table above, the first transition series stretches form Sc to Zn and the atomic numbers range from 21 for Sc to 30 for Zn. They are in period four of the periodic table.

Electron configuration

Element	Atomic Number	Electron arrangement	
		Other electrons	**3d electrons**
Scandium	21	[Ar] $4s^2$	↑
Titanium	22	[Ar] $4s^2$	↑ ↑
Vanadium	23	[Ar] $4s^2$	↑ ↑ ↑
Chromium	24	[Ar] $4s^1$	↑ ↑ ↑ ↑
Manganese	25	[Ar] $4s^2$	↑ ↑ ↑ ↑ ↑
Iron	26	[Ar] $4s^2$	↑ ↓ ↑ ↑ ↑ ↑
cobalt	27	[Ar] $4s^2$	↑ ↓ ↑ ↓ ↑ ↑ ↑
Nickel	28	[Ar] $4s^2$	↑ ↓ ↓ ↑ ↓ ↑ ↑ ↑
Copper	29	[Ar] $4s^1$	↑ ↓ ↑ ↓ ↑ ↓ ↑ ↓ ↑
Zinc	30	[Ar] $4s^1$	↑ ↓ ↑ ↓ ↑ ↓ ↑ ↓ ↑ ↓

We can see that for chromium and copper there is a difference in the expected arrangement of electrons. These differences occur when d orbitals are either full or half full and this is because half full or completely full d subshells constitute or render some stability. We also notice from the electron configurations table that copper and zinc have completely filled 3d sub-shell or orbitals and hence these elements are not strictly transition elements.

Electron arrangement and Energy



Electron energy diagram

You will notice from the energy diagram above that as the shells get further from the nucleus the energy difference between shells gets less until there is an energy overlap between the 4th and 3rd shells. In fact, as shown, the 3d orbitals have higher energy than the 4s orbitals

Ion formation in transition metals.

As you know ions are formed from metal atoms by loss of outermost electrons and so one would expect electrons to be lost first from the 3d subshell rather than form the 4s subshell. However, the reverse is true which means that electrons are lost from the 4s subshell first and not from the 3d subshell. The reasons for this unexpected observation is that once electrons occupy the 3d sub-shell they tend to repel the 4s electrons further from the nucleus. Hence the grip of the nucleus on these 4s electrons will be weaker rendering the electrons easier to lose. Since transition elements lose electrons when they ionize they will exhibit similar chemical properties.

Trends across the 1st transition series.

Trends in atomic radii

Metal	Metallic (atomic radii/(nm)
Potassium	0,24
Calcium	0,20
Scandium	0,16
Titanium	0,15
Vanadium	0,14
Chromium	0,13
Manganese	0,14
Iron	0,13
Cobalt	0,13
Nickel	0,13
Copper	0,13
Zinc	0,13

You will notice that generally the atomic radii of transition metals are small. This is because the electrons are added to the 3d sub-shell which is nearer to the nucleus and therefore experience greater nuclear attraction than the 4s electrons. Furthermore, the electrons are added to inner orbitals, there is a nullifying effect on increase in nuclear charge leading to more or less consistent atomic size. The atomic radii of potassium and calcium are comparatively larger because the 4s electrons are outermost.

Ionic radii

Ion	**1onic radii (nm)M^{2+}**
Calcium	0,094
Scandium	-
Titanium	0,090
Vanadium	0,088
Chromium	0,084
Manganese	0,080
Iron	0,076
Cobalt	0,074
Nickel	0,072
Copper	0,070
Zinc	0,074

It is clear from the table that generally the radii are the same though they tend to be smaller from Sc to Cu. As you know this is due to increased nuclear attraction from Sc to Cu which is intensified by removal of electrons. Further more, the 3d electrons constitute a poor screen from nuclear attraction for the outer electrons. You would then expect the +3 or more oxidation states ions to be even smaller.

Ionisation Energy

Metal	1st Ionisation energykJmol^{-1}
Scandium	630
Titanium	660
Vanadium	650
Chromium	650
Manganese	720
Iron	760
Cobalt	760
Nickel	740
Copper	750
Zinc	910

As you know ionisation energy is the energy required to remove an electron from an atom or ion in the gaseous state. The first-ionization energy can be represented by:

$$M_{(g)} \rightarrow M^{+}_{(g),} + e^{-}$$

Notice from the table above that the first ionization energies of the transition elements are more or less similar. You would expect the ionization energy to increase across the transition series due to an increase in nuclear charge. However this is offset by the additional screening of the nuclear charge by additional d electrons. The screening is poor for zinc hence a larger ionisation energy. Generally one would expect the ionisation energies to increase from 1st to 2nd to 3rd and so on. This is due to the increase in effective nuclear attraction for the remaining electrons which will be harder and harder to remove. This is shown by the ionisation energies of titanium and vanadium

Element	Ionisation	Value
Titanium ($4s^2\ 3d^2$)	1st	660
	2nd	1310
	3rd	2680
	4th	4170
	5th	9750
Vanadium ($4s^2\ 3d^3$)	1st	650
	2nd	1415
	3rd	2860
	4th	4620
	5th	6290
	6th	12450

Looking at the successive ionisation energies above, the values increase gradually until all the 4s and 3d electrons have been removed. This explains the existence of multiple oxidation states. After all the 4s and 3d electrons have been removed the next are the 3p electrons and you will notice the large jump in energy. If you look at the electron energy diagram we have already referred to you will find that it explains this large energy jump.

Melting points, density and electrical or thermal conductivity.

Transition elements have higher melting and boiling points as shown in the table than potassium and calcium. Due to their stronger metallic bonding the interatomic forces are hard to break.

This is coupled with the small atomic radii which results in enhanced nuclear attraction. The metallic bond formed by attraction between metallic ionic cores and delocalized d electrons is hard to break. Bonding in potassium and calcium is weak due to the presence of only a few s electrons in the delocalized system.

Metal	M.pT°C	b.pT°C
Potassium	64	770
Calcium	850	1490
Scandium	1540	2730
Titanium	1680	3260
Vanadium	1900	3400
Chromium	1890	2480
Manganese	1240	2100
Iron	1540	3000
Cobalt	1500	2900
Nickel	1450	2 730
Copper	1080	2 600
Zinc	420	910

Densities of transition elements are generally high compared to the s block metals (K and Ca) in the same period. Again we consider the atomic size (atomic radii) which are small in transition elements due to more intense nuclear attraction. This reduces the atomic size and enables the atoms to be more closely packed whereas in calcium the atoms are large and therefore not so closely packed in the crystal lattice. Hence the density of calcium is less than that of the transition metals. The table below shows the densities.

Metal	Density (g/cm^3)
Calcium	1.54
Scandium	3.0
Titanium	4,5
Vanadium	6.1
Chromium	7,2
Manganese	7,4
Iron	7,9
Cobalt	8,9
Nickel	8,9
Copper	8,9
Zinc	7,1

Except for zinc there is a general increase in density corresponding to a decrease in atomic size. Do you still remember why the atomic size is decreasing Sc-Co? Transition metals are good conductors of heat and electricity and this is due to mobile d delocalized electrons. The electrons are loosely bound to metallic ion cores and can move readily under a thermal or potential difference. Due to their mobility the electrons can readily be promoted to the conduction band.

As we have seen, calcium has fewer delocalized s electrons and hence the metal is not as good a conductor as the transition elements.

Oxidation states and electron configuration

As we saw earlier in the electron energy level diagram, 3d and 4s electrons have more or less similar energy and so an element can lose electrons from 3d and 4s sublevels. This enables the atom to form ions with different charges. You will find that the elements Sc to Cu can assume two or more oxidation states. Do you still remember what is meant by oxidation state? In simple ionic components the oxidation state of an element is the same as the charge on its ion. Thus in iron (iii) chloride the iron has an oxidation state of +3.

However in more complex groups, the oxidation state of the atom is the charge the atom would carry taking into account the oxidation state of the more electronegative atom with which it is combined. For example in the ion $MnO_{4,}^{-}$ the oxidation state of oxygen is -2 in this example the total oxidation state of O_4 is -2x4 = -8, but the overall or net charge is 1-. Therefore oxidation state of Mn- 8= -1 this gives +7 as the oxidation state of Mn. The table shows the oxidation states of Mn.

Ion or compound	Oxidation state of Mn.
MnO_4^-	+7
MnO_4^{2-}	+6
MnO_4^{3-}	+5
MnO_2	+4
$\left[Mn(CN)_6\right]^{3-}$	+3
Mn^{2+}	+2

You will find that other transition elements also have a number of oxidation states. The maximum value for elements scandium to manganese are shown.

Element	Maximum Oxidation state
Sc	+3
Ti	+4
V	+5
Cr	+6
Mn	+7

After Mn the values are irregular. Some of the oxidation states of transition elements are differently coloured and this makes it possible to tell whether the values are increasing or decreasing. Remember a decrease in the oxidation state corresponds to the addition of an electron and an increase corresponds to the removal of an electron. Effectively this corresponds to a redox system. Generally, the +3 oxidation states are more common at the start of the series (Sc- Cr) While the + 2 oxidation state is more common from Cr- Zn. It has also been found that the elements exhibit their highest oxidation states when combined with highly electro-negative elements like oxygen. The highly electro-negative atom is able to "dig deeper" into the metallic atom for electrons.

Redox systems and E^{θ} Values

Due to the small energy difference between the 4s and 3d sub levels electrons can be lost. readily from these sublevels to form +2 and +3 oxidation states. In a mixture containing ions of the same element in both state +2 and +3, which oxidation state would be more stable? The standard electrode potentials of the system $M^{+3}{}_{(aq)} / M^{2+}{}_{(aq)}$ can be used to predict the position of equilibrium in the system.

$$M^{3+}{}_{(aq)} + e^{-} \rightleftharpoons M^{2+}_{(aq)}; E^{\theta}_{v}$$

The table shows the E^{θ} values for the system $\left(M^{3+}_{(aq)} \big/ M^{2+}_{(aq)} \right)$ for elements Ti → Co.

Element $M^{3+}_{(aq)} \big/ M^{2+}_{(aq)}$	E^{θ} / V
Ti	-0,37
V	-0,26
Cr	-0,4
Mn	+1,51
Fe	+0,77
Co.	+1,82

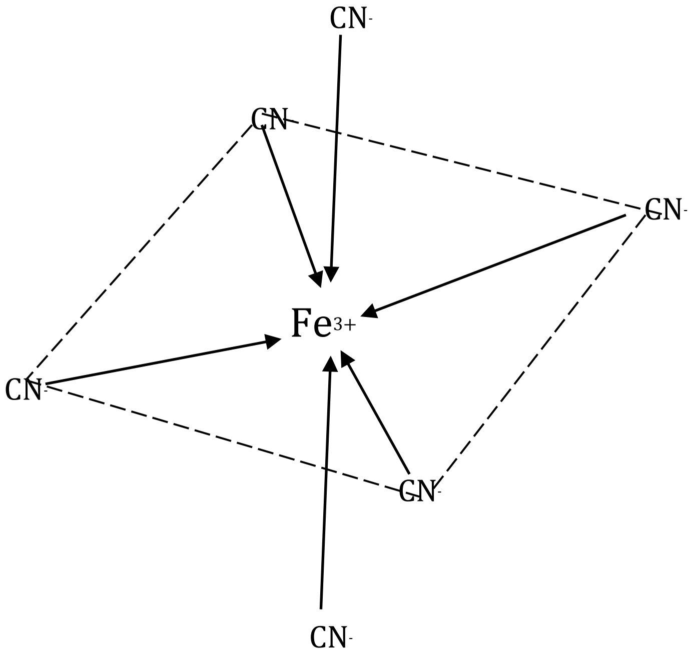
Notice from the table that there is a gradual rise in E^{θ} values from Ti-Co, but there is an unexpected high value for Mn and an equally unexpected low value for Fe. Generally the more positive the E^{θ} value the less stable the $M^{3+}_{(aq)}$ in the presence of $M^{2+}_{(aq)}$.

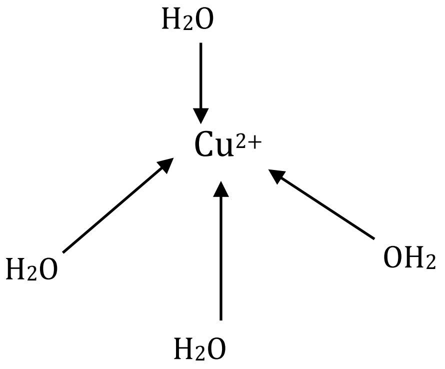
Hence the low value of E^{θ} for Ti, V, Cr and Fe mean the $M^{3+}_{(aq)}$ is more stable than the $M^{2+}_{(aq)}$. Also the table tells us that the Mn^{3+} and Co^{3+} would be less stable than the +2. In order to explain the stability of $Mn^{2+}_{(aq)} and Fe^{3+}_{(aq)}$ we will recall that half filled 3d orbitals offer stability. Check them from the electronic configuration of these elements.

Ligand Formation

Complex ions are formed from anions or neutral molecules and a central cation being of a transition element. What is a ligand? It is a molecule or ion with at least one lone pair of electrons which is available for dative bond formation with the metal atom or ion. However the electron pairs tend to alter the arrangement of electrons in the central atom/ion (orbital splitting) and also the physical properties the central atom/ion. One of the physical properties altered is colour. Some of the common anion ligands are Cl^{-}, F^{-}, CN^{-}, OH^{-}. Non ionic ligands include H_2O, $NH_3 and$ CO. Some of the complexes and their structures are:

Complex	**Structure**
$\left[Fe(CN)_6\right]^{3-}$	Octahedral
$\left[Ti(H_2O)_6\right]^{3+}$	Octahedral
$\left[Cu(H_2O)_4\right]^{2+}$	Tetrahedral





In the complex $\left[Ti(H_2O)_6\right]^{3+}$ the central Ti^{3+} ion will assume the electron configuration

$\left[Ar\right]3d^1(4s^2 and 3d^1)$ used in bonding

Colour formation

This involves $d \rightarrow d$ electron transitions. If a d electron is at a low energy level and absorbs enough energy it can jump to a higher energy level. If the energy is acquired from the visible region of the electromagnetic spectrum, the colour corresponding to the wavelength of the energy goes missing from the white light and the remaining colours are transmitted. For example in the complex $\left[Ti(H_2O)_6\right]^{3+}$ energy of wavelength $5x10_M^{-7}$ is able to promote one electron in Ti^{3+} from a low energy level to a highest energy level orbital. Green light has a wave length of $5x10_M^{-7}$. So green goes missing from white light resulting in the transmission a purple colour which is seen.

Ligand exchange

Different ligands have different bonding strengths. Some ligands form stronger bonds than others. For a particular central ion, stronger ligands will displace weaker ones. For example copper (II) ions form the complex $\left[Cu(H_2O)_6\right]^{2+}$ which is blue in an aqueous solution. Addition of concentrated hydrochloric acid leads to the replacement of the H_2O ligands by the Cl^- ligands. The displacement reactions are shown.

1. $\left[Cu(H_2O)_6\right]^{2+} + 4Cl^- \rightarrow \left[CuCl_4\right]^{2-} + 6H_2O$

The colour of the solution is seen to change from blue to yellow as more H_2O ligands are replaced by Cl^- ligands. The displacing power decreases in the order.

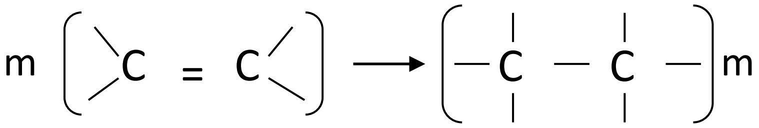
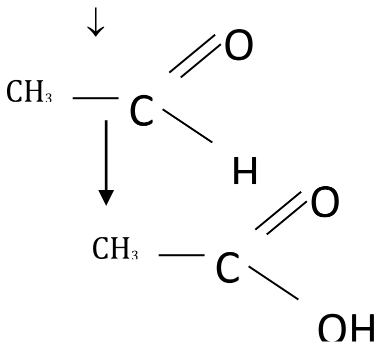
H_2O, NH_3, x^-, CN^- where x^- is a halide ion.

The displacement of a ligand by another is important in life processes where it involves absorption of oxygen by haemoglobin. In the presence of carbon monoxide a stronger ligand than oxygen, the carbon monoxide forms a stable complex with haemoglobin (carboxy haemoglobin). Oxygen being a weaker ligand than carbon monoxide is not able to displace it from the haemoglobin complex whose central ion is iron. So the blood of the organism is unable to absorb oxygen.

Catalysis

Transition elements and their compounds are catalysts. It is believed that their catalytic activities are due to the variable oxidation states. The catalysts provide a lower energy route for reactions and during the reactions there are changes in the oxidation states of the elements. The catalyst is regenerated at the end of the reaction.

The table shows some of the industrially important catalysts

Transition Element	**Catalysts**	**Reaction**
Ti	$T_1Cl_3 / A1_2O_3$	
V	V_2O_5	$2SO_2 + O_2 \rightarrow 2S0_3$
Fe	Fe / Fe_2O_3	$N_2 + 3H_2 \rightarrow 2NH_3$
Ni	*Ni*	$-CH = CH + H_2$ $-CH_2 - CH_3$
Cu	Cu / CuO	$CH_3CH_2OH + \frac{1}{2}O_2$ 
Pt	*Pt*	$2SO_2 + O_2 \rightarrow 2SO_3$
Pt	*Pt*	$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

<u>**Summary**</u>

1. Transition elements are elements that form one or more stable ions with incomplete d orbitals.
2. Atomic radii and ionic radii decrease across the transition series.
3. Ionisation energies increase across the series.
4. Melting points, boiling points and densities of transition elements are higher than those of s block elements.
5. Transition elements form compounds which exhibit various oxidation states.
6 Transition elements form complexes with ligands.
7. Transition elements form coloured ions.
8. The lower the E^{θ} values for redox reactions the more stable the resulting ions.
9. Strong ligands displace weaker ones from complexes.
10. Transition elements or their compounds are catalysts.

Examination Type Questions

1. Draw the electron configurations of the following ions
V^{3+}, Cu^{2+}, Mn^{2+}, Cr^{3+}.
2. What are the oxidation states of the metal ion in the following.
$Cr_2O_7^{2-}$, $Cr_2O_7^{2-}$, $KMnO_4$, V_20_5, Fe_2O_3

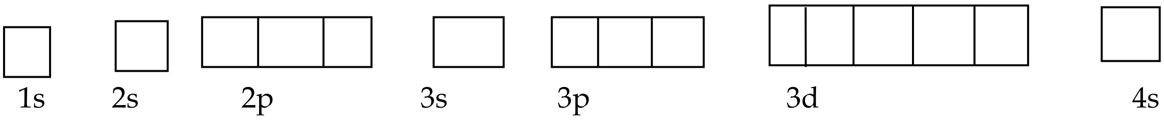
3. Complete the following equations

a) $MnO_4^- + H^+ \rightarrow Mn^{2+} + H_2O$

b) $Cr_2O_7^{2-} + H^+ \rightarrow Cr^{3+} + H_2O$

c) $Fe^{3+} \rightarrow Fe^{2+}$

4. Draw the electron configuration of atomic chromium by filling in the boxes



5. Using the electron configuration given at the beginning of the chapter, predict the possible oxidation states of the following: cobalt, vanadium, nickel and manganese.

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