

Ministry of Education and Sports

HOME-STUDY LEARNING



CHEMISTRY

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This material has been developed as a home-study intervention for schools during the lockdown caused by the COVID-19 pandemic to support continuity of learning.

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FOREWORD

Following the outbreak of the COVID-19 pandemic, government of Uganda closed all schools and other educational institutions to minimize the spread of the coronavirus. This has affected more than 36,314 primary schools, 3129 secondary schools, 430,778 teachers and 12,777,390 learners.

The COVID-19 outbreak and subsequent closure of all has had drastically impacted on learning especially curriculum coverage, loss of interest in education and learner readiness in case schools open. This could result in massive rates of learner dropouts due to unwanted pregnancies and lack of school fees among others.

To mitigate the impact of the pandemic on the education system in Uganda, the Ministry of Education and Sports (MoES) constituted a Sector Response Taskforce (SRT) to strengthen the sector's preparedness and response measures. The SRT and National Curriculum Development Centre developed print home-study materials, radio and television scripts for some selected subjects for all learners from Pre-Primary to Advanced Level. The materials will enhance continued learning and learning for progression during this period of the lockdown, and will still be relevant when schools resume.

The materials focused on critical competences in all subjects in the curricula to enable the learners to achieve without the teachers' guidance. Therefore effort should be made for all learners to access and use these materials during the lockdown. Similarly, teachers are advised to get these materials in order to plan appropriately for further learning when schools resume, while parents/guardians need to ensure that their children access copies of these materials and use them appropriately. I recognise the effort of National Curriculum Development Centre in responding to this emergency through appropriate guidance and the timely development of these home study materials. I recommend them for use by all learners during the lockdown.

Àlex Kakooza

Permanent Secretary

Ministry of Education and Sports

ACKNOWLEDGEMENTS

National Curriculum Development Centre (NCDC) would like to express its appreciation to all those who worked tirelessly towards the production of home-study materials for Pre-Primary, Primary and Secondary Levels of Education during the COVID-19 lockdown in Uganda.

The Centre appreciates the contribution from all those who guided the development of these materials to make sure they are of quality; Development partners - SESIL, Save the Children and UNICEF; all the Panel members of the various subjects; sister institutions - UNEB and DES for their valuable contributions.

NCDC takes the responsibility for any shortcomings that might be identified in this publication and welcomes suggestions for improvement. The comments and suggestions may be communicated to NCDC through P.O. Box 7002 Kampala or email admin@ncdc.go.ug or by visiting our website at http://ncdc.go.ug/node/13.

Grace K. Baguma

Director,

National Curriculum Development Centre

ABOUT THIS BOOKLET

Dear learner, you are welcome to this home-study package. This content focuses on critical competences in the syllabus.

The content is organised into lesson units. Each unit has lesson activities, summary notes and assessment activities. Some lessons have projects that you need to carry out at home during this period. You are free to use other reference materials to get more information for specific topics.

Seek guidance from people at home who are knowledgeable to clarify in case of a challenge. The knowledge you can acquire from this content can be supplemented with other learning options that may be offered on radio, television, newspaper learning programmes. More learning materials can also be accessed by visiting our website at www.ncdc.go.ug or ncdc-go-ug.digital/. You can access the website using an internet enabled computer or mobile phone.

We encourage you to present your work to your class teacher when schools resume so that your teacher is able to know what you learned during the time you have been away from school. This will form part of your assessment. Your teacher will also assess the assignments you will have done and do corrections where you might not have done it right.

The content has been developed with full awareness of the home learning environment without direct supervision of the teacher. The methods, examples and activities used in the materials have been carefully selected to facilitate continuity of learning.

You are therefore in charge of your own learning. You need to give yourself favourable time for learning. This material can as well be used beyond the home-study situation. Keep it for reference anytime.

Develop your learning timetable to ca ter for continuity of learning and other responsibilities given to you at home.

Enjoy learning



PHYSICAL CHEMISTRY

LESSON 1 THE STRUCTURE FUNCTIONING OF THE MASS SPECTOMETER

LEARNING OBJECTIVE:

By the end of this section you be able to;

- 1. State what a mass spectrometer is
- 2. Draw a labelled diagram of the mass spectrometer
- 3. Describe how the mass spectrometer works

Key Terms:

Spectrum pattern; of a sample is a pattern representing the distribution of ions by mass (more correctly: mass-to-charge ratio) in a sample.

Mass/charge ratio: the mass-to-charge ratio of an ion is a physical quantity used to identify isotopic or molecular ions produced in the mass spectrum. They are used find the molecular weight of the sample.

INTRODUCTION

At this level you are already aware that matter is made of entities/units that are particles in nature. Particles of matter can be atoms, molecule or ions. Individual particles are too small to be seen. A single particle of matter is more than 100,000 times smaller than the width of the human hair. Every form of matter has its own particles, having a particular mass. Despite their small size the mass of particles of matter can be determined using an instrument called the mass spectrometer. The sample of matter must first be broken down into free gaseous particles before introducing it into the mass spectrometer. In this lesson you are going to learn about mass spectrometer and it's in determining mass of particles.

KEY INQUIRY QUESTION;

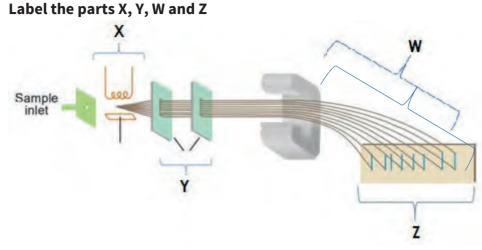
Why do you think equal volumes of different substances have will always have different masses/weight?

Activity 1 To find out about the stages through which the particle pass in mass spectrometer.

1. Carefully read the information in the table below. It contains information about the main parts of the mass spectrometer the function of the part. The order in which the parts are placed in the table does not represent the correct stages/steps through are acted on in the mass spectrometer.

PART OF THE MASS	FUCTION
SPECTROMETER	
A computerized,	This can be used to identify the particles (atoms or
electrical	molecules) in the original sample. It records in a
detector/Recorder	spectrum pattern how many ions arrive for each mass/charge.
	NB: In early spectrometers photographic ddetectors
	were used instead, producing a chart of peaked
	lines called a mass spectrograph. In modern
	spectrometers, you slowly vary the magnetic field
	so each separate ion beam hits the detector in turn.
Ionisation Chamber	The gaseous particles of the sample whose masses
	are being determined are hit/bombarded with a
	beam of high-speed electrons. The high-speed
	electrons cause the particles (atoms or molecules)
	turn into ions. This is because the high-electron
	knock out electron from the particle of the sample
	to form positive ions. This process is
	called ionization. For a particle represented by the
	symbol X the ionization equation is written as;
Definition Chambridge	X(g) + e → X(g) + 2e
Deflection Chamber	The accelated beam bean of ionized are directed
	into a magnetic field (the invisible, magnetically
	active region between the poles of a magnet). When this moving beam of particles having positive
	5 . 5.
	electric charge enter a magnetic field, they <i>bend</i> into an arc. The degree/extent of bending
	depends on the on mass and charge on the ion. The
	lighter particles (and more positively charged ones)
	bending more than heavier ones. In this region the
	ions formed from the sample split into a spectrum.
	This means each different type of ion bent to a
	different degree according to its mass and its
	electrical charge (mass/charge ratio).
Acceleration chamber	The ions formed from the gaseous move into a
	powerful electric field. This region has two metal
	plates charged to high voltages which ions to
	accelerate or gain some speed/velocity.

- 2. Re-write the names of the parts and their functions in the correct order in which samples are acted upon in the mass spectrometer. Number them in their respective order/stages from 1 to the last (4)
- 3. Diagram in figure below is a sketch of the cross section through the mass spectrometer



Conclusion/Comment

From the activity you have carried out, make a conclusion by filling in the spaces below;

The mass spectrometer is an instrument used for determining...... of matter.

Before the sample the sample of matter is	s introduced into mass spectrometer it must
be	The mass spectrometer is made up
Parts. These parts are;	
••••••	••••••

Summary

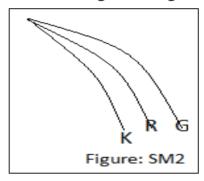
The mass spectrometer is an evacuated/vacuum tube

In the mass spectrometer the vaporized sample undergoes the following important stages/steps

- 1. It is bombarded by a stream of highspeed electrons and ionized to form positive ions
 - Note; Particles with large molecular size, containing many atoms will be fragmented/broken into different sizes of molecular ions whose results may be reliable
- 2. The positive ions are accelerated so that they gain a certain velocity a d move in form of a beam of positive ions into the magnetic field.
- 3. In the magnetic field the ions are deflected according to charge/mass ratio.
- 4. On the detector, ions with same charge-mass ratio are detected and recorded on a particular position at mass scale unit. For a particular element the ions resulting from the different isotopes are recorded as relative or percentage abundance/frequencies.

Revision questions

- 1. Explain why the region having the region of the mass spectrometer having the magnetic field is curved into an arc
- 2. Why do you think the mass spectrum cannot be suitable to determine mass of particles of the following substances?
 - a) Substances with very high boiling and sublimation points
 - b) Organic substances with large molecules like proteins, carbohydrate.
- 3. An element has three isotopes as; isotope-51, Isotope-49 and Isotope-54. The vapor of the element was passed through the mass spectrometer, the path produced is represented in the diagram in Figure SM2 below



- a) Identify the paths K, R and G in relation to each of the isotopes
- b) Give reason for your answer in (a) above

LESSON 2 INTERPRETING THE MASS SPECTRUM

LEARNING OBJECTIVE:

By the end of this section you be able to;

- 1 Interpret data in the mass spectrometer
- 2 Use data in the mass spectrum to determine relative atomic/molecular masses and carry out calculations

Key Terms:

Relative abundance/frequency

INTRODUCTION

You are already aware that in the mass spectrometer, the different ions are separated according to their masses. The number of ions represented by each of the masses are counted or compared and represented as a fraction of the total or percentage. This fraction or percentage is known as relative frequency or abundance or intensity. I can be given in figures or in graphical form. In this ln this activity you will learn how to interpret result produced in the mass spectrum and use it compute the relative atomic mass

Activity 2 To find out about the stages through which the particle pass in mass spectrometer.

Read the information below. It's a brief outline of the results obtained when chlorine was analysed in the mass spectrometer

The total number of isotopic ions produced were 992

248 ions of this total (992) were Isotopes recorded at position of mass unit 37.

The rest of the ions; 744 in number were recorded at mass scale unit 35 **Summary:**

Mass of Isotope	Number of Isotopes recorded						
35	744						
37	248						
Total number of ions: 744	+ 248 = 992						

- 2. Express the number of each of each isotope as; fraction, decimal number and percentage. In each case compute the sum of the terms you have expressed for all the Isotopes.
 - a) Summarise your working in the table below

Terms of Expression	Isotope 35	Isotope 37	Sum
Fraction			
Decimal number			
Percentage			

b) Use the decimal numbers or percentages representing the frequencies of the different isotopes to sketch graphical outline of relative frequencies'

<u>NB:</u> The values you have obtained in the table are relative/percentage frequencies/abundance/intensities

3 Using the hint given below and the results from your table above, calculate the relative atomic mass of chlorine.

<u>Hint:</u> Relative atomic mass of elements that have isotopes is calculated as the average of the masses of all the isotopes.

The sum of all the values for the expression:

Mass of Isotope x Relative/percentage frequency

Relative atomic mass = \sum Mass of Isotope x Relative/percentage frequency.

Conclusion/Comment

The data/information produced on the recorder of the mass spectrometer is called a mass spectrum.

When an element is analysed	, the mass spectrum gives info	rmation about
and	all the different	present
in the element. This informat	tion is then used to calculate th	ne relative atomic mass of
the element		

Revision questions

1. The table shows the mass numbers and the percentage abundance of an element Q.

MASS	PERCENTAGE
	ABUNDANCE
54	5.84
56	91.68
57	2. 17
58	.31

Calculate the relative atomic mass of Q

- 2. Copper has a relative atomic mass of 63.55 and consists of two isotopes of mass number 63 and 65. Calculate the percentage composition of the isotopes.
 - 3. The mass spectrum of chlorine shows peaks at masses 70, 72, and 74. the heights of the peaks are in ratio of 9:6:1

Calculate: a) The average atomic mass of chlorine

b) The relative abundance of 35Cl and 37Cl. (3 marks)

LESSON 3 INTRODUCTION TO MOLE AND HOW ITS RELATED TO FORMULA

LEARNING OBJECTIVE:

By the end of this section you be able to;

- 1. Explain the term mole as unit of measurement in relation to Avogadro number.
- 2. Calculate molar masses
- 3. Apply conversion factors in calculations

Key Terms:

Relative atomic or molecular mass

Molar Mass

Moles

Pre-requisite knowledge

- Avogadro number
- Formula

INTRODUCTION

In your last lesson you learnt how mass of a particle (atoms, molecules, ions) of mater can be determined using a mass spectrometer. There was little emphasis put on the unit for measurement of mass of an atom or molecule using the scale of mass spectrometer. This was partly because an atom or molecule is very minute.

Therefore, the unit of measurement of mass used in the mass spectrum is far smaller than micro levels of ordinary/common units of measurements such as grams. On the mass spectrum the smallest and lightest atom has a mass of 1 (unit.) You can refer to this unit as relative atomic mass unit (amu). This is could be taken as basic unit for the mass spectrum. The mass a hydrogen atom in grams is $1.66 \times 10^{-22} \, \text{g}$. You may then ask yourself; if mass of a hydrogen atom from mass spectrum is 1amu ($1.66 \times 10^{-22} \, \text{g}$) how many hydrogen atoms are there in 1g of hydrogen atom? In this section you are going to find out about the relationship between relative atomic mass, molar mass, moles, Avogadro Constant N_A

Activity 1 Part A: To find out how molar mass, relative atomic mass, Avogadro's constant are related.

In this activity you will be asked to carry out some numerical computation. The results from the numerical computation will help you in making decisions or conclusion at the end of the activities. You can use the following hint to guide you in the calculations

Hint

- 1. Relative atomic mass (rmm) of an element refers to the mass of a single atom. It has no unit. In this case relative atomic mass of any other element is a measure of number of times its atom is heavier than a hydrogen atom.
- 2. Mass of a single atom in gram of any element is given by the expression;

Mass in g of Single atom in g = Mass of H-atom in g x Relative atomic mass (rmm) of the atom

- Mass of a hydrogen atom in grams is 1.66 x 10 -22 g
- Relative atomic mass of an element is a measure of number of times its atom is heavier than a hydrogen atom
- 3. Molar mass is the mass of one mole of particles(atoms). It has units in grams. It is numerically equal to relative atomic mass.

Materials you will need

- Calculator
- Periodic Table

1.	Copy	the	table	M1	given	below
- •	COPY	CIIC	tabte	1417	SIVCII	DCION

		ıss(rmm)	n grams	Mass in g of Single at atom in g x Relative (rmm) of the atom	tom in g = Mass of H- molecular mass	Number atoms present in molar mass (N _A) $NA = \frac{Molar\ mas}{Mass\ atoms\ in\ g}$			
	Element	Relative atomic mass(rmm)	(rmm) of the atom Calculation Calculation Calculation Answer/Res		Answer/Result	Calculation Answer/			
1	Carbon	14	14	(1.66 x 10 ⁻²² X 14)g	= (2.324 x 10 ⁻²³) g	$\left(\frac{14}{2.324 \times 10^{-23}}\right)$	= 6.02 x 10 ²³		
2						Z.SZ 1 X 10			
3									
4									
5									
6									
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9									
10									
11									
12									
13									
14									
15			1						

- 2. With the help of a Periodic Table, fill the names elements of your choice, their respective relative atomic and numerically same values in grams for molar mass.
- 3. Carry out calculation to fill the remaining spaces in the table.
- 4. Describe your finding from the calculation about the number particles in one mole of an element
- 5. Write a statement that defines one mole of a substance in terms of number of particles

Activity 1 Part B: How to calculate relative atomic mass, molar mass and moles
In this activity you will learn about relative molecular/relative formula mass and
how to use it to calculate moles of a substance

1. (i)Carefully read the information given brief text and the illustrative calculation attached to the text.

"A molecule is a particle that contains two or more atoms chemically combined together. The mass of a molecule is known as its relative atomic mass. If the atoms combined together are the same, then it's a molecule of an element; (examples include O_2 , H_2 , N_2 , Cl_2). If the atoms are different then it's a molecule of a compound

(H₂O, CO₂, Na₂O₃). Molecules are represented by the formula of the compound or polyatomic element. Relative molecular mass can be computed from the relative formula mass. Relative formula mass is the sum of the relative atomic masses of all the atoms in represented in the formula. The molar mass of compound or element has unit in gram and is numerically equivalent to relative molecular/formula mass. Molar mass of a compound is the mass of one mole of the compound and contains Avogadro number of molecules. Therefore, moles of a substance in any given mass is the ratio in grams of the substance to the molar mass of the substance. The mathematical expression for moles is given as;

$$Moles = \frac{\textit{Mass in grams}}{\textit{Molar mass}} "$$

Illustration: To find relative formula mass, percentage composition, molar mass of sulphuric acid (H_2SO_4) and moles of 4.9 g of sulphuric acid

➤ Finding relative atomic mass and molar mass Formula of sulphuric acid; H₂SO₄

Relative atomic masses of the atoms in H_2SO_4 : H = 1, S = 32, O = 16

Number of each atom in the formula H₂SO₄, and their resulting relative mass:

2 atoms of Hydrogen resulting relative mass = 2 x 1= 2

1 atom of sulphur resulting relative mass = 1 x 32= 32

4 atoms of oxygen resulting relative mass = 4 x 6 = 64

Sum of relative masses (hence relative molecular/formula mass) = 2 + 32 + 64 = 98

Molar mass (mass of one mole) of sulphuric acid (with formula; H₂SO₄) is 98g

Finding moles of sulphuric acid in 4.9g

The percentage of each element in a compound is given by the expression;

Percentage composition =
$$(\frac{Sum\ of\ relative\ atomic\ masses\ of\ the\ element}{Relative\ molecular\ mass\ of\ the\ compound}\ x\ 100)\%$$

Therefore; - Percentage of hydrogen in sulphuric acid = $(\frac{2}{98} \times 100)$ %

Percentage of Sulphur in sulphuric acid = $(\frac{32}{98} \times 100)$ %

Percentage of Oxygen in sulphuric acid = $(\frac{64}{98} \times 100)$ %

➤ Finding moles of sulphuric acid in 4.9g Molar mass of sulphuric acid (H₂SO₄) is 98g

98g of sulphuric acid contains has 1 mole

1g of sulphuric acid contains has $(\frac{1}{98})$ moles,

4.9g of sulphuric acid contains has ($\frac{1}{98}$ x 4.9) moles,

Which is equal to 0.05 moles

Conclusion/Comments

The mole is a concept used for measurement amounts of matter. One mole as a unit of

measurement contains...... Particles. The mass of a single atom is known as

..... of the atom. Mass of one mole of atoms is known as the of the atom of the element. The relative atomic mass and molar mass are similar in, but differ in that

Evaluation

- 1. Find:
 - a) Number of carbon atoms in 6 grams of carbon rod (C=12).
 - b) Mass of 1.505 x 10^{23} atoms of Sulphur (S=32)
 - c) (i) molecules of chlorine (ii) atoms atoms of chlorine 3.55 g of gaseous chlorine; Cl₂? (35.5)
- 2. Find the moles of the following
 - a) 5.3g of anhydrous sodium carbonate; Na₂CO₃ (Na = 23, C = 12, O = 16)
 - b) 15g of Aluminium sulphate; $(Al)_2(SO_4)_3$ (Al = 27, S= 32. O = 16)
- 3. a) How many moles of Sulphur dioxide molecules are present in 16 g of Sulphur dioxide, SO₂?
 - b) What mass of magnesium (Mg = 24) would contain the same number of atoms as 4 g of carbon.
- c) Calculate the mole of each element present in 18.4 g of iron (III) sulphate.
- 4. Calculate the percentage;
 - a) composition by mass of magnesium oxide, (Mg = 24, O = 16).
 - b) of water of crystallization in hydrated sodium carbonate, $Na_2CO_3.10H_2O.$

LESSON 4 CONCENTRATION OF SOLUTION

LEARNING OBJECTIVE:

By the end of this section you be able to;

- 1. Explain the concept of concentration in terms of amount of substance dissolved in a solvent
- 2. Interpret the meaning of percentage composition by volume (v/v) and percentage composition by mass (m/m)
- 3. Carry out calculations involving concentration.

Pre-requisite Knowledge

- Relative atomic mass
- Molar mass

Key Terms:

- Concentration
- Molarity

INTRODUCTION

In this lesson you learn how to apply the knowledge you gained about moles in measuring amount of solute in a given solution. The amount of solute in per unit amount of solution is called concentration (How much solute is present in one unit of the solute).

Mathematically concentration can be expressed as the ratio of amount of solute to amount of solution. Concentration can be expressed in many terms depending on units used to measure amount solute and amount of solution. In this lesson you going to find out about some the terms used to express concentration

Activity: To find out how to express the concentration of solutions of salt dissolved in water

Materials you will need

- Calculator
- Periodic Table
- Common Salt
- Clean water
- Small weighing scale or small spoon
- cups
- Stirrer
- Any container you can use to estimate volume'

Steps

- 1. Weigh any three different portions of salt (for example 20g, 40g and 60g.)
 You can estimate the masses/weight of the salts arbitrarily using a small spoon
- 2. Measure equal volume of water (for example 500ml/half a litre into the separate cups. Label them as cup A, cup B and cup C.

- 3. Add one of the portions into one, another portion into the next cup and the third portion into the third cup. Stir each of the mixtures until the salts dissolve into a uniform solution. Taste each of the solution and describe the difference. This is how difference in concentration feels.
- 4. Carry out the following calculations on the solution in each cup.
 - (i) Find the amount of salt in grams present in one centimeter cubed in each cup and give the units

Hint: You use the methods below:

```
Mass of salt in 1 \text{cm}^3 = \left(\frac{Mass \ in \ grams}{Volume \ in \ cm^3}\right)
```

OR (Use first principle)

500 cm³ of solution dissolved 30g,

1 cm³ of solution dissolved

- (ii) Change the masses salt dissolve into moles and find the amount of salt in moles present in one centimeter cubed. Give the units (Na= 23, Cl=35.5)
- (iii) Convert the volume of solution into decimeters cubed/litres and find the amount of salt in grams present in one decimeter cubed/litres. Give the units
- (iv) Find the amount of salt in moles present in one decimeter cubed/litre. Give the units. This concentration on moles per decimeter cubed or per litre is also known as MOLARITY. The unit for molarity molar and abbreviated as M. Compare the values of the molarity with strength of taste you felt for each solution.
- (v) Given the density of solution is 1gcm⁻³, Convert the volume of solution into kilograms and find the amount of salt in moles present in one kilogram of solution. Give the units

Conclusion/Comments

Concentration of a solution is a measure amount of solute present in a solution.

Concentration can be expressed in various terms depending on the units used to measure

amount of solute and amount of solution. One of the terms used to express concentration is Molarity. Molarity is a term used to express concentration when the amount of the

solute is measured in, ant that of the solution is measure	d in
, The unit for molarity is	abbreviated as

Evaluation

- 1. Calculate the molarities of
 - a) 7g of potassium hydroxide KOH, in 250cm³ solution
 - b) 9.8g of sulphuric acid in 2 dm³ of solution
 - c) of 21.2 g of sodium carbonate dissolved in 10 litres of solution (Na=23, C=12,
- 2. Find the mass of

- (a) sodium sulphate, in 100cm³ of 2 M solution.
- (b) potassium carbonate, K₂CO₃ in 50cm³ of 0.2 M solution
- 3. Calculate the concentration in grams per litre;
 - a) of 0.02 moles of nitric acid dissolved in 200 cm³ of solution
 - b) of 0.005 moles of sodium carbonate dissolved in 25 cm³ of solution

INORGANIC CHEMISTRY

SENIOR FIVE SELF STUDY MATERIAL

TOPIC ONE: PERIODIC TABLE

Lesson 1.1: The third short period of the Periodic Table

Learning Outcomes: By the end of this lesson, you should be able to:

- (a) State the elements in the short period of the Periodic Table.
- (b) Plot graphs and explain the following observed trends as you go across the period;
 - Atomic number and nuclear charge
 - Valence electrons
 - Atomic radius
 - First ionisation energy

Introduction

- The original form of the Periodic Table was first put forward by Mendeleev in 1869 when he arranged the known elements in the order of their relative atomic masses.
- The horizontal rows of the Periodic Table are called periods. Period 3, or the third period, refers to the third row from the top of the Periodic Table.
- There are only 2 gaseous elements in period 3; chlorine and argon. These are definitely non-metals since metals do not exist as gases at room temperature and pressure. We cannot classify any of the other elements as metals or non-metals based on their state at room temperature and pressure because both metals and non-metals can exist as solids.
- Elements in period 3 of the Periodic Table show variation across the period in regard to their atomic number, nuclear charge, atomic radii, electronegativity, first ionisation energy, melting and boiling points, and metallic lustre.

Materials you need:

Periodic Table, pen, and book/paper.

Activity 1.1 Identifying the elements in period 3 of the Periodic Table.

In this activity, you will Write the electronic configuration of the elements you have identified I the Periodic Table.

IA 1 H 1.00794	IIA											IIIA	IVA	VA	VIA	VIIA 1 H 1.09794	VIIIA 2 He 4.002602
3 Li 6941	4 Be 9.012182											5 B 10.811	6 C 12.00+7	7 N 14.04674	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
11 Na 22.989770	12 Mg 24.3059	ШВ	IVB	VB	VIB	VIIB		VIIIB		IB	IIB	13 A1 26.981538	14 Si 28.0855	15 P 30.973761	16 S 32,066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.5961	25 Mn 54.938049	26 Fe 55.845	27 Co 58.933200	28 Ni 51.6934	29 Cu 63.546	30 Zn 65.39	31 Ga 69.725	32 Ge 72.61	33 As 74.92160	34 Se 78.96	35 Br 79.904	36 Kr 85.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr *1.224	41 Nb 92.90638	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126,90447	54 Xe 131.29
55 Cs 132.90545	56 Ba 137.327	57 La* 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.96655	80 Hg 200.59	81 Tl 204.3833	82 Pb 267.2	83 Bi 208.98098	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac** (227)	104 Rf (251)	105 Db (282)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Ds (269)	111 Uuu (272)	112 Uub (277)		114 Uug (289) (287)		116 Uuh (289)		118 Uuo (295)
	* Lant serie	hanide s	58 Ce 140.116	59 Pr 140.90765	60 Nd 14424	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 16250	67 Ho 164.93092	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04	71 Lu 174.967	
	** Acti seri	inide es	90 Th 232.0381	91 Pa 231,03588	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (263)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)	

Activity 1.2: Analysing the variation of melting and boiling point across period 3 elements in the Periodic Table.

Procedure:

2. The table below gives the melting point and boiling point of period 3 elements. Let's see if we can classify each of the elements of period 3 as either a metal or a non-metal as well:

Name of Element and (Symbol)	Sodiu m (Na)	Magne sium (Mg)	Alumi nium (Al)	Silicon (Si)	Phosp horus (P)	Sulph ur (S)	Chlori ne (Cl)	Argon (Ar)
Melting Point (°C)	98	639	660	1410	44	113	-101	-189
Boiling Point (°C)	883	1090	2467	2680	280	445	-35	-186

- 3. (i) Describe the trend in boiling and melting point across period 3 elements.
 - (ii) Plot a graph to represent the above data
- 4. Explain the shape of your graph.

Hint on graph work. A good chemistry graph should have, title (heading), good scale, axis correctly labelled, correctly plotted points and a line or curve.

Discussion

Name of Element (Symbol)	Sodiu m (Na)	Magne sium (Mg)	Alumi nium (Al)	Silicon (Si)	Phosp horus (P)	Sulph ur (S)	Chlori ne (Cl)	Argon (Ar)
Melting Point (°C)	98	639	660	1410	44	113	-101	-189
Boiling Point (°C)	883	1090	2467	2680	280	445	-35	-186
Trend:	higher			highes t	lower			

Conclusion or Summary.

The following general trends are observed as you go across period 3 from left to right:

- Atomic number, and therefore charge on the nucleus (nuclear or core charge) increases
- Number of valence electrons increases
- Atomic radius decreases
- First ionisation energy increases
- electronegativity increases (excluding argon)
- elements on the left are metals, elements on the right are non-metals⊗
- melting points change from high to low
- boiling points change from high to low
- electrical and heat conductors on the left to insulators on the right
- metallic lustre on the left to dull on the right
- colour changes from grey on the left to coloured on the right

Follow up activity.

- a) Research on the trend in the following physical properties across the period and down the group in the Periodic Table?
 - i) atomic radius
 - ii) ionization energy
 - iii) electronegativity
 - iv) melting and boiling points
- b) State and explains the factors that affect the values of atomic radius, ionization energy, electronegativity.

TOPIC 2: CHEMISTRY OF GOURP II ELEMENTS IN THE PERIODIC TABLE

Lesson 1.3 Physical properties of group II elements in the Periodic Table.

Lesson Outcome; by the end of the lesson a learner should be able to identify the elements in group II and describe the trend in physical properties down the group.

Introduction: In this lesson we shall identify the elements in group II of the Periodic Table and learn about the trend in physical properties down the group.

Inquiry question: How does the physical property such as ionization energy, atomic radius, melting point, density, vary down group II elements?

Materials needed; Periodic Table, pen graph paper, book.

Activity.1. Studying the Periodic Table

- i) Identify the elements in group II of the Periodic Table and state their atomic number.
- ii) Write the electronic configuration of each of the elements.
- iii) Deduce the electronic structure of the elements in group II of the Periodic Table.

Activity 2. Study the trend in physical property of group II elements in the table below

Table 2. Group II elements.

Element	Ве	Mg	Ca	Sr	Ва
Ist I.E (KJmol-1)	900	740	590	550	500
2 nd I.E(KJmol ⁻¹)	1800	1460	1150	1060	970
Atomic radius(nm)	0.11	0.16	0.20	0.21	0.22
Melting point (°C)	1280	650	838	768	714
Density(gm ⁻³)	1.86	1.74	1.55	2.60	3.50

- a) State the trend in the following physical properties
 - i) ionization energy
 - ii) atomic radius
 - iii) melting point
 - iv) density.
- b) Explain the trends stated in (i) above.

Recap.

The following general trends are observed as you go across period 3 from left to right:

- Atomic number, and therefore charge on the nucleus (nuclear or core charge) increases
- Number of valence electrons increases
- Atomic radius decreases

- First ionization energy increases
- electronegativity increases (excluding argon)
- elements on the left are metals, elements on the right are non-metal
- melting points change from high to low
- boiling points change from high to low
- electrical and heat conductors on the left to insulators on the right
- metallic lustre on the left to dull on the right
- colour changes from grey on the left to coloured on the right

TOPIC. CHEMICAL REACTIONS OF GROUP I and II ELEMENTS.

Lesson 1.3. Comparing Chemical Properties Of Group I And II Elements

Learning Outcome: By the end of this lesson a learner should be able to compare the chemical properties of group I and II elements.

Introduction: The elements in this block have their valence electrons placed in the Sorbital. The outer most configurations are: Group I (Alkali metals) -nS¹, group II (Alkaline earth metals)-nS² where n is principal quantum number.

Inquiry question. Compare the physical and chemical properties of group I and II elements.

Activity1. From the Periodic Table, identify the elements in group I and II and write the electronic configuration of each of the elements.

2. Discuss the chemical properties of group I and II elements.

Discussion. Reaction with,

(a). Hydrogen

The hot metals react with dry hydrogen gas to form ionic hydrides i.e.

$$2Na (s) + H2 (g) \longrightarrow 2 NaH (s)$$

$$Mg (s) + H2 (g) \longrightarrow MgH2 (s)$$

(b). Water

All the elements except Beryllium react with water with increasing vigour down the group to liberate hydrogen gas.

Reactivity of group (II) elements with water increases down the group as atomic radius increases due to increase of Electro positivity.

Magnesium reacts slowly with cold water but vigorously with steam

$$Mg(s) + H2O(g)$$
 MgO(s) + $H2(g)$

Calcium, Barium Strontium reacts readily with water to form the hydroxide and hydrogen gas.

$$M(s) + 2 H2O(l)$$
 \longrightarrow $M(OH)2 (aq) + H2 (g)$

Where M= Ca, Ba and Sr.

All group I elements readily react with cold water to form strong alkaline solution e.g.

$$2K(s) + 2H_2O(l) \longrightarrow 2KOH(aq) + H_2(g)$$

(C). Acids

Group I elements react violently with dilute mineral acids to form salt and hydrogen gas.

$$2M(s) + 2H^{+}(aq) \rightarrow M^{+}(aq) + H_{2}(g)$$

Group II elements react but the reaction becomes more vigorous down the group except with dilute sulphuric acid. e.g.

Mg (s) + 2 H⁺(aq)
$$\rightarrow$$
 Mg²⁺ (aq) + H₂ (g)

Calcium, Strontium and Barium react slowly with dilute sulphuric acid due to formation of sparingly soluble salt which prevent further reaction e.g.

Ba (s)
$$+ H_2SO_4$$
 (aq) \longrightarrow BaSO₄ (s) $+ H_2$ (g)

Magnesium, Calcium and Barium react with very dilute nitric acid to liberate hydrogen gas e.g.

$$Mg(s) + 2HNO_3(aq) \longrightarrow Mg(NO_3)_2(aq) + H_2(g)$$

Question. Compare the reaction of beryllium and barium with sulphuric acid

(d). Oxygen

Group II elements form normal oxides .i.e.

$$2M(s) + O_2(g) \longrightarrow 2MO(s)$$

However barium and Strontium can form peroxides when the normal oxide is heated in more oxygen .e.g.

Group I elements burn in excess oxygen to form variable oxides .i.e.

Lithium forms only a normal oxide .i.e

$$4 \text{ Li (s)} + O_2 (g)$$
 2 Li₂O (s)

Sodium forms a yellow normal peroxide .i.e.

$$2Na(s) + O_2(g) \rightarrow Na_2O_2(s)$$

Potassium, Caesium and Rubidium form super oxides when burnt in excess in oxygen e.g.

$$K(s) + O_2(g) \longrightarrow KO_2(s)$$

All the oxides are basic except beryllium oxide which is amphoteric .i.e.

BeO(s) + 2 H⁺ (aq)
$$\rightarrow$$
 Be²⁺ (aq) + H₂O (l)

The peroxides form hydroxides and hydrogen peroxides when dissolved in water

$$Na_2O_2(s) + 2 H_2O(l)$$
 \longrightarrow $2NaOH(aq) + H_2O_2(aq)$

The super oxides liberate oxygen gas, hydrogen peroxide and the hydroxide when dissolved in water.

$$2KO_2(s) + 2H_2O(l)$$
 \longrightarrow $2KOH(aq) + O_2(g) + H_2O_2(aq)$

Question. (a) Be, Mg, Ca and Ba belong to group II of the Periodic Table. Describe the reactions of the elements with;

- (i) Water
- (ii) Air
- (b) Explain why Lithium doesn't form peroxide or superoxide when burn in oxygen.
- (c) State what is observed when potassium super oxide is dropped in water. Write the equation of reaction.
- (e). Chlorine (Halogens)

The hot metals directly combine with chlorine to form ionic halides except beryllium i.e.

$$Ca(s) + Cl_2(g)$$
 \longrightarrow $CaCl_2(s)$

The anhydrous chlorides are ionic except beryllium chloride which is covalent

NOTE: Beryllium behaves differently from the rest of the elements.

Follow up activity; Research on the qualitative analysis of group II cat ions i.e.Mg²⁺, Ca²⁺, Ba²⁺. In each case, state the reagent used and your observation. Write an equation for the reaction.

SELF STUDY MATERIAL 5

TOPIC. CHEMISTRY OF GROUP II ELEMENTS IN THE PERIODIC TABLE.

Lesson 5. Diagonal relationship between elements.

Learning outcome: By the end of the lesson a learners should be able to discuss the diagonal relationship among elements in the Periodic Table.

Introduction

Inquiry question. Define the term diagonal relationship?

Diagonal relationship is the similarity in chemical properties between elements in period two to their diagonal neighbours in period three and adjacent groups.

The pairs of elements with similarity in chemical properties include:

- Lithium and Magnesium
- Beryllium and Aluminum
- Boron and Silicon

The similarity in chemical properties is due to following reasons:

- Similar polarizing power or charge density
- Similar electronegativity
- Similar electropositivity
- Similar electrode potential

Similarities in chemical properties include:

Li and Mg	Be and Al	B and Si
Both react with nitrogen on heating to form nitrides.	Oxides and hydroxides are amphoteric. Be(OH) ₂ (s) + 2OH ⁻ (aq) \longrightarrow Be(OH) ₄ ²⁻ (aq) Al(OH) ₃ (s) + OH ⁻ (aq) \longrightarrow Al(OH) ₄ ⁻ (aq)	Both form acidic oxide as B ₂ O ₃ and SiO ₂
Their hydrogen carbonates exist in solution	Both react with Conc. Sodium hydroxide solution to form a complex and hydrogen gas. Be(s)+2OH ⁻ (aq)+2H ₂ O(l) \longrightarrow Be(OH) ₄ ²⁻ (aq) + H ₂ (g) 2Al(s)+2OH ⁻ (aq)+6H ₂ O(l) \longrightarrow 2Al(OH) ₄ ⁻ (aq) + H ₂ (g)	Both form series of covalent hydrides.
Both form normal oxides when heated in oxygen (air)	Their chlorides and bromides are covalent and dimerize in vapour phase as Be ₂ Cl ₄ and Al ₂ Cl ₆ . 2AlCl ₃ (s) Al ₂ Cl ₆ (g)	Both form chlorides which hydrolyse readily.

Their hydroxides and carbonates are sparingly soluble in water	Both form ionic carbides which hydrolyse to form methane. Be ₂ C (s) + 4H ₂ O(l) \longrightarrow CH ₄ (g) + Be(OH) ₂ (aq) Al ₄ C ₃ (s) + 12H ₂ O(l) \longrightarrow 3CH ₄ (g) + 4Al(OH) ₃ (aq)	Form covalent compounds.
Carbonates, hydroxides, peroxide decompose on heating to give an oxide.	Both are rendered passive concentrated nitric acid.	Form borides and silicides with metals.
Nitrates decompose on heating to give an oxide, nitrogen dioxide and oxygen.	Both form fluoro complexes. e.g. BeF ₄ ² -	
Halides (except fluorides) and chlorates(VII) are soluble in organic solvent.		

Follow up activity

State three properties in which:

- (a) Lithium differs from the rest of group I elements.
- (b) Beryllium differs from the rest of group II elements.
- (c) Boron differs from the rest of group III elements.
- (d) Beryllium resembles other elements in groupie of the Periodic Table

TOPIC: THE CHEMISTRY OF GROUP IV ELEMENTS.

Lesson 5.1. Physical properties of group IV elements.

Learning Outcome: At the end of the lesson, a learner should be able to discuss the trend in physical properties of group IV elements.

Introduction; The elements in group IV of the Periodic Table include, Carbon, Silicon, Germanium, Tin, and Lead. Write their electronic configuration. The outer most electronic configuration is nS²nP²where n is the principal quantum numbers.

Inquiry question; How do these elements exist?

Prediction. Carbon exists as graphite, diamond and amorphous carbon. Silicon occurs as Silica (SiO₂). Tin exist as grey tin and white tin. Lead occurs as a ore in form of galena (PbS)

Activity 1. Table below shows the variation of melting point and density among group IV elements in the Periodic Table. Study it carefully and answer the given questions.

Elements	Melting point (°C)	Density	
Carbon	4000	2.25 (graphite), 3.5(Diamond)	
Silicon	1680	2.33	
Germanium	1210	5.35	
Tin	505	7.28(white), 5.75(grey)	
Lead	600	11.3	

Discussions

Question. State and explain the trend in the melting and density of the elements in group IV.

The melting points of group IV elements depend on the structure. Carbon and Silicon have giant atomic structures which require a lot of energy to break. However the melting point of silicon is lower than that of carbon since the covalent bonds in silicon atoms are longer thus weaker.

Germanium is a Metalloid with an intermediate giant atomic structure.

Tin and Lead are weak metals with a metallic structure however lead is more metallic than tin hence has a higher melting point.

Other physical properties include,

Electropositivity. Increases down the group thus metallic character also increases.

Electronegativity, decreases down the group

Oxidation states, the elements exhibit both +2 and +4 oxidation states. The +4-oxidation state is attained by promoting one S- electron to an empty P orbital to avail four electrons.

Down the group, the nS² electrons become more reluctant to participate in bonding. This is called inert pair effect. Therefore, the stability of +2 oxidation state increases while that of +4 decreases.

Question: Explain the cause of inert pair effect

Solution: As the radius of the atoms increase down the group there is increasing tendency for the two bonding electrons in the S- Sub energy level to resist taking part in bonding.

Carbon behaves differently from the rest of the group members due:

- Small Atomic radius
- High electronegativity
- Lack of vacant orbital

Some of the properties in which Carbon differs from the rest of the members include:

- It forms stable multiple bonds with itself and with other non-metals.
- Carbon can form a number of hydrocarbons because it can catenate. Catenation is the ability of the element to form bonds between atoms of the same element.
- It forms gaseous oxides unlike other members
- The halides are stable to hydrolysis.

TOPIC: CHEMISTRY OF GROUP IV ELEMENTS

Lesson 5.2. Chemical properties of group IV elements.

Learning Outcome: By the end of the lesson a learner should be able to discuss the chemical properties of the group IV elements.

Discussion. Listen attentively to the conversation between Henry and Rose below

Rose: How do group IV elements react with Water?

Henry: When heated, coke reacts with steam to form water gas.

$$H_2O(g)$$
 + $C(s)$ \longrightarrow $CO(g)$ + $H_2(g)$

Ge and Sn do not react with water.

Hot silicon reacts with steam to form silicon dioxide and hydrogen gas I.e.

$$Si(s) + 2H_2O(g)$$
 \longrightarrow $SiO_2(s) + 2H_2(g)$

Lead reacts slowly with soft water in presence of air (oxygen) to form lead (II) hydroxide

2Pb (s) + 2
$$H_2O(l) + O_2(g)$$
 — Pb(OH)₂ (s)

Rose: What about reaction with Air?

Henry: The elements burn in air to form dioxides except lead which forms lead (II) oxide

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

$$Si(s) + O_2(g) \longrightarrow SiO_2(s)$$

However in limited amount of air, Carbon forms carbon monoxide

Rose: Now I know how to write the equations, and I can discuss the reactions with acids and alkalis.

Henry: I believe you can discuss them Rose.

Rose: The elements do not react with dilute acids except tin which reacts with dilute nitric acid as:

$$NO_3^-(aq) + 4 Sn(s) + 10 H^+(aq)$$
 \longrightarrow $4 Sn^{2+}(aq) + NH_4^+(aq) + 3 H_2O(l)$

Silicon reacts with only with hydrofluoric acid to form hexafluoro silicic acid and Hydrogen gas

Si (s) + 6 HF (aq)
$$\longrightarrow$$
 H₂SiF₆ (aq) + 2 H₂ (g)

Hot nitric acid oxidizes tin, germanium and Carbon to dioxide and itself reduced to oxides of nitrogen

$$3Sn(s) + 4HNO_3(aq) \longrightarrow 3SnO_2(s) + 4NO(g) + 2H_2O(l)$$

Lead forms lead (II) nitrate, nitrogen monoxide and water

3Pb (s) + 8HNO₃ (aq)
$$\longrightarrow$$
 3Pb (NO₃)₂ (aq) + 2NO (g) + 4H₂O (l)

Rose: With alkalis

All the elements except Carbon react with Conc. Alkali to form complex salts and hydrogen gas.i.e.

$$Si(s) + 2OH^{-}(aq) + H_2O(l)$$
 \longrightarrow $SiO_3^{2-}(aq) + 2H_2(g)$

Henry: Finally, they react with Non-metals.

When heated, the elements react with Sulphur, chlorine, fluorine and hydrogen chloride. e.g.

$$Sn(s) + 2HCl(g)$$
 \longrightarrow $SnCl_2(s) + H_2(g)$

Follow up activity.

Question1.(a). Discuss the chemical reactions of group IV elements with,

- (i) air
- (ii) water
- (iii) acids

- (iv) alkalis
- (b) In each case write a balanced equation for the reaction.

TOPIC: COMPOUNDS OF GROUP IV ELEMENTS.

Lesson 5.3 Physical properties of the compounds of group IV. These are the chlorides, Hydrides, and Oxides.

Learning Outcome;

By the end of this lesson, you should be able to describe the trend in physical properties of the chlorides, Hydrides, and Oxides.

Discussion. Group IV elements form different types of oxides. These include:

(a) Monoxides: CO and SiO are covalent compounds with simple molecular structure.

GeO, SnO and PbO are amphoteric oxides with giant ionic structure

Some of the reactions of the monoxide according to equations include:

With alkaline solution

PbO (s) +2 OH⁻ (aq) + H2O (l)
$$\longrightarrow$$
 Pb(OH)₄²⁻ (aq)
SnO (s) + 2OH⁻ (aq) + H₂O (l) \longrightarrow Sn (OH)₄²⁻ (aq)
CO (g) + NaOH (aq) $\xrightarrow{150^{\circ}\text{C}}$ HCOONa (aq)

With Acids

SnO (s) + 2 H⁺ (aq)
$$\longrightarrow$$
 Sn²⁺ (aq) + H₂O (l)

(b) Dioxides

Lead (IV) is prepared by reacting di lead (II) lead (IV) oxide with dilute nitric acid.

$$Pb_3O_4(s) + 4HNO_3(aq)$$
 \longrightarrow $2Pb(NO_3)_2(aq) + PbO_2(s) + 2H_2O(l)$

The dioxides are more stable than the monoxides except lead (IV) oxide. i.e.

$$2PbO_2(s)$$
 \longrightarrow $2PbO(s) + O_2(g)$

The table below shows the nature of the dioxides

Oxide	Nature	Structure
CO ₂	Acidic	Simple molecular
SiO ₂	Acidic	Giant molecular
GeO ₂	Amphoteric	Intermediate
SnO ₂	Amphoteric	Giant ionic and giant
PbO ₂	Amphoteric	Metallic

Lead (IV) oxide oxidizes strong hot concentrated hydrochloric acid to chlorine gas

$$PbO_2(s) + 4HCl(aq)$$
 \longrightarrow $Cl_2(g) + PbCl_2(s) + H_2O(l)$

When excess concentrated hydrochloric acid is reacted with lead (IV) oxide at 0°C it forms a complex ion

Addition of concentrated ammonium chloride to the complex produces a yellow precipitate. i.e.

2. Hydrides

The elements form covalent tetra hydrides whose thermo-stability decreases down the group.

3. Chlorides

(a) Tetrachlorides

These are covalent liquids with simple molecular structure and become less stable down the group due to an increase in M-Cl bond length

Research on: Preparation of the tetrachloride's of group (IV) elements.

Note. Lead (IV) chloride readily decomposes to form chlorine and lead (II) chloride

Question: Explain why Lead (IV) iodide does not exist.

Reactions of tetrachlorides with water

Carbon tetrachloride does not react with water because of lack of vacant d-orbital.

Other chlorides react with water rapidly to liberate hydrogen chloride. For silicon tetrachloride, the second product depends on the degree of hydration.

$$SiCl_4(l) + 2H_2O(l)$$
 \longrightarrow $SiO_2(s) + 4HCl(g)$

$$SnCl_4(s) + 4H_2O(l)$$
 \longrightarrow $SnO_2.2H_2O(s) + 4HCl(g)$

(b) Dichlorides

The stable chlorides in the +2 oxidation states are only formed by tin and lead

Sn (s)
$$+ 2HCl(g)$$
 \longrightarrow SnCl₂(s) $+ H2(g)$

Pb (s) +
$$Cl_2$$
 (g) Pb Cl_2 (s)

Tin (II) chloride reacts with water to form a basic chloride and hydrochloric acid. i.e. it undergoes hydrolysis

$$SnCl_2(s) + H_2O(l)$$
 \longrightarrow $Sn(OH)Cl(s) + HCl(aq)$

However, in excess hot water tin (II) hydroxide is formed.

$$SnCl_{2}(s) + 2H_{2}O(l)$$
 \longrightarrow $Sn(OH)_{2}(s) + 2HCl(aq)$

Lead (II) Chloride is sparingly soluble in water and does not undergo hydrolysis. However, it dissolves on heating since solubility increases with temperature.

$$PbCl_2(s)$$
 \longrightarrow $Pb^{2+}(aq) + 2Cl^{-}(aq)$

Note. Lead (II) chloride is more soluble in concentrated hydrochloric acid than in water due to formation of a soluble complex of tetrachloro plumbate (II)

$$PbCl_{2}(s) + 2Cl^{-}(aq)$$
 Pb $Cl_{4}^{2-}(aq)$

Note. A solution containing tin (II) ions and lead (II) ions react with hydrogen sulphide gas to precipitate the metal sulphide (black)

$$Sn^{2+}$$
 (aq) + S^{2-} (aq) \longrightarrow SnS (s)

$$Pb^{2+}(aq) S^{2-}(aq) \longrightarrow PbS(s)$$

ORGANIC CHEMISTRY

TOPIC 1: INTRODUCTION TO ORGANIC CHEMISTRY

Key Words

alkane isomerization alkene polymerization catalytic cracking reforming fractional residfining

distillation

Sources of carbon

The fractional distillation of crude oil

- Fractional distillation is one of several processes used to refine crude oil. Refining converts crude oil into a range of useful pro
- Crude oil is a complex mixture of hydrocarl During fractional distillation, this mixture is separated into a series of fractions (compo on the basis of boiling point.
- The crude oil is passed through a furnace, where it is heated to 400°C and turns most vapour. The gases pass into a distillation of within which there is a gradation of tempe The column is hottest at the bottom and co at the top.
- bubble cap

 gasoline (110°C)

 kerosine (180°C)

 diesel oil (260°C)

 heater

 crude oil

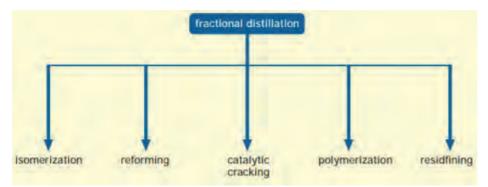
 gasoline and chemical feedstock
- Hydrocarbons with the highest boiling points are the first to condense at the bottom of the column, along with any remaining liquid residue from the crude oil. This fraction provides bitumen for use in road building.
- Rising up the column, other fractions condense out: first diesel oil, then kerosene, and finally gasoline. All of these fractions are used as fuels.
- The hydrocarbons with the lowest boiling points remain as gases and rise to the top of the column. This fraction is used as a fuel in the refinery.
- The hydrocarbon vapor moves up the column through a series of bubble caps. At each level, the hydrocarbon vapour passes through condensed hydrocarbon liquid. This helps to ensure a good

separation into the various fractions.

Crude oil composition

 Crude oil varies in composition, depending on where it was obtained. Fractional distillation of different crude oils provides different proportions of the various fractions.

Other refining processes



Other refining processes are used to modify the products of fractional distillation. These include isomerization, reforming, catalytic cracking, polymerization, and residfining.

Isomerization

Isomerization changes the shape of hydrocarbon molecules. For example, pentane is converted into 2- methlybutane.

$$\begin{array}{c} \operatorname{CH_3-CH_2-CH_2-CH_2-CH_3} \longrightarrow \operatorname{CH_3-CH_2-CH_2-CH_-CH_3} \\ \operatorname{CH_3} \\ \operatorname{pentane} \end{array}$$

Reforming

Reforming converts straight chain molecules into branched molecules in order to improve the efficiency of gasoline. One type of reaction involves the dehydration of saturated compounds to unsaturated compounds. Another involves the cyclization of hydrocarbons.

Dehydration

$$\begin{array}{c} \mathsf{CH_3} \\ \mathsf{CH} \\ \mathsf{CH} \\ \mathsf{CH_2} \\ \mathsf{CH_3} \\ \mathsf{CH_2} \\ \mathsf{CH_3} \\ \mathsf{CH_2} \\ \mathsf{CH_3} \\ \mathsf{CH_2} \\ \mathsf{CH_3} \\ \mathsf{CH_2} \\ \mathsf{CH_2} \\ \mathsf{CH_3} \\ \mathsf{CH_2} \\ \mathsf{CH_3} \\ \mathsf{CH_2} \\ \mathsf{CH_2} \\ \mathsf{CH_3} \\ \mathsf{CH_3} \\ \mathsf{CH_2} \\ \mathsf{CH_3} \\ \mathsf{CH_3} \\ \mathsf{CH_3} \\ \mathsf{CH_4} \\ \mathsf{CH_3} \\ \mathsf{CH_3} \\ \mathsf{CH_4} \\ \mathsf{CH_5} \\ \mathsf{C$$

Cyclization

$$\begin{array}{c} \text{CH}_3\\ \text{CH}_3\\ \text{CH}_2\\ \text{CH}$$

Catalytic cracking

In general, smaller hydrocarbon molecules, such as those in gasoline, are in greater demand than larger ones. Catalytic cracking redresses this balance by breaking (cracking) large alkane molecules into smaller alkane and alkene molecules.

Polymerization

Polymerization combines small molecules to form larger molecules that can be used to make various products.

Two propene molecules combine to form hexene
$$\begin{array}{c} \mathsf{CH_3CH=CH_2} + \mathsf{CH_3CH=CH_2} \to \mathsf{CH_3CH_2CH_2CH=CH_2} \\ \mathsf{propene} & \mathsf{propene} \end{array}$$

Residfining

residfining is the process used on the residue fraction to convert it into usable products. It also removes impurities that would damage the catalyst used in catalytic cracking.

Carbon chains

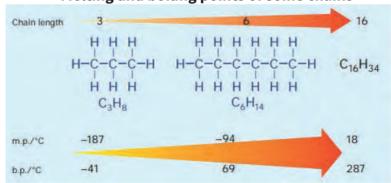
Catenation

Carbon has the ability to form long chains of carbon atoms in its compounds. This
is called catenation.

Melting and boiling points

Forces of attraction, called van der Waals forces, exist between molecules. As molecular size increases, there is more overlap between the molecules, and the intermolecular forces of attraction increase.

Melting and boiling points of some chains



• In order to melt and to boil, the forces of attraction between molecules must be overcome. The greater these forces, the more energy is needed. This is reflected in a steady increase in melting point and boiling point as molecules increase in size.

Types of bonds

 A carbon atom may form one, two, or bonds with another carbon atom in its compounds. These bonds are describe single bonds (C-C), double bonds (C=C), and triple bonds ($^{C}\equiv ^{C}$).

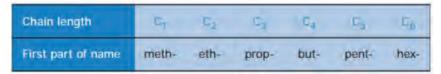
- Alkanes contain only carbon-carbon single bonds.
- Alkenes contain a carbon-carbon double bond.
- Alkynes contain a carbon-carbon triple bond.
- Alkanes, alkenes, and alkynes are all hydrocarbons since they consist only of hydrogen and carbon atoms.

Naming hydrocarbons

 The name of a hydrocarbon indicates the number of carbon atoms in the molecule and what sort of carbon-carbon bonds is present.

Chain length

• The first part of name is determined by the number of carbon atoms in the molecule. The same prefixes are used for all groups of organic compounds.



Functional group

- The second part of the name is determined by the type of carbon-carbon bonds present. Each functional group has a unique suffix.
- The position of the functional group in a carbon chain is identified by numbering the carbon atoms in the carbon chain.



Examples of compound names

- The first two examples in the diagram are alkanes. If there is one carbon atom in the molecule it is: "meth" (1 carbon atom in the chain) + "ane" (for alkane): methane. If there are four carbon atoms in the molecule it is: "but" (4 carbon atoms in the chain) + "ane" (for alkane): butane.
- The third example is propane, an alkene with three carbon atoms: "pro" (3 carbon atoms in the chain) + "ene" (for alkene).
- The fourth example is ethyne, an alkyne with a two-carbon chain: "eth" (2 carbon atoms in the chain) + "yne" (for alkyne).



ALKANES

The first six alkanes

- The alkanes form an homologous series of compounds that have the general formula C_nH_{2n+2}, where n is a positive integer. Each alkane molecule differs from the previous one in the series by -CH₂-.
- They have similar chemical properti and show a gradation of physical properties, such as melting point an boiling point, as the molecular size increases.
- Alkane molecules are attracted to electric other by van der Waals forces. As molecular size increases, there is more overlap between the molecules, and the intermolecular forces of attraction increase.
- Alkane molecules are frequently show as having a flat two-dimensional structure because this is easy to draw but in reality, the four bonds around each carbon atom are directed towar the corners of a tetrahedron. The ang between any two bonds is 109.5°.
- Alkanes are relatively unreactive substances when compared with oth groups of hydrocarbons. Their most important reaction is combustion, and they are the main constituent of range of fuels. Natural gas is largely composed of methane:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

In a good supply of air, hydrocarbons burn to give carbon dioxide and water. In a restricted supply of air, carbon monoxide and/or carbon may be formed:

$$C_2H_6 + 2O_2 \rightarrow CO + C + 3H_2O$$

Alkane	Methane	Ethano	Propane
Formula	CH ₄	C ₂ H ₆	C ₃ H ₈
Structural formula	H-C-H	H H H-C-C-H H H	H H H H-C-C-C-H H H H
Boiling point (°C)	-164	-87	-42
Physical state at room temperature	Gas	Gas	Gas
Molecular model	000	3	200

Alkane	Butane	Pentane	Hexane
Formula	C ₄ H ₁₀	C ₅ H ₁₂	C ₆ H ₁₄
Structural formula	H H H H H-C-C-C-C-H H H H H	H H H H H H-C-C-C-C-C-H	H H H H H H
Boiling point (°C)	0	36	69
Physical state at room temperature	Gas	Liquid	Liquid
Molecular model	33399	33000	3333

Alcohols and Organic Acids Alcohols

- A homologous series containing the -OH functional group: hydroxyl group (OH group is covalent. It is different from OH ions in bases).
- They have the general formula, C_nH_{2n+1}OH.
- Each member differs from the member before it by CH₂.
- Names of alcohol ends with -ol.
- Alcohols are soluble in water, colourless liquids and have low boiling points.
- As the number of carbon atoms \uparrow , boiling point \uparrow , but solubility in water \downarrow .
- Ethanol is the most common alcohol.

Homologous series

Activity

By doing your own research, provide the meaning of "homologous series". What are the characteristics of such a series? Illustrate your answer by using examples of alkanes, alcohols, carboxylic acids.

When members of a class of compounds having similar structures are arranged in order of increasing molecular mass, they are said to constitute a homologous series.

Each member of such a series is referred to as a "homologous" of its immediate neighbours. For example, the following sequence of straight chain of alcohols forms a homologous series.

CH₃-OH: Methyl alcohol

CH,-CH,-OH: Ethyl alcohol

CH₃-

CH,-CH,-CH,-OH: Butyl alcohol etc.

Characteristics of a homologous series

- 1. Any member of the series differs from the next by the unit -CH2(methylene group)
- 2. The series may be represented by a general formula of alcohols which is C_nH_{2n+1} OH where n =1,2,3, etc.
- 3. The chemical properties of the members of a homologous series are similar, though in some series the first members show different behaviour.
- 4. The physical properties such as density, melting point and boiling point generally, increase within the molecular mass.

Self - Check

- 1. Give a precise definition of "functional group".
- 2. Indicate the functional group in the following compounds:
- 3. a) CH₂=CH₂ b) CH₃-CH₂OH c) CH₃-COOH d) CH₃-CH₃ e) CH₂CH₂CH₂CH₃
- 4. Predict which one of the two compounds a) and e) in 2) has the higher boiling point and explain why

General rules of nomenclature of organic compounds according to IUPAC

Activity

By your own research, describe the rules that are applied to name the organic compounds. Your answers can be given as a form of a report.

The organic compounds are named by applying the rules set by the International Union of Pure and Applied Chemistry (IUPAC). The purpose of the IUPAC system of nomenclature is to establish an international standard of naming compounds to facilitate the common understanding.

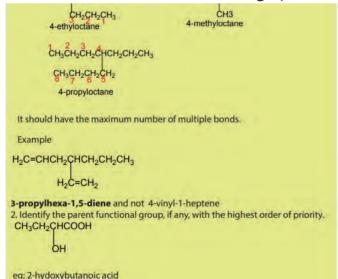
In general, an IUPAC name has three essential parts:

- A prefix that indicates the type and the position of the substituents on the main chain.
- The base or root that indicates a major chain or ring of carbon atoms found in the molecule's structure. e.g. Meth- for one carbon atom, eth- for 2 carbon atoms, prop- for 3 carbon atoms, hex- for six carbon atoms, etc.
- The suffix designates the functional group.
 Example -ane for alkanes, -ene for alkenes, -ol for alcohols, -oic acid for carboxylic acids and so on.

Steps followed for naming organic compounds:

1. Identify the parent hydrocarbon:

It should have the maximum length, or the longest chain



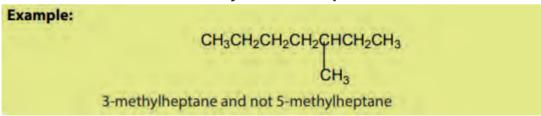
2. Identification of the side chains.

Side chains are usually alkyl groups. An alkyl group is a group obtained by a removal of one hydrogen atom from an alkane. The name of alkyl group is obtained by replacing -ane of the corresponding alkane by -yl.

Nomenclature of alkyl group

Formula of alkyl group	Corresponding alkane	Name of the alkyl group
C _n H _{2n+1} -	Alkane	Alkyl
CH ₃ -	Methane	Methyl
CH ₂ CH ₂ -(C ₂ H ₅ -)	Ethane	Ethyl
CH,CH,CH,-	Propane	Propyl
СН₂СНСН₃	Propane	Isopropyl
CH,CH, CH,CH,-	Butane	Butyl
CH ₂ CHCH ₂ CH ₃	Butane	Sec-(s-) butyl
CH ₃ CHCH ₂ — CH ₃	Methylpropane (isobutene)	Isobutyl
сн _з ссн _з	Methylpropane (isobutene)	Tertio-(t-) butyl
CH,CH, CH, CH,CH,-	Pentane	Pentyl

A side chain must be identified by the smallest possible numbers.



3. If the same substituent occurs two or more times, the prefix di, tri, tetra, ...is attached to substituent's name. Its locants separate the prefix from the name of the substituent.

4. Identify the remaining functional groups, if any, and name them. Different side chains and functional groups will be listed in alphabetical order.

The prefixes di, tri, tetra,...are not taken into consideration when grouping alphabetically. But prefixes such iso-, neo- are taken into account. Example:

Identify the position of the double/triple bond.

Example:

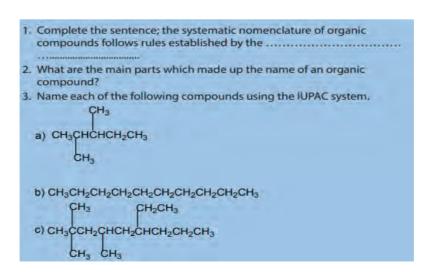
Number the chain (left to right) or right to left.

The sum of the numbers which show the location of the substituents is the possible smallest.

The correct name will be the one which shows the substituents attached to the third and fifth carbon, respectively and not to the fourth and the fifth carbon atom.

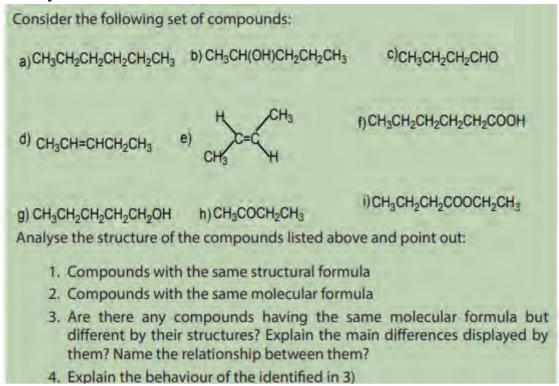
Numbers are separated by commas Hyphens are added between numbers and words. Successive words are merged in one word.

Self - Check



Isomerism in organic compounds

Activity



Isomerism is the existence of compounds that have the same molecular formula but different arrangements of atoms; these compounds are called "isomers".

Isomers have different physical or/and chemical properties and the difference may be great or small depending on the type of isomerism.

There are two main classes of isomerism: Structural isomerism and stereoisomerism.

Structural isomerism

Activity

- 1. Referring to the previous activity 1.5 above, what is the relationship between compounds: a), o and p) in the list of the activity 1.5?
- 2. Identify the relationship between compounds b) and g) in the activity 1.5?
- 3. Relate the relationship between compounds: b) and J) in the activity 1.5?
- 4. Estimate the relationship between compounds c) and h) in the activity 1.5?
- 5. Investigate if there is a relationship between compounds d) and k) in the activity 1.5?

Structural isomers are compounds of the same molecular formula but with different structural formula.

1. Position isomerism

Position isomers are compounds with the same molecular formula but different positions of the functional group or substituent(s).

Examples:

2. Chain isomerism

Chain isomers are compounds with the same molecular formula, belonging to the same homologous series, with chain of carbon atoms of different length.

3. Functional isomerism

Functional (group) isomers are compounds which have the same molecular formula but different functional groups.

Examples:

Stereoisomerism

1. Geometrical isomerism

Geometrical isomers or cis-trans isomers are compounds with the same molecular formula, same arrangement of atoms but differ by spatial arrangements.

This type of isomers is mainly found in alkenes due to the restricted rotation around the carbon-carbon double bond.

The necessary condition for an alkene to exhibit geometrical isomerism is that each carbon doubly bonded has two different groups attached to it.

2. Optical isomerism

Activity

- 1. Look at your hands or the figure showing hands and chairs and discuss the relationship between them.
- 2. What are the necessary conditions for such pairs of organic compounds to exhibit that relationship?
- 3. What name is given to such compounds?

Optical isomers are compounds with the same molecular formula and arrangements

of atoms but have different effect on the plane polarised light.

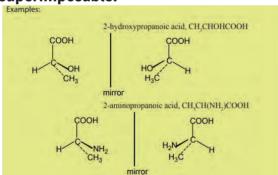
- A compound that rotates the plane polarised light is said to have an optical activity.
- This type of isomerism occurs in compounds containing an asymmetric (asymmetrical) carbon atom or chiral centre.
- When a molecule has chiral centre, there are two non-superimposable isomers that are mirror images of each other.
- Such compounds are called enantiomers.



Mirror images

In a mirror, the left hand is the image of the right hand and they are non superimposable, i.e. they are enantiomers. An achiral object is the same as its mirror

image, they are no superimposable.



Self - Check

- 1. What is meant by "isomers"
- Using examples, distinguish structural isomers and stereoisomers. Describe the sub-classes of each type of isomers.
- Explain how the nature of the C=C bond gives rise to cis-trans isomerism.
- 4. Identify which of the isomers of hexene exhibit geometrical isomerism.

ALKANES

Learning objectives

By the end of this lesson, you should be able to;

- name straight chain alkanes up to carbon-20
- define homologous series
- use IUPAC system to name straight and branched alkanes
- describe the preparation methods of the alkanes

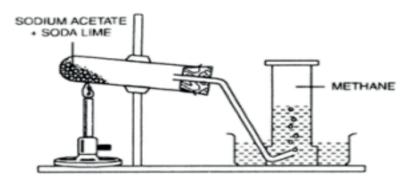
INTRODUCTION

Alkanes are the simplest class of organic compounds. They are made of carbon and hydrogen atoms only and contain two types of bonds, carbon-hydrogen (C-H) and carbon-carbon (C-C) single covalent bonds. They do not have functional groups. Alkanes form a homologous series with the general formula C_nH_{2n+2} where n is the number of carbon atoms in the molecule. The first member of the family has the molecular formula CH_4 (n=1) and is commonly known as methane and the second member with molecular formula is C_2H_6 (n=2) is called ethane.

These compounds are also known as saturated hydrocarbons. This name is more descriptive than the term "alkane" because both their composition (carbon and hydrogen) and the fact that the four single covalent bonds of each carbon in their molecules are fully satisfied or "saturated".

Preparation of alkanes

Lab preparation of methane gas



Requirements
Stand and accessories
Delivery tube

NaOH(s)
calcium oxide(s)

Procedure

Prepare a mixture of the reagents in ratio 1:1. Weight about 3 grams of sodium acetate and the same quantity as soda lime. Mix them thoroughly in a beaker.

Place about 4 grams of the mixture into a boiling tube.

Seal the boiling tube with a stopper with a gas-delivery tube. The gas-delivery tube should look upwards.

Fix the boiling tube on a stand.

Heat the test-tube gently with the cold part of the flame. To avoid local overheating keep the flame in motion.

After a while the gas starts liberating.

Prepare an empty test-tube. Collect some gas keeping this test-tube on top of the gas delivery tube.

Methane is a flammable gas. To set it on fire turn the covering test tube and hold a burning match to the end of the gas delivery tube.

The gas burns with a blue (red) fire.

Methane can be prepared by the reaction between sodium acetate and sodium hydrox

ide solid according to the equation:

$$CH_3COONa(s) + NaOH(s) \xrightarrow{CaO(s)} CH_4(g) + Na_2CO_3(s)$$

It is collected by the downward displacement of water.

The general equation for preparation of alkanes:

RCOONa(s) + NaOH(s)
$$\frac{\text{CaO(s)}}{\text{heat}}$$
 RH(g) + Na₂CO₃(s)

Note: The reaction is practically used to reduce by one carbon the length of carbon chain. It is referred as decarboxylation of sodium carboxylates.

Other reactions used for the preparation of alkanes are the following:

1. Addition reaction of hydrogen to alkenes and alkynes in the presence of catalyst like Nickel, Palladium or platinum produces alkanes: this reaction is called hydrogenation reaction of alkenes and alkynes; it is also called a reduction reaction of alkenes and alkynes.

R-CH=CH R' + H₂
$$\xrightarrow{\text{Ni}}$$
 R-CH₂-CH₂-R' alkene Alkane

2. From halogenoalkanes or Alkyl halides

On reduction of alkyl halides with Zn and concentrated hydrochloric acid, alkyl halides are converted to alkanes.

a)
$$2RX + Zn \xrightarrow{H'} 2RH + Zn^{2+} + 2X$$

E. g: $CH_3 - CH_2CHBr - CH_3 \xrightarrow{Z_B \cap H^+} CH_3CH_2CH_3$
 $R-X+Li \rightarrow RLi \xrightarrow{CBX} R_2CuLi \xrightarrow{R'X} R - R^n$
 $CH_3CH_2Cl + Li \rightarrow CH_3CH_2Li + Cul \rightarrow (CH_3-CH_2)_2Cul + CH_3 (CH_2)_5CH_2Br \rightarrow CH_3 (CH_2)_7CH_3$
n- nonane
 $R-X+H_3 \xrightarrow{Pd} RH + HX$

3. From carbonyl compounds

Reduction of carbonyl compounds, with amalgamated Zinc (alloy made of zinc and mercury) and HCl. This is the Clemmensen reduction).

$$CH_3CH_2COCH_3 \xrightarrow{Zn(Hg)/HCknnc} CH_3 - CH_2 - CH_2 - CH_3 + H_2O$$

Under special conditions, reduction also is realized by use of H_2 and Raney Nickel or using hydrazine (NH_2NH_2) and KOH. This is called Wolf Kushner reduction.

Physical properties of alkanes

Alkanes	Melting Point ^o C	Boiling Point [©] C	Density	Physical state
CH ₄	-182.6	-162,0	and now that	
C ₂ H ₆	-172.0	-89.0	0.4240	gas
C ₃ H ₈	-157.1	-44.0	0.5463	
	-135.0	-0,5	0.5824	
C ₄ H ₁₀	-135,0	-0,5	0.5933	
C _s H ₁₂	-129.7	36.2	0.6264	
C ₆ H ₁₄	-94.5	69.0	0.6594	
C ₇ H ₁₆	-90,5	98.4	0.6837	
C _s H ₁₈	-57.0	125.6	0.7028	
C ₉ H ₂₀	-53.7	150.7	To the second	
C ₁₀ H ₂₂	-29.7	174.0	0.7179	
			0.7298	







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www.ncdc.go.ug



Ministry of Education and Sports

HOME-STUDY LEARNING



CHEMISTRY

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This material has been developed as a home-study intervention for schools during the lockdown caused by the COVID-19 pandemic to support continuity of learning.

Therefore, this material is restricted from being reproduced for any commercial gains.

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FOREWORD

Following the outbreak of the COVID-19 pandemic, government of Uganda closed all schools and other educational institutions to minimize the spread of the coronavirus. This has affected more than 36,314 primary schools, 3129 secondary schools, 430,778 teachers and 12,777,390 learners.

The COVID-19 outbreak and subsequent closure of all has had drastically impacted on learning especially curriculum coverage, loss of interest in education and learner readiness in case schools open. This could result in massive rates of learner dropouts due to unwanted pregnancies and lack of school fees among others.

To mitigate the impact of the pandemic on the education system in Uganda, the Ministry of Education and Sports (MoES) constituted a Sector Response Taskforce (SRT) to strengthen the sector's preparedness and response measures. The SRT and National Curriculum Development Centre developed print home-study materials, radio and television scripts for some selected subjects for all learners from Pre-Primary to Advanced Level. The materials will enhance continued learning and learning for progression during this period of the lockdown, and will still be relevant when schools resume.

The materials focused on critical competences in all subjects in the curricula to enable the learners to achieve without the teachers' guidance. Therefore effort should be made for all learners to access and use these materials during the lockdown. Similarly, teachers are advised to get these materials in order to plan appropriately for further learning when schools resume, while parents/guardians need to ensure that their children access copies of these materials and use them appropriately. I recognise the effort of National Curriculum Development Centre in responding to this emergency through appropriate guidance and the timely development of these home study materials. I recommend them for use by all learners during the lockdown.

Àlex Kakooza

Permanent Secretary

Ministry of Education and Sports

ACKNOWLEDGEMENTS

National Curriculum Development Centre (NCDC) would like to express its appreciation to all those who worked tirelessly towards the production of home-study materials for Pre-Primary, Primary and Secondary Levels of Education during the COVID-19 lockdown in Uganda.

The Centre appreciates the contribution from all those who guided the development of these materials to make sure they are of quality; Development partners - SESIL, Save the Children and UNICEF; all the Panel members of the various subjects; sister institutions - UNEB and DES for their valuable contributions.

NCDC takes the responsibility for any shortcomings that might be identified in this publication and welcomes suggestions for improvement. The comments and suggestions may be communicated to NCDC through P.O. Box 7002 Kampala or email admin@ncdc.go.ug or by visiting our website at http://ncdc.go.ug/node/13.

Grace K. Baguma

Director,

National Curriculum Development Centre

ABOUT THIS BOOKLET

Dear learner, you are welcome to this home-study package. This content focuses on critical competences in the syllabus.

The content is organised into lesson units. Each unit has lesson activities, summary notes and assessment activities. Some lessons have projects that you need to carry out at home during this period. You are free to use other reference materials to get more information for specific topics.

Seek guidance from people at home who are knowledgeable to clarify in case of a challenge. The knowledge you can acquire from this content can be supplemented with other learning options that may be offered on radio, television, newspaper learning programmes. More learning materials can also be accessed by visiting our website at www.ncdc.go.ug or ncdc-go-ug.digital/. You can access the website using an internet enabled computer or mobile phone.

We encourage you to present your work to your class teacher when schools resume so that your teacher is able to know what you learned during the time you have been away from school. This will form part of your assessment. Your teacher will also assess the assignments you will have done and do corrections where you might not have done it right.

The content has been developed with full awareness of the home learning environment without direct supervision of the teacher. The methods, examples and activities used in the materials have been carefully selected to facilitate continuity of learning.

You are therefore in charge of your own learning. You need to give yourself favourable time for learning. This material can as well be used beyond the home-study situation. Keep it for reference anytime.

Develop your learning timetable to ca ter for continuity of learning and other responsibilities given to you at home.

Enjoy learning



PHYSICAL CHEMISTRY

TOPIC: 1.0 PHYSICAL EQUILIBRIA

GENERAL OBJECTIVE: The learner should be able to comprehend the concept of interconversion of phases due to changes in the physical conditions and its applications.

LESSON 1.1 Systems, Phases and components

By the end of this lesson, you should be able to;

- explain the concept of physical equilibrium
- distinguish between the terms, phases, components and systems.
- discuss the characteristics of a system, phases and component
- mention different types of component systems
- give examples of one component system.
- explain the cooling curves for pure substances
- explain the term phase diagram
- draw phase diagrams for a one component system
- explain what the different regions of a phase diagram represent.

INTRODUCTION

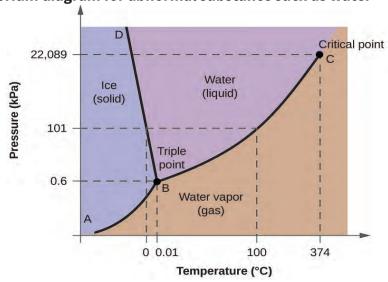
PHYSICAL EQUILIBRIA

It deals with balance of phases. A phase is any homogenous and physical distinct part if systems which can be separated from other part by definite boundary surface e.g. miscible liquids have one phase, immiscible liquids have two phases while water can exist in three phases. The word phase can replace the word state.

Phase equilibrium diagrams.

A phase equilibrium diagram is one that shows the relationship between the vapour pressure of a substance and temperature.

A phase equilibrium diagram for abnormal substance such as water



AB- sublimation curve, BC- evaporation / condensation CURVE

BD- Melting /freezing curve.

B- triple point. It is a point where all the three phases coexist in equilibrium. Along AB, ice and water vapour are in equilibrium. This curve represents the effects of pressure on ice as temperature various.

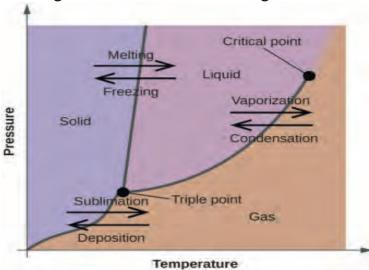
Along **OC**, vapour and liquid co-exist in equilibrium. It represents the effects of increased pressure on boiling point of water.

OB- ice and liquid co-exist in equilibrium. OB represents the effects of increased pressure on the melting point of ice. It slopes towards the left (pressure axis) indicating that increase in pressure decreases the melting point and volume of ice.

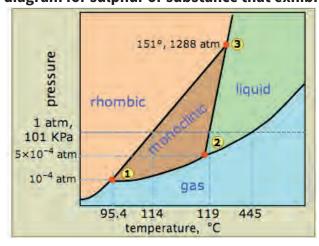
Point C is the critical point i.e point beyond which the liquid and vapour phases are indistinguishable. The pressure exerted by one mole of a substances at this point is called the critical pressure and corresponding temperature is called the critical temperature. Above this point, the vapour cannot be liquefied no matter what pressure is applied.

Critical temperature is the minimum temperature above which the vapour cannot be liquefied under all conditions of temperature and pressure.

A phase equilibrium diagram for normal substance e.g carbon dioxide.



A phase equilibrium diagram for sulphur or substance that exhibit allotropy



The diagram is complicated by the fact that sulfur can exist in two crystalline forms: rhombic and monoclinic.

Let's look first at the four areas:

- **Pink** only rhombic sulfur
- **Brown** only monoclinic sulfur
- **Green** only liquid sulfur
- Blue gaseous sulfur

The corresponding curves are:

- **lower left to** (1) the sublimation curve of rhombic S: $S(rhombic) \rightleftharpoons S(g)$
- (1) to(2) the sublimation curve of monoclinic S: S(monoclinic) ⇒ S(g)
- 2 to upper right the vapour pressure curve of liquid S: S(l) ⇒ S(g)
- (1) to (3) the transition curve for S(rhombic) ⇒ S(monoclinic)
- 2 to 3 the melting point curve for $S(monoclinic) \rightleftharpoons S(l)$
- 3 to top the melting point curve for $S(rhombic) \rightleftharpoons S(l)$

There are three **triple points**:

- (1) (95.4 °C,1×10-4 atm) rhombic S is in equilibrium with monoclinic S, and both have the same vapour pressure.
- ② (119 °C,5×10-4 atm) monoclinic S melts; this is the triple point for Sm\(\Rightarrow\)Sl\(\Rightarrow\)Sg.
- (3) (151 °C, 1288 atm) rhombic, monoclinic, and liquid S are at equilibrium.

The **critical point** — where liquid and gaseous S have the same density — is off to the right at 1041 °C and 203.3 atm

Research work

By use of internet or text book,

- Sketch cooling curves of pure substances.
- Explain the cooling curves for pure substances.
- Draw phase diagrams for mixtures
- Explain the phase diagrams for mixtures
- Explain concept of eutectic mixtures
- Compare the behaviour of eutectic mixture and a pure compound
- Give examples of substances which form eutectic mixtures.

LESSON 1.2: LIQUID-LIQUID MIXTURE

SPECIFIC OBJECTIVES:

By the end of this lesson, you should be able to;

- give examples of two component system.
- explain the different types of two component systems
- identify the different types of two component systems
- state Raoult's law
- explain what ideal solution is.

- give characteristics and examples of ideal solutions
- draw vapour composition diagrams for ideal solutions and real solutions.
- interpret the vapour pressure composition diagrams.
- carry out calculations on Raoult's law

INTRODUCTION

Previously you learnt that an example of **one-component system** is a **system** involving one pure **chemical** while **two-component systems**, such as mixtures of water and ethanol, have **two** chemically independent **components** and so on. Typical phases are solids, liquids and gases.

One phase system solution (miscible liquids)

Miscible liquids are liquids which dissolve in one another in all proportions to form a uniform solution. The solubility of a liquid in a liquid is governed by the same principle as a solid in a liquid, but when a liquid dissolve in another liquid, we use the word **miscible instead of soluble**.

Activity

- a) Identify examples of mixtures of miscible Liquids.
- b) Define each of the following terms:
 - i) Solution,
 - ii) Solvent
 - iii) Solute
 - iv) Saturated solution
 - v) unsaturated solution

Liquid – liquid mixtures which form ideal solutions

There are hardly any liquids which form an ideal solution when mixed but some do form nearly an ideal solution.

An ideal solution is one that obeys Raoult's law exactly and possesses the following properties;

- i) The intermolecular forces of attractions between like molecules (molecules of one compound) or those between the unlike molecules (molecules of the different components) in the mixture are exactly equal and therefore the escaping tendency of the molecules of each component does not change compared to that in the pure state at the same temperature. Therefore, the boiling point of the solution is between that of two components.
- ii) When the two liquids are mixed, there is no enthalpy change.
- iii) When the two liquids are mixed to form an ideal solution, the total volume of the solution is equal to the sum of the volumes of the individual components

Raoult's law:

States that the partial vapour pressure of any volatile component of an ideal solution is equal to the vapour pressure of the pure component multiplied by the mole fraction of that component in the solution.

This law can be expressed mathematically as follows:

Suppose P^O_A, P_A and X _A are respectively the vapour pressure of pure A, Partial vapour pressure of component A in the solution, and the mole fraction of A in the solution, then

$$P_A = X_A P_A^o$$

Similarly, for liquid B we have: $P_B = X_B P_B^o$

$$X_B P^{O_B}$$

Partial vapour pressure of a component is defined as the pressure that component will exert on the walls of the container which was originally occupied by components.

For two components A and B that form on ideal solution, the total vapour pressure of the mixture at a particular temperature:

$$P_T = P_A + P_B$$

= $(X_A P_A^o) + (X_B P_B^o)$

Mole fraction of a component in solution is the number of moles of that component in the mixture divided by total moles in the mixture. Note that the sum of the mole fractions of all components in a mixture is 1.

$$X_A + X_B = 1$$

Thus, $X_A = 1 - X_B$
 $P_T = (P_A^o X_A) + (P_B^o X_B)$
Becomes
 $P_T = P_A^o (1 - X_B) + (P_B^o X_B)$
 $P_T = P_A^o - P_A^o X_b + (P_B^o X_B)$
 $P_T = P_A^o + (P_B^o - P_A^o) X_B$ Note: $X_A = \frac{nA}{nA + nB}$ and $X_B = \frac{nB}{nA + nB}$

Where, nA = moles of A in a mixturenB = moles of B in mixture

Activity

Components A and B form an ideal solution. The vapour pressure of pure A and pure B is 900mmHg and 500mmHg respectively at a temperature of 25°c and pressure of 760mmHg.

Calculate the mole fraction of each component

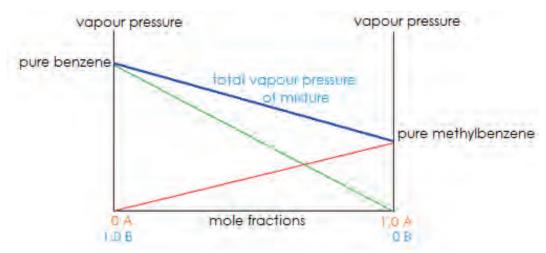
- i) In the solution. (Answer: $X_A = 0.65$, $X_B = 0.35$)
- ii) In the vapour above the mixture. (Answer $X_A = 0.77$ and XB = 0.23)

Vapour pressure - composition diagram for an ideal solution

The vapour pressure of a pure liquid increases when temperature is increased until it reaches atmosphere pressure when it begins to boil at constant temperature

For an ideal solution, the force of attraction between the molecules of individual components is the same as that between the molecules of different components.

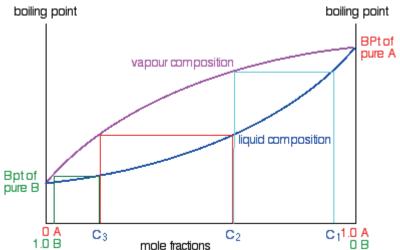
Therefore, the escaping tendency of each molecule into the vapour form is uniform.



Let A = methylbenzene B = benzene

Temperature (boiling point) – composition curve corresponding to the above vapour pressure-composition curve is given below.

Notice that component A that had a lower vapour pressure than B now has higher boiling point than B.



If you boil a liquid mixture C₁, you will get a vapour with composition C₂, which you can condense to give a liquid of that same composition (the pale blue lines).

If you re-boil that liquid C₂, it will give a vapour with composition C₃. Again, you can condense that to give a liquid of the same new composition (the red lines).

Re-boiling the liquid C₃ will give a vapour still richer in the more volatile component B (the green lines). You can see that if you were to do this once or twice more, you would be able to collect a liquid which was virtually pure B.

The secret of getting the more volatile component from a mixture of liquids is obviously to do a succession of boiling-condensing-re-boiling operations.

It isn't quite so obvious how you get a sample of pure A out of this. That will become clearer in a while.

This process is called fractional distillation and the description above illustrates the principal of fractional distillation.

Fractional distillation is a technique of separating completely volatile miscible liquids by taking into account the different in their boiling points.

Effective separation can be achieved by using a long vertical column (fractionating column) attached to a distilling flask and filled with glass beads vapour from the liquid that is heated rise up the column until it condenses in the cooler parts and runs back into the vessel.

The rising vapour in the column has a more volatile component towards the top and the less volatile components at the bottom. Various fractions of the mixture can be drawn off at points of the column.

Activity

- a) explain the term fractional distillation and state its principle
- b) State the importance of fractional distillation.
- c) Draw a labeled diagram for the setup of apparatus that can be used to separate a mixture of miscible liquids

Summary

- Miscible liquids are liquids that dissolve in one another in all proportions to form a uniform solution.
- Fractional distillation is used to separate a mixture of miscible liquids.
- No mixture of mixture of miscible liquids is perfectly ideal.

LESSON1.3: NON-IDEAL SOLUTION

Specific objectives: By the end of this lesson you should be able to:

- explain what real solution is
- give characteristics and examples of real solutions
- draw vapour composition diagrams for real solutions.
- differentiate between negative and positive deviation from Raoult's law.
- explain what is meant by the terms azeotropic mixtures and azeotropes
- explain what distillation is.
- explain the separation of components of azeotropes.

INTRODUCTION

A non-ideal solution (real solution) does not obey Raoult's law. The intermolecular forces of attraction between the like molecules are completely different from intermolecular forces of attraction between the unlike molecules.

The formation of non-ideal solutions is accompanied by change in total volume of mixture and evolution or absorption of heat such as solution is solid to.

There are two types of deviation from Raoult's law i.e. positive deviation and negative deviation.

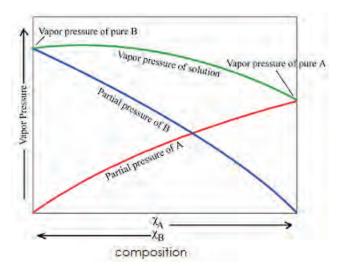
Positive deviation

It arises when the intermolecular forces of attraction between like molecules are stronger than intermolecular forces of attraction between unlike molecules. As a result, there is increased repulsion between the molecules and this increase the escaping tendency of each type of molecules from solution into the vapour phase giving a maximum vapour composition curve and a corresponding minimum boiling point composition curve.

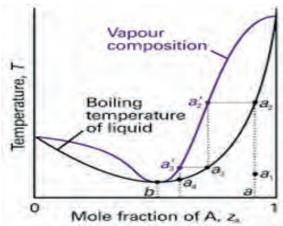
Formation of a solution which deviates positively from Raoult's law is accompanied by absorption of heat and increase in total volume of the mixture.

Most of the liquids which deviate positively from Raoult's law, one or two must be able to form hydrogen bonds e.g. water and ethanol.

Positive Deviations from Raoult's Law Weak solute-solvent interaction results in a vapour pressure higher than expected.



The boiling point composition diagram for a mixture that deviates positively from Raoult's law.



The liquid of composition **b** is called an azeotrope /azeotropic mixture/constant boiling point mixture and in this case the minimum constant boiling point mixture.

When this mixture is boiled, the temperature remains constant until all the liquid has turned into vapour and when the vapour is cooled, it forms a liquid of the same composition as one originally distilled. In this way, the azeotropic mixture behave as if it is a pure liquid yet it is not because when the external pressure is changed, the composition of the azeotropic mixture changes.

An azeotropic mixture is a mixture whose composition and boiling point remains constant at a given confining pressure with continued distillation of the mixture.

Distillation of mixture that deviates positively from Raoult's law

Fractional distillation of this mixture cannot separate the components completely because they form an azeotropic mixture. However, from the above diagram if the mixture distilled

has a composition to the right of **b** the distilled is still the azeotrope and the residue mainly **A**.

Separation of azeotropic mixtures.

- 1. Distillation with a third component. To separate azeotropic mixture of X and Y, a third component is introduced in which Y must be readily soluble to form an ideal solution and X must be immiscible with the third component such that a separating funnel can be used to separate the two and Y in the third component is obtained by fractional distillation e.g. an azeotropic consisting water and ethanol, benzene can be introduced as a third component.
- 2. By chemical method. Azeotropic mixture of ethanol and water can be separated by adding of calcium oxide which absorbs the water.
- 3. By absorption. It is done by addition of charcoal which absorbs one of the components.

Follow up activity.

- a) Ethanol-water system deviates positively from Raoult's law. Draw a vapour pressurecomposition curve for ethanol – water system and label the phases. (Water boils at higher temperature than ethanol)
- b) Name at least three pairs of liquids whose solution deviates positively from Raoult's law.
- c) (C) Explain how negative deviation from Raoult's law arises. Draw labeled vapour pressure- composition diagram and the corresponding boiling point-composition diagram for a mixture of liquids that deviates negatively from Raoult's law.
- d) State what is meant by the term a zeotropic mixture.
- e) Use internet or text book to research and write down the description of methods of separating components of an azeotropic mixture.

LESSON 1.4: Immiscible liquids

SPECIFIC OBJECTIVES

- Explain the total vapour of immiscible liquid mixture in terms of the vapour of the components.
- Calculate the composition of the vapour above a mixture of two immiscible liquids.
- Calculate the composition of the distillate.
- State industrial application of steam distillation

Introduction

Immiscible liquids are liquids which when mixed in any proportion form two distinct layers e.g. water and nitrobenzene

The total vapour pressure above the mixture of two immiscible liquids is equal to the sum of the vapour pressure of the liquids at a given temperature.

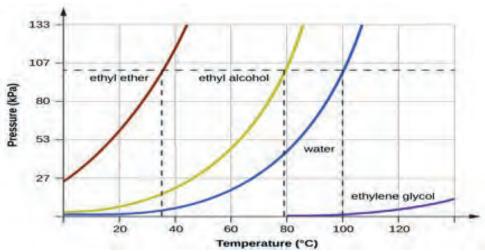
This total vapour pressure is independent of the relative amounts of the two components present i.e. if A and B are two immiscible liquids forming a binary mixture, then

$$P_T P_A^0 + P_B^0$$

where, P_A^o and P_B^o are saturated vapour pressure of components A and B respectively at a given temperature.

A liquid boil when it's vapour pressure reaches the value exerted by the external pressure thus the total vapour pressure extend by an immiscible mixture of liquid will reach atmospheric pressure at a temperature below liquids the boiling point of the most volatile constituent.

Below is the vapour pressure curves of two liquids that are immiscible e.g water and nitrobenzene.



Activity

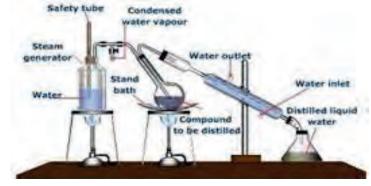
1. The vapour pressure of water and of an immiscible liquid x at different temperature are given in the table below.

Temperature / °C	92	94	96	98	100
V.P of x / kPa	6	8	12	15	17
$V.P of x H_2O / kPa$	74	80	88	94	109

- a) On the same axes, plot graphs of vapour pressure against temperature for each liquid.
- b) Determine the vapour pressure of the mixture of \mathbf{x} and water at the temperature given in the table above.
- c) On the same axes of the graph in (a) plot a graph of the vapour pressure of the mixture versus the temperature.
- d) (d) The distillate from the mixture at 101kPa contained 16g of water and 1.1g of x. calculate the R.M.M of x using the information from the graph you have drawn.

Steam distillation (distillation of immiscible liquids)

- Pass steam from the steam jacket through a mixture containing the desired organic compound in a flask that is being maintained at a temperature just below the boiling point of water.
- When the mixture in this flask boils, it gives off steam and a vapour of the desired organic compound. The steam and the vapour are condensed and collected as a distillate.



Since water and organic compound are immiscible, they are separated by means of a separating funnel or a drying agent which removes water.

Conditions for a compound to be separated by steam distillation

- The compound must be immiscible with water.
- It must have a high relative molecular mass.
- It must be able to exert high vapour pressure near the boiling point of water.
- Any impurities mixed with it must be non-volatile.

Analysis of the distillate (composition of the distillation)

The mass of each liquid in the distillate is proportional to the product of its relative molecules mass and the vapour pressure at a particular temperature i.e.

 $W_A \propto RMM_A \times Vapour \ pressure \ A$ $W_A = k \ RMM \ of \ A \ vapour \ of \ A \dots (i)$

Similarly

 $W_B = kRMM \text{ of } B \times vapour \text{ of } B \dots (ii)$

$$\frac{W_A}{W_B} = \frac{RMM \ of \ B \ vapour \ of \ A}{RMM \ of \ A \times \ vapour \ of \ B}$$

Where, $W_A = mass of component A in the distillate.$

 W_B = mass of component b in the distillate.

Examples

A mixture of naphthalene and water was steam distilled at 98.3°C and 753mmHg.
 Calculate the percentage of by mass of naphthalene in the distillated (vapour pressure of water at 98.3°C is 715mmHg).

Let the percentage of $C_{10}H_8$ in distillate be X Then let the percentage of H_2O in distillate be (100-X)

But,
$$\frac{\times}{100-\times} = \frac{RMM \text{ of } C_{10}H_9 \times vapour \text{ pressure of } C_{10}H_9}{RMM \text{ of } H_2O \times vapour \text{ pressure of } H_2O}$$

$$\frac{\times}{100-\times} = \frac{120 \times (753-715)}{18 \times 715}$$

$$\frac{X}{10-X} = \frac{4864}{12870}$$

$$1287 = 100-X \text{ (4864)}$$

$$12870 \text{ X} = 486400 - 486X$$

$$X = 27.43$$

2. A compound x was steam distilled at 80°C at 760mmHg and the distillate was found to contain 90.8% of x (vapour pressure of water at 80°C is 240mmHg) calculate the molecules mass of x.

$$\frac{90.8}{100-90.8} = \frac{\text{RMM of X vapour pressure of x}}{\text{RMM of H2O X vapour pressure of H2O}}$$

$$\frac{90.8}{9.2} = \frac{\text{RMM of X} \times 760 - 240}{18 \times 240}$$

$$90.8(18X240) = 520 \text{ RMM of x.}$$

$$392,256 = 4784 \text{ RMM of x.}$$

$$\mathbf{RMM of x} = \mathbf{82}$$

Activity

- a) State the principle used in steam distillation.
- b) Give
 - i) the advantages of stem distillation
 - ii) the uses of steam distillation

LESSON 1.5: The Distribution/Partition law.

By the end of this lesson, you should be able to:

- explain the concept of distribution law.
- experimentally determine K_D.
- carry out calculations involving distribution law.
- explain the application in; chromatography, solvent extraction and ion exchange

INTRODUCTION

This law deals with the distribution of solute between two immiscible solvents in contact with each other. It starts that when a solute irrespective of its amount is shaken between two immiscible solvents in contact with each other the solute distributes itself such that at equilibrium, the ratio of the concentrations of the solute in the two layers is constant at any given temperature.

Distribution law.

i.e.
$$K_D = \frac{c_1}{c_1}$$

Where, C_1 is the concentration of the solute in solvent 1.

 C_2 is the concentration of the solute in solvent 2.

 K_D is known as the distribution or partition coefficient.

Solvents 1 and 2 are immiscible.

The distribution coefficient is defined as the ratio of concentration of a solute in one solvent to its concentration in another solvent for two immiscible solvents in contact at a particular /constant temperature.

Limitation of the law

- The solute must not dissociate or associate in any one of the solvents.
- The solute must not chemically react with any of the solvents.
- The partition law only holds at a particular temperature.
- The solute must not saturate any of the solvents.

Generally, the law only holds when the solute remains in the same molecular form in the two solvents.

Application of the partition law

- Solvent extraction
- Determination of the formula of a complex.
- Purification of the metals.

Solvent extraction

This is a process of separating substances especially organic substances from aqueous solution in which they are soluble by shaking the mixture with a suitable solvent which is immiscible with water in which the solute is more soluble in.

ACTIVITY

 $100cm^3$ of aqueous solution containing 20g of substance **x** was shaken once with $50cm^3$ of ether.

- i) Calculate the mass of **x** extracted by ether.
- ii) Calculate the mass of \mathbf{x} that would be extracted by shaking the mixture twice with 25cm^3 of ether (K_D of \mathbf{x} between ether and water is 4).

2. The determination of formula a complex ion

The partition coefficient is used to determine the structure of a complex ion i.e. the determination of number of ligands coordinated with the metal ion.

Experimental determination of a number of ligands complexed with a metal ion

E.g. number of moles of Ammonia that form a complex ion with copper (ii) ion.

A known volume of a standard solution of excess ammonia is shaken with a standard solution of Cu^{2+} to form a complex of formula; $[Cu(NH_3)_n]^{2+}$.

The resultant solution is then shaken with CHCl₃ in a separating funnel repeatedly for about 5minutes while releasing pressure at intervals.

The mixture is the allowed to stand until the two layers are separate completely.

The upper deep blue aqueous layer contains both free Ammonia and ammonia that has formed a complex i.e. ammonia in a complex, in equilibrium with the free ammonia in trichloromethane layer below.

ACTIVITY

- a) Describe the application of K_D in the determination of formula of a complex.
- b) (b)Excess aqueous ammonia was shaken with equal volume of CHCl₃ and 0.05M aqueous solution of Copper(II) Sulphate was added. The mixture was shaken and allowed to stand until two separate layers completely formed. It was found out that the concentration of NH₃ in CHCl₃ and aqueous layer were 0.21 mol l¹ and 0.725 mol l¹ respectively. If distribution coefficient of NH₃ between water and trichloromethane is 25 Determine the value of n in the complex [Cu(NH₃)_n]²⁺
- c) The table below shows the result of partition of amino ethane and 0.1M Copper sulphate solution.

[CH₃NH₂(CHCl₃)]	0.87	1.10	1.33	1.57	1.80		
CH ₃ NH ₂ (CHCl ₃)]	0.02	0.03	0.04	0.05	0.06		

- i) Plot a graph of CH₃NH₂[(0.1MCuSO₄)]
- ii) Determine the number of moles of aminomethane that has formed complex with Copper (ii) ions.

TOPIC 2.0 CHEMICAL EQUILIBRIUM

GENERAL OBJECTIVE:

By the end of this topic the learner, should be able to explain the concept of reversible reactions and its applications.

LESSON 2.1 THE CONCEPT OF CHEMICAL EQUILIBRIUM AND COMPARISON BETWEEN $K_{\text{\tiny c}}$ and $K_{\text{\tiny p}}$

SPECIFIC OBJECTIVES:

By the end of this lesson, you should be able to:

- explain the concept of chemical equilibrium
- distinguish between reversible and irreversible reactions
- explain dynamic equilibrium
- differentiate between homogenous and heterogeneous reversible system
- restate the law of mass action and apply it in writing equilibrium expressions
- derive a general expression relating K_c and K_p
- carry out calculations involving use of K_c and K_p
- compare concentration equilibrium constant and pressure equilibrium constant [Kc and K_D]
- compare Q and Kc to determine the direction of chemical reaction
- interpret the magnitude of value of Kc or Kp in relation to the equilibrium position

INTRODUCTION

Equilibrium exists when two opposing forces or rates balance each other.

In everyday life, such equilibrium exists in a balanced se-saw, weighing scale, when a person walks at a right speed up a down moving elevator. In chemistry, many reactions do not go to completion. The reactants combine to form a product and a point is reached when the product decomposes to form the reactants.

A point is then reached when the rate at which reactants are forming products is equal to the rate at which the product is decomposing into reactants. This is said to be the equilibrium state of the system.

The equilibrium reached is dynamic and not static because there is a constant interchange between the products and reactants and the reaction is said to be reversible.

NB: A dynamic equilibrium can be established in either an isolated system or a closed system.

Definition:

- 1. Isolated system- is one which does not exchange matter or energy with the surrounding.
- 2. Closed system is one which does not exchange matter with the surrounding but exchange energy.
- 3. Open system is one that exchanges both matter and energy with the surrounding therefore a dynamic equilibrium cannot be obtained in an open system.

In a closed system, a reaction will reach a state of equilibrium when the rate of the forward reaction is equal to the rate of the backward reaction.

Consider the reaction;

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

$$R_f = K [A] [B]$$

$$R_b = K_2[C][D]$$

At equilibrium, $R_f = R_b$ $K_1[A][B] = K_2[C][D]$

$$\frac{K_1}{K_2} = \frac{[C][D]}{[A][B]}$$

$$K_C = \frac{[C][D]}{[A][B]}$$

K_c is called **equilibrium constant** in terms of concentration of the participating.

Equilibrium constant K_C is the ratio of the product of the concentration of the products of reaction to the product of concentration of the reactants raised to their respective stoichiometric powers when the concentrations are in moldm⁻³ Generally, for the reaction;

$$n A + mB \longrightarrow x C + y D$$

$$K_c = \frac{[C]^x [D]^y}{[A]^n [B]^m}$$

K_c is the equilibrium constant in terms of concentration of the participating species

If the reactants and products are all gases, then equilibrium constant can be conveniently given in terms of pressures e.g.,

$$N_2(g) + 3H_2(g \implies 2NH_3(g)$$

$$K_p = \frac{P_{NH_3}^2}{(P_{N_2})(P_{H_2}^3)}$$

Where P is partial pressure and the units for K are atm⁻².

In terms of concentration; $K_c = \frac{[NH_3]^2}{[N_2]^2[H_2]^3}$

NB: However, if the reactants and products are I aqueous state equilibrium constant is only expressed in terms of concentration of the participating species e.g.

a.
$$CH_3COOH(aq) + CH_3CH_2OH(I) \rightleftharpoons CH_3CO_2CH_2CH_3(aq) + H_2O(I)$$

$$K_c = \frac{[CH_3CO_2CH_2CH_3][H_2O]}{[CH_3CH_2OH][CH_3CO_2H]}$$

The above reaction in which all the reactants and products are in same phase are called **homogenous equilibrium reactions.** However, in reactions where the reactant and products have different state are called **heterogeneous reactions** e.g.

a)
$$CaCO_3(s) \leftarrow CaO(s) + CO_2(g)$$

The concentrations of the solids hardly change and therefore are taken to be constant. Concentrations of solids hardly appear in the expression of equilibrium constant. Therefore, the above reaction;

$$K_C = [CO_2].$$

In terms of the partial pressures, since the pressure exerted by a solid or liquid is negligible, then in heterogeneous equilibrium reactions, expression for K_P does not include solids and liquids e.g. in the above reaction;

$$K_P = P_{CO2}$$

b) $3Fe_{(s)} + 4H_2O(g)$ Fe₃O₄ (s) + H₂(g)

$$K_C = \frac{[H_2]^4}{P_{H_2O}^4}$$
 $K_p = \frac{P_{H_2}^4}{[H_2O]^4}$

Note: K_C or K_P value is only affected by changes in temperature and its units depend on the expression for the KC or KP and on the concentration units used or pressure with used.

LESSON 2.2 Factors that affect equilibrium reactions

SPECIFIC OBJECTIVES

By the end of this lesson, you should be able to;

- explain Le' Chatelier's principle and apply it in explaining the effects of various factors on the equilibrium of reversible chemical reaction
- experimentally determine K_c using esterification reaction
- show the importance of equilibrium constant factors on industrial processes

INTRODUCTION

Le Chatelier's principle

It states that when a system in equilibrium is subjected to any change, it will shift the equilibrium position in a direction that causes an opposite change.

1. Concentration

Consider the reactions;

$$N_{2(g)} + 3H_2(g) = 2NH_3(g)$$

When Nitrogen gas is added to the above equilibrium mixture, the position of equilibrium will shift to the right. This is the direction in which the Nitrogen added is used up by its reaction with Hydrogen to form Ammonia in attempt to restore equilibrium.

On the other hand, if some Ammonia is removed from the equilibrium mixture, the equilibrium will be distorted and hence the position of equilibrium system. Then the products will have to dissociate faster in order to replace the reactant being removed and have restore the equilibrium.

2. Pressure

Increasing pressure on a system in equilibrium will cause the equilibrium position to shift in a direction which will bring about the lowering of pressure.

Considering;

$$N_2(g) + 3H_2(g) \implies 2H_3(g)$$

Total number of moles of reactants = 4

Moles of products = 2

Therefore, increase in pressure on the system will shift the position of equilibrium from left to right because the forward reaction proceeds with a decrease in volume i.e since PV = constant, increase in pressure can only be achieved through the corresponding decrease in volume of the system.

Note: For reactions where total number of moles of reactants = total number of moles products, pressure changes have no effect on equilibrium position. These reactions include;

$$H_{2(g)} + I_{2(g)} = 2HI_{(g)}$$

3. Temperature

The increase in temperature of a system in equilibrium will cause the position of equilibrium to shift in a direction which proceeds with absorption of heat i.e to the endothermic side.

Effect of temperature on attainment of equilibrium

Increases in temperature increases the rate of attainment of equilibrium irrespective of whether the reaction is exothermic or endothermic.

This is because increase in temperature increases the speed of reacting particles which leads to increase in their kinetic energy have more frequent collisions which are energetic will occur leading to increase in the rate of reaction and hence attainment of equilibrium in a shorter time.

Effect of concentration on attainment of equilibrium.

At high concentration of reactants, the equilibrium is attained in a shorter time. This is because when the concentrations are high, the reacting particles are close to one another and therefore the chances of frequent collusions increase which increases the rate at which the reactants are converted to products.

Effects of a catalyst on attainment of equilibrium.

A catalyst does not change the composition of equilibrium mixture therefore it has no effect on the position of equilibrium. It also has no effect on the value of equilibrium constant. However, the catalyst affects both forward and backwards reaction to the same extent and their equilibrium position is attained more rapidly in the presence of catalyst.

Note: Pressure, concentration changes in equilibrium reaction do not have any effect on the value of the equilibrium constant because when the factors changes, there is no equilibrium in the system momentarily, but it is established after the change has been countered.

However, changes in temperature do affect the value of equilibrium constant in that;

- 1. If the reaction under consideration is endothermic, increase in temperature will lead to formation of more products from the reactants which means the K_C value (equilibrium constant value) will increase with increase in temperature.
 - 2. On the other hands, if the reaction under in equilibrium constant.

Determination of equilibrium constant between ethanol and ethanoic acid.

$$CH_3CO_2H$$
 (aq) + CH_3CH_2OH aq) \longrightarrow $CH_3CO_2CH_3$ (aq) + H_2O (aq)

Known volume of ethanol and ethanoic acid are mixed and then heated to about 60°C

It is then allowed to stand for about 8 hours in a flask in order to keep the temperature constant.

A fixed volume of the mixture is pipette and titrated with a standard solution of Sodium hydroxide using phenolphthalein indicator.

The amount of ethanoic acid present in equilibrium mixture is determined and then the equilibrium amount of other species present at equilibrium is deduced as shown below.

Let **a** and **b** be the initial moles of ethanoic acid and ethanol respectively.

$$K_{C} = \frac{[CH_{3}CO_{2}CH_{2}CH_{3}][H_{2}O]}{[CH_{3}CO_{2}H][CH_{3}CH_{2}OH]}$$

$$= \frac{[x][x]}{[(\frac{a-x}{V})][(\frac{b-x}{V})]}$$
$$= \frac{x^2}{(a-x)(b-x)}$$

ACTIVITY

When 8.28g of ethanol was mixed with 60g ethanoic acid and the mixture heated and allowed to reach equilibrium, the amount of ethanoic acid present at equilibrium, determined by titrating the mixture with a standard solution of Sodium hydroxide using phenolphthalein indicator was 49.74g.

Calculate the equilibrium constant.

If 12g of ethanoic acid were instead mixed with 13.8g of ethanol at the same temperature as in a, calculate the mass of ethylethanoate present at equilibrium.

$$CH_3CH_2OH = (12X2) + 16$$

= **46**

46g is the mass of 1mole of ethanol.

8.28g is the mass of 1mole $\frac{1}{4} \times 8.28$

= 0.18moles

$$CH_3CO_2H = 12\times2+16\times2+4\times1$$

= 60

60g is the mass of 1mole of ethanoic acid.

$$CH_3CO_2CH_2CH_3 = (4x120 + (8x1) + (12x6)$$

= 128

128g is the mass of 1mole of ethylethanoate

49.74g is the mass of $1 \text{mole} \frac{1}{128} \times 49.74$

= 0.389moles

$$CH_{3}CO_{2}H_{(aq)} + CH_{3}OH_{(aq)} \qquad CH_{3}CH_{2}CH_{3}_{(aq)} + H2O_{(l)}$$
Initial moles 1 0.18 0 0
$$Equilibrium moles 0.829 \quad 0.089 \qquad 0.171 \quad 0.171$$

$$K_{C} = \frac{[CH_{3}CO_{2}CH_{2}CH_{3}][H_{2}O]}{[CH_{3}CO_{2}H][CH_{3}CH_{2}OH]}$$

$$K_{C} = \frac{(0.171)(0.171)]}{(0.829)(0.09)}$$

ACTIVITY

0.3 moles of Hydrogen and 0.14 moles of Iodine were heated to 630K. if 0.2 moles of Hydrogen Iodide were formed at equilibrium. Calculate the value of equilibrium constant K_c . Determine the mole composition at equilibrium of the system if 0.4 moles of Hydrogen and 0.1 moles of Iodine were heated at 630K. (K_c = **0.5**)

Degree of dissociation

It is the fraction of 1 mole of a compound that is converted to a new substance(s) when the system has attained equilibrium.

Example.

Consider the dissociation of phosphorous pentachloride. If \propto is the degree of dissociation and n is the initial moles, then at equilibrium;

 $PCl_{5\,(g)} \qquad \qquad PCl_{3\,(g)} + Cl_{2\,(g)}$ Initial moles $\qquad \qquad 0 \qquad \qquad 0$ Equilibrium $n(1-x) \qquad \qquad n \propto \qquad n \propto$

Total moles at equilibrium = $n - n \propto + n \propto + n \propto$.

= n+ n∝.

At constant temperature, PV = nRT for no dissociation of PCl₅.

However, on dissociation,

$$=(n+n\propto)RT$$

Hence, PV = nRT

But, total moles = $n + n \propto$

$$PV - nRT = n - \times RT$$

$$\propto = \frac{PV - nRT}{nRT}$$

$$\frac{PV}{mPT}$$
 - V

Consider the dissociation of ammonia.

$$2NH_3(g)$$
 \Longrightarrow $3H_2(g) + N_2(g)$

Initial moles n

0 (

Equilibrium mole
$$n(1-x)$$
 $\frac{3}{2} n \propto \frac{1}{2} n \propto$

Total moles at equilibrium = n - $n \propto + \frac{3}{2} n \propto + \frac{1}{2} n \propto$

From PV = n + n
$$\propto$$
 RT $\propto = \frac{PV}{nRT} - 1$

Example

- 1. 1 mole of phosphorus pentachloride was placed in a 10dm³ vessel at 400°C.
 - i) Calculate the pressure inside the vessel assuming that phosphorus pentachloride did not dissociate (R= 0.08 atml⁻¹ K⁻¹)

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

$$=\frac{1\times0.082\times(400+273)}{10}$$

= 5.52atm

ii) When phosphorus pentachloride was allowed to dissociate, the equilibrium mixture had a total pressure of 26 atmospheres with no change in volume and temperature. Calculate the degree of dissociation if 4 moles of phosphorus pentachloride were originally used under these conditions.

$$PCl_5(g)$$
 \longrightarrow $PCl_3(g) + Cl_2(g)$
oles 4 0 0

Initial moles 4

Ü

Equilibrium $4(1-\infty)$ 4∞ 4∞

Total number moles at equilibrium = $4 - 4 \propto + 4 \propto + 4 \propto$

From PV = nRT.

$$PV = 4 + 4 \propto + RT$$

$$\propto = \frac{PV}{4RT} - 1$$

$$= \frac{26 \times 10 - 1}{4 \times 0.082 \times (400 \times 273)}$$

Effect of an inert gas on the equilibrium position of a reversible reaction.

- 1. A reaction in which $\Delta n = 0$ e.g. $H_{2(g)} + I_{2(g)} \Longrightarrow 2HI_{(g)}$
 - i) At constant volume addition of an inert gas to the equilibrium reaction above at constant volume has no effect on equilibrium position. This is because the inert gas its own pressure in the vessel bit pressure has no effect on the position of equilibrium for such reactions, that proceed no change in volume.
 - ii) at constant pressure in the inert gas exerts pressure but since the reaction proceeds without change in volume, it will have not affect the partial pressures of the equilibrium mixture hence it does not affect the equilibrium position.

Reactions in which
$$\Delta n > 0$$
 e.g.
 $2SO_{2(g)} \longrightarrow 2SO_{2(g)} + O_{2(g)}$

- iii) Addition of an inert gas at constant volume.
 - At constant volume, the concentration of species present is not affected because inert gas goes not take part in the reaction: addition of inert gas does not affect equilibrium positions of the reaction. The concentration of inert gas not takes part in the equilibrium constant expression and therefore has no effect on the value of equilibrium constant.
- iv) At constant pressure inert gas exerts to its own pressure and at constant pressure it results in the reduction of partial pressures of the species in equilibrium mixture which therefore leads to increase in volume of the reaction mixture.
- v) This favours the forward reaction which proceeds with an increase in volume or number of gaseous molecules.
- 2. Reaction is which $\Delta n > 0$ e.g. $N_2(g) + 3H_2(g) \longrightarrow 2H_3(g)$

<u>Discuss</u> the effect of adding oxygen on the o the position of equilibrium and on the value of equilibrium constant for the above reaction;

- i) At constant volume.
- ii) At constant pressure.

At constant volume, the total pressure of the system increase. This is increase the frequency of collision amongst Hydrogen, Nitrogen and Ammonia. The equilibrium is attained with a decrease in volume; the forward reaction is favored by pressure increase hence the position of equilibrium is shifted to the right. The equilibrium constant is not affected.

At constant pressure – when Argon is added, the pressure of the system increases. To keep the pressure constant, the volume must increase. There is reduced frequency of collision hence rate of attaining equilibrium decreases. The backward reaction is favored by increase in volume and so the position is shifted to the left. The equilibrium constant is not affected.

TOPIC 3.0: IONIC EQUILIBRIA

GENERAL OBJECTIVE:

By the end of this topic, you should be able to describe behaviour of acids, bases, and salts in aqueous solutions

LESSON 3.1: ACIDS, BASES AND SALTS

By the end of this lesson, you should be able to;

- explain the concept of acids and bases according to various theories.
- explain the concept of conjugate bases and conjugate acids.
- classify acids and bases on the basis of their degree of ionization.
- explain the ionisation constants for weak acids and weak bases K_a and K_b
- derive general expression for K_a and K_b
- correctly apply knowledge about K_a and K_b in calculations.
- explain auto ionization (self-ionization) of water.
- derive an expression for K_w.
- explain the concept of pH of 1-14.

INTRODUCTION

An acid is:

• A substance that donates a proton.

A base is:

- A substance that accepts a proton.
- When an acid also called the <u>conjugate acid of the base</u> donates a proton, a base called the <u>conjugate base of an acid</u> is formed. For example: for H₂SO₄ acid, the conjugate base is HSO₄⁻

ACTIVITY: Copy and complete the following table:

	3
Conjugate acid	Conjugate base
HCl	
HNO_3	
H_2O	
NH_4^+	
$[Al(H_2O)_6]^{3+}$	

 When bases accept protons, they form the conjugate acids of the bases. For example, ammonia accepts a proton to form the ammonium ion which by definition is a conjugate acid of ammonia.

$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$$

Strength of acids and bases

- The strength of an acid is measured by the ease with which it releases a proton.
- *Strong acids:* easily release protons and are completely ionized in the solvents.

 Weak acids: do not easily release protons, and are partially ionized in the solvents.

Factors affecting acid strength

Nature of the solvent

- The more basic the solvent, the stronger will be the acid in such a solvent because the acid will easily donate its proton. If the solvent is of weaker base strength, the acid cannot easily donate its proton to it, hence behaving as a weak acid instead.
- Hence, ethanoic acid will show much more acid properties when dissolved in ammonia than when dissolved in water, because ammonia is stronger base than water.

Proton - conjugate base bond strength

- The stronger the proton conjugate base bond, the weaker the acid will be.
 This is because it is difficult to break the bond and release the proton.
- The weaker the proton base bond, the stronger the acid will be. This is because the bond can be easily broken and the proton easily released
- Hence HI is a stronger acid in aqueous solution than HF because the H-I bond is weaker than the H-F bond and can easily be broken to release protons more readily than that in H-F

Comparing acid strength

By using their degree of dissociation.

- Degree of dissociation is the fraction of each mole of an electrolyte that exists as ions. It can also be expressed as a percentage.
- A stronger acid has a higher degree of dissociation compared to a weak one.

By using their dissociation constants, K_{α} , (weak acids)

- Since a weak acid partially ionizes, a solution of a weak acid has the ions and the molecules of an acid present in equilibrium with each other.
- Hence the law of mass action can be applied to give the dissociation constant.
 i.e. for a weak acid HX,

$$HX(aq) \leftrightharpoons H^+(aq) + X^-(aq)$$

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

• An acid with a higher K_a value would have ionized more than the one with the lower value. Hence an acid with a higher K_a value is a stronger acid than the one with a lower value.

Dissociation of water

 Water is a weak electrolyte because it is slightly ionized

$$H_2O(l) \leftrightharpoons H^+(aq) + OH^-(aq)$$

 By applying the law of mass action the equation obtained is

$$K = \frac{[H^+][OH^-]}{[H_2O]} \dots \dots \dots \dots (1)$$

• But since the dissociation of water is very small,

$$[H_2O] \approx 1$$

• Hence, equation (1) becomes

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

- Which is called the *the ionic product of water*
- The numerical value of the ionic product of water is given by

$$K_w = 1 \times 10^{-14} mol^2 dm^{-6}$$

рΗ

• This is defined as the negative logarithm to base 10 of the hydrogen ion concentration of a given solution

i.e.
$$pH = -\log_{10}[H^+]$$

pH of water

- From $K_w = [H^+][OH^-] = 1 \times 10^{-14}$
- But $[H^+] = [OH^-]$

$$\therefore [H^+]^2 = 1 \times 10^{-14}$$

$$[H^+] = \sqrt{(1 \times 10^{-14})}$$

$$pH$$

$$= -\log_{10} \left(\sqrt{(1 \times 10^{-14})} \right)$$

pH of acids

Strong acids

- These are completely ionized in aqueous solution.
- Thus their $pH = -\log[H^+]$

Weak acids

• Weak acids do not completely dissociate even in very dilute solution. The $[H^+] \neq [Acid]$.

The hydrogen ion concentration depends on the degree of dissociation of the

Consider a weak acid HX which ionizes in aqueous solution as follows

HX(aq)

 $H^+(aq)$ $+ X^{-}(aq)$

Initial moles:

1

0

0

Equilibrium moles:

1-∝

 \propto

Equilirium • concetration

Applying the law of mass action:

$$K_a = \frac{[H^+][X^-]}{HX}$$

$$=\frac{\left(\frac{\alpha}{V}\right)\left(\frac{\alpha}{v}\right)}{\left(\frac{1-\alpha}{v}\right)}$$

$$K_a = \frac{\alpha^2}{v(1-\alpha)}$$

But

$$\frac{1}{v} = c$$

For weak acids, the degree of dissociation is very small such that

$$(1-\infty) \approx 1$$

Hence

$$ka = C \propto^2$$

From the above equation it can be seen that

$$[H^+] = C \propto$$

Also

$$[H^+] = \sqrt{CK_a}$$

pH of bases

Strong bases

These are assumed to be completely ionized. In solution, these produce hydroxide ions in the solution and not hydrogen ions. For this reason, the pH of the solution is determined indirectly from the ionic product expression. i.e.

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

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

Introducing

 $-\log_{10}$ both sides

$$-\log[H^+] = -\log\left(\frac{K_w}{\lceil OH^- \rceil}\right)$$

Hence
$$pH = pK_w - pOH$$

But

$$p \, Kw = 14$$

Therefore

$$pH = 14 - pOH$$

Weak bases

These are partially dissociated in solution. The hydroxide ion concentration in the solution as it was with the weak acids is dependent on the base dissociation constant, K_b or the degree of dissociation (\propto)

Hence
$$K_b = C \propto^2$$
 and $[OH^-] = C \propto$ or $[OH^-] = \sqrt{(K_b \times 1/C)}$

LESSON 3.2 SALTS

SPECIFIC OBJECTIVES: The learner should be able to:

- Explain the concept of salt hydrolysis.
- Derive an expression for K_h.
- Identify the various types of salts.
- Correctly apply knowledge of K_h in calculations.
- Explain the pH of the resultant solutions derived from hydrolysis of salts.

INTRODUCTION

Salt Hydrolysis

- Is the reaction of a salt with water to give a solution, containing the acid and base that reacted to form it, and whose pH is greater or less than seven
- Typically, salts are thought to give neutral solutions when dissolved in water. However, this is only true for salts derived from strong acids and strong bases. Other combination of salts when dissolved in water, give solutions whose pH is not exactly seven.
- Hydrolysis can occur in three different ways, all of which produce changes in pH

Salts of strong bases and weak acids

- When such salts are dissolved in water, they give alkaline solutions. (pH is greater than seven)
- Examples include: sodium ethanoate, potassium fluoride, sodium carbonate, potassium cyanide, sodium sulphite.
- The anion being a conjugate base of a weak acid, easily accepts protons from the water molecules to form an unionized weak acid and the hydroxide ion in solution. This makes the solution alkaline. Consider a salt such as sodium methanoate.
- Sodium methanoate in water dissociates into sodium and methanoate ions.

$$HCOONa(aq) \rightarrow HCOO^{-}(aq) + Na^{+}(aq)$$

• The methanoate ions then react with water molecules

$$HCOO^{-}(ag) + H_{2}O(l) = HCOOH(ag) + OH^{-}(ag)$$

• The free hydroxide ions in the solution make it alkaline.

 From the above equation, the law of mass action can be applied, to give

$$K = \frac{[HCOOH][OH^-]}{[HCOO^-][H_2O]}$$

• But since water is in large excess, its concentration does change much so that at equilibrium $[H_2O] \approx 1$.

Hence

$$K_h = \frac{[HCOOH][OH^-]}{[HCOO^-]}$$

The above expression is called the expression for the hydrolysis constant, K_h , of the salt, sodium methanoate.

 K_h is called the hydrolysis constant

pH of the solution

From the expression,

$$K_h = \frac{[HCOOH][OH^-]}{[HCOO^-]}$$

But

$$[HCOOH] = [OH^-]$$
$$[HCOO^-] \approx [salt]$$

Hence

$$K_h = \frac{[OH^-]^2}{[salt]}$$

$$[OH^-] = \sqrt{(K_h[salt])}$$

And

$$pH = 14 - pOH$$

Note

$$K_h = \frac{[HCOOH][OH^-]}{[HCOO^-]}$$

 Multiplying through the numerator and denominator by [H+]

$$K_h = \frac{[HCOOH][OH^-]}{[HCOO^-]} \times \frac{[H^+]}{[H^+]}$$

Re-arranging

$$K_h = \frac{[HCOOH]}{[HCOO^-][H^+]} \times [H^+][OH^-]$$

But

$$\frac{[HCOOH]}{[HCOO^-][H^+]} = \frac{1}{K_a}$$

And

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

Therefore

$$K_h = \frac{K_w}{K_a}$$

Salts of weak bases and strong acids

- When such salts are dissolved in water, they give acidic solutions. (pH is less than seven)
- Examples include: ammonium chloride, ammonium nitrate, methylammonium chloride, dimethylammonium nitrate.
- The cation of the salt being a conjugate acid of a weak base, easily releases protons to form an unionized weak base and a proton in solution. This makes the solution acidic
- For example, a solution of ammonium chloride is acidic will react with strongly electropositive metals such as zinc to liberate hydrogen. This is because
- Ammonium chloride dissociates fully in water

$$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

• The ammonium ions then react with water to form an acidic solution.

$$NH_4^+(aq) + H_2O(l) \iff NH_3(aq) + H_3O^+(aq)$$

 The oxonium ions produced then react with the metal to liberate hydrogen gas

$$Zn(s) + 2H_3O^+(aq) \rightarrow Zn^{2+}(aq) + H_2(q) + 2H_2O(l)$$

 From the above equation, the law of mass action can be applied, to give

$$K = \frac{[NH_3][H_3O^+]}{[NH_4^+][H_2O]}$$

 But since water is in large excess, its concentration does change much so that

pH of the solution

From the expression,

$$K_h = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

• But $[NH_3] = [H_3O^+] \text{ and } [NH_4^+] \approx [salt]$

Hence

at equilibrium $[H_2O] \approx 1$.

$$K_h = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

• The above expression is called the expression for the hydrolysis constant, K_h , of the salt, ammonium chloride

$$K_h = \frac{[H_3 O^+]^2}{[salt]}$$

$$[H_3O^+] = \sqrt{(K_h[salt])}$$

And

$$pH = -\log[H^+]$$

Note

It is also true that

$$K_h = \frac{K_w}{K_h}$$

Salts containing heavily hydrated cations

• A number of normal salts when dissolved in water give an acidic solution for example iron(III) chloride. This is because; the hydrated metal ion behaves as an acid. The high charge density of the cation causes greater attraction of the lone pairs in the water molecules. This attraction extends to O-H bonds which becomes weaker, so that a proton is lost to the solution

$$[Fe(H_2O)_6]^{3+}(aq) \qquad \Leftrightarrow \qquad [Fe(H_2O)_5OH]^{2+}(aq) \quad + \quad H^+(aq)$$

LESSON 3.2: BUFFER SOLUTION

SPECIFIC OBJECTIVES

By the end of this lesson, you should be able to;

- explain the concept of a buffer solution.
- classify buffers and give examples of each type.
- explain the action of a buffer.
- describe the preparation of a buffer.
- derive the Henderson-Hasselbalch equation.
- carry out calculations of pH of buffers.
- explain application of buffers.

This is a solution of definite pH which resists a change in its pH when a small amount of acid or alkali is added.

• A buffer solution consists of either a weak acid and its salt with a strong base or a weak base and its salt with a strong acid

Types of Buffers

Acidic buffers

• These contain a weak acid and its salt with a strong base. For example, methanoic acid and potassium methanoate, ethanoic acid and sodium ethanoate, carbonic acid and sodium carbonate.

Action of an acidic buffer

- Consider a buffer solution made of ethanoic acid and sodium ethanoate.
- Sodium ethanoate salt, ionizes fully in aqueous solution

$$CH_3COONa(aq) \rightarrow CH_3COO^{-}(aq) + Na^{+}(aq)$$

Ethanoic acid, a weak acid partially ionizes.

$$CH_3COOH(aq) \Leftrightarrow CH_3COO^{-}(aq) + H^{+}(aq)$$

- The presence of ethanoate ions from the salt suppresses the ionization of ethanoic acid further so that the solution contains large amount on ethanoate ions and ethanoic acid molecules.
- If a small amount of the acid is added to the solution, the hydrogen ions added react with ethanoate ions to ethanoic acid molecules.

$$CH_3COO^-(aq) + H^+(aq) \rightarrow CH_3COOH(aq)$$

• If a small amount of the alkali is added, the excess ethanoic acid molecules react with the hydroxyl ions added to form the salt and water.

$$CH_3COOH(aq) + OH^{-}(aq) \rightarrow CH_3COO^{-}(aq) + H_2O(l)$$

• Hence the pH of the solution remains unchanged

pH of an acidic buffer

 Ethanoic acid in the solution is partially ionized.

$$CH3COOH(aq) \leftrightharpoons CH3COO^{-}(aq) + H^{+}(aq)$$

By law of mass action,

$$Ka = \frac{[CH3COO^-][H^+]}{[CH3COOH]}$$

• But since the acid is only slightly ionized,

$$[CH3COO^{-}] \approx [salt]$$

 $[CH3COOH] \approx [acid]$

Therefore

$$K_a = \frac{[salt][H^+]}{[acid]}$$

$$[H^+] = \frac{K_a[acid]}{[salt]}$$

But
$$pH = -\log[H^+]$$

Basic buffers

 These contain a weak base, and its salt with a strong acid. For example, ammonia solution and ammonium chloride, methylammonium nitrate and methylamine solution.

ACTIVITY:

Explain the action of a basic buffer such as on consisting of ammonia solution and ammonium chloride.

pH of an acidic buffer

• Ammonia in the solution is partially ionized.

$$NH_3(aq) + H_2O(l)$$

$$\Leftrightarrow NH_4^+(aq)$$

$$+ OH^-(aq)$$

By law of mass action,

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3(aq)]}$$

But since the acid is only slightly ionized,

$$[NH_4^+] \approx [salt]$$

 $[NH_3] \approx [base]$

Therefore

$$K_b = \frac{[salt][OH^-]}{[base]}$$

$$[OH^{-}] = \frac{K_b[base]}{[salt]}$$

But
$$pH = 14 - pOH$$

Applications of buffer solutions

- Maintain constant pH of blood and tissue fluids
- In fermentation buffers prevent pH changes that would reduce the activity of enzymes
- In medicine, Solutions for intravenous injections are buffered so that pH does not change.
- in biochemical assays depend on enzymes and buffers are used to maintain the pH constant
- in industrial products such as shampoos and lotions
- in manufacture of drugs

LESSON 3.3: SOLUBILITY PRODUCT

SPECIFIC OBJECTIVES:

By the end of this lesson, you should be able to;

- explain the concept of dynamic equilibrium in a saturated solution.
- explain the factors that affect solubility of sparingly soluble salts.
- derive an expression for solubility product.
- carry out an experiment to determine solubility product.
- calculate K_{sp}. and carry out calculations involving K_{sp}.
- explain relationship between ionic product, K_{sp}, and precipitation.
- explain the applications of K_{sp}.
- explain the concept of common ion effect.
- explain the application of common ion effect.

INTRODUCTION

Solubility product concept.

- This applies to a sparingly soluble salt.
- When a sparingly salt such as lead (II) sulphate is added to water, little of it
 dissolves and produces ions in the solution while most of it remains **not**dissolved. Thus equilibrium is set up between the solid and its ions in
 solution. Consider a sparingly soluble salt, MX which dissolves in water
 according to the equation.

$$MX(s) \leftrightharpoons M^+(aq) + X^-(aq)$$

- Since the ions are in contact with the solid, the solution is said to be saturated.
- By law of mass action,

$$K = \frac{[M^+][X^-]}{[MX]}$$

- But since the solubility of the salt is very small, the $[MX] \approx 1$.
- Hence the equation becomes

$$K_{sp} = [M^+][X^-]$$

- Which is the solubility product expression for a sparingly soluble salt, MX.
- The K_{sp} is called the solubility product constant.
- The <u>solubility product</u> of a sparingly soluble ionic compound is the product of the molar concentration of the ions produced by the compound raised to their stoichiometric powers in a saturated solution at a given temperature.

• Solubility of a solute

Is the mass of a solute in grams required to saturate specified amount solvent {e.g. 100g of water} at a given temperature.

• Saturated solution:

Is a solution that cannot dissolve any more solute at a given temperature in the presence of un-dissolved solute.

• The solubility of a sparingly soluble salt can be determined by conductivity measurements e.g. for barium sulphate or titration and the solubility product calculated e.g. magnesium hydroxide, calcium iodate.

Note:

When

- $K_{sp} = [M^+][X^-]$; The solution is said to be saturated
- $K_{sp} > [M^+][X^-]$; The solution is unsaturated
- $K_{sp} < [M^+][X^-]$; Precipitation occurs

<u>Determination of the solubility product of sparingly soluble salt such as silver oxalate</u>

• This can be done by titration method.

Procedure

- Excess silver oxalate is added to a given volume of water in a container.
- The container is stoppered and shaken occasionally for about two hours.
- The solution is filtered to removes the excess solid
- An aliquot of the filtrate is pipetted into a conical flask and to above 60°C.
- The **hot** solution is titrated with a standard solution of potassium manganate(VII).
- The concentration of the oxalate ions in the solution is calculated.

Treatment of results

$$Ag_2C_2O_4(s) \iff 2Ag^+(aq) + C_2O_4^{2-}(aq)$$

• Let
$$[C_2O_4^{2-}] = x$$

• $[Ag^+] =$
• $X_{sp} = [Ag^+]^2[C_2O_4^{2-}]$
• $X_{sp} = (2x)^2x$
• $X_{sp} = (2x)^2x$

Factors which affect the solubility of a sparingly soluble salt

Formation of complex ion

Consider a sparingly salt such as silver oxalate.

$$Ag_2C_2O_4(s) = 2Ag^+(aq) + C_2O_4^{2-}(aq)$$

• The solubility of this salt can be increased by adding ammonia solution. This is because ammonia reacts with silver ions to form the diamminesilver(I) complex ions.

$$Ag^{+}(aq) + 2NH_{3}(aq) \rightarrow [Ag(NH_{3})_{2}]^{+}(aq)$$

- This reduces the concentration of silver ions in equilibrium. And in order to restore the K_{sp} , more silver oxalate dissolves.
- Hence, <u>formation of a complex ion increases the solubility of a sparingly</u> soluble salt.
- The solubility of lead(II) chloride is higher in concentrated hydrochloric acid than water or dilute hydrochloric acid du formation of a complex ion, tetrachloroplumbate(II).

$$PbCl_2(aq) + 2Cl^-(aq) \rightarrow [PbCl_4]^{2-}(aq)$$

• Copper(I) salts are also more soluble in aqueous ammonia than water because of formation of the complex ion, diamminecopper(I) ion.

$$Cu^{+}(aq) + 2NH_{3}(aq) \rightarrow [Cu(NH_{3})_{2}]^{+}(aq)$$

Common ion effect

- This is the precipitation of a sparingly soluble ionic solute from its saturated solution by adding to the solution another electrolyte containing an ion common to that of the sparingly soluble compound.
- The <u>common ion effect reduces the solubility of a sparingly soluble salt</u>.
- Consider a sparingly soluble salt such as silver chloride.

$$AgCl(s) \iff Ag^+(aq) + Cl^-(aq)$$

- When silver nitrate is added to such a solution, the concentration of silver ions in the solution increases, the ionic product exceeds the K_{sp} , the excess silver ions react with chloride ions to form silver chloride solid and the K_{sp} is restored.
- The same thing would occur if sodium chloride was added to a saturated solution of silver chloride

Applications of common ion effect

Purification of common salt.

Common salt contains calcium and magnesium chloride as impurities.
 Bubbling hydrogen chloride through a saturated solution of impure sodium chloride will precipitate sodium chloride while leaving calcium and magnesium chlorides in the solution

Salting out of soap

• In the preparation of soap, a concentrated solution of sodium chloride is added to the reaction mixture to precipitate soap.

Selective precipitation of compounds in qualitative analysis

- This also uses the knowledge of solubility product and common ion effect, for example the precipitation of sulphides.
- Certain metal sulphides are precipitated by passing hydrogen sulphide into a solution of the metal ion in presence of an acid while others in the presence of alkali.
- The choice of the conditions depends on the solubility product of the sulphide.
- Precipitation of sulphides such as *ZnS*, *MnS*, and *NiS* occurs in alkaline medium (presence of dilute ammonia).
- Hydrogen sulphide ionizes in water as follows

$$H_2S(aq) \leftrightharpoons 2H^+(aq) + S^{2-}(aq)$$

• In the presence of an alkali, hydrogen sulphide reacts with the alkali the hydrogen ions react with the hydroxide reducing their concentration in equilibrium. This causes further ionization of hydrogen sulphide and the concentration of the sulphide ions increases. The high K_{sp} of the sulphides is reached which enables them to precipitate.

• While, sulphides such as CuS, SnS and CdS with low K_{sp} values are precipitated in acidic medium (presence of dilute hydrochloric acid). The hydrogen ions from the acid suppress the ionization of hydrogen sulphide. Very low concentration of sulphide ions occur in solution but enough to reach the K_{sp} of the metal sulphides hence precipitated.

Use of potassium chromate (IV) in silver titration

- When silver nitrate solution is titrated with sodium chloride solution containing a little potassium chromate(IV), only silver chloride is precipitate as long as there are any chloride ions in the solution. The red precipitate of silver chromate(VI) appears when all the chloride ions are reacted.
- This is explained by the solubility products of the two silver salts.

$$K_{sp}(AgCl) = 1 \times 10^{-10} mol^2 dm^{-6}$$
 and $K_{sp}(Ag_2CrO_4) = 2.5 \times 10^{-12} mol^3 dm^{-9}$.

• Suppose the concentration of Cl^- and CrO_4^{2-} are both $0.1 \ mold m^{-3}$ then the concentration of silver ions needed to precipitate silver chloride

$$= \frac{1 \times 10^{-10}}{0.1} = 1 \times 10^{-9} \, moldm^{-3}$$

• Concentration of silver ions needed to precipitate silver chromate

$$= \sqrt{\left(\frac{2.5 \times 10^{-12}}{0.1}\right)} = 5 \times 10^{-6} \ moldm^{-3}$$

 Thus even if the concentration of chloride and chromate ions in the solution is the same, it is easier by adding silver ions to reach the solubility product of silver chloride than that of silver chromate in spite of the lower solubility product of the latter.

LESSON 3.4: ACID - BASE INDICATORS

By the end of this lesson, you should be able to;

- explain the action of an indicator.
- give examples of indicators.
- describe how an indicator works.
- explain the concept of pH range.
- choose a suitable indicator for acid-bases titration.
- carry out acid-bases titration.
- sketch different types of pH volume curves for acid-bases titration.

INTRODUCTION

- Acid base indicators are substances which can change colour according to the hydrogen ion concentration of the liquid in which they are placed.
- They are weak acids; hence they are slightly dissociated when dissolved in water. The colour of the indicator depends on the colour of the undissociated molecules and the colour of the ions produced.

Action of an indicator

• Consider an indicator, HIn, when put in water, it ionizes as follows

$$HIn(aq) \leftrightharpoons H^+(aq) + In^-(aq)$$

- And at this point, there are indicator molecules (*HIn*) and ions in the solution and the colour of the solution will be an intermediate of the two. e.g. in water methyl orange is orange, while phenolphthalein is colourless.
- **Addition of an acid**, increases the hydrogen ion concentration in the solution. These combine with the In^- in the solution to form the unionized HIn indicator molecules. The HIn molecules of litmus and methyl orange are red, while those of phenolphthalein are colourless.
- Addition of an alkali, provides hydroxide ions which react with the hydrogen ions from the indicator. This reduces the concentration of the hydrogen ions in equilibrium. More of the indicator molecules ions, increasing the concentration of the In^- ions in the solution, hence the colour of the solution also changes to that of the In^- ions. e.g. the In^- ions of litmus are blue, methyl orange are orange, and phenolphthalein pink

Choice of an indicator

- The true point of neutralization in any titration occurs when the amounts acid and base added together are chemically equivalent to each other. i.e. complete neutralization has taken place and a salt and water have been produced.
- However sometimes, the pH is not equal to 7 even at this point. This is because the salt formed at endpoint may undergo hydrolysis. The choice of the indicator will therefore depend on the pH of the solution at end point.
- Every indicator has a definite range of pH over which it changes colour, and if the pH at the end point of the titration falls within this range, then the indicator will be the ideal choice.

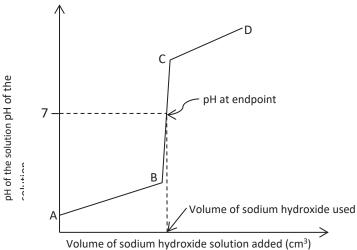
Table showing the ranges of some common indicators

Indicator	pH range
Methyl orange	2.9 – 4.6
Phenolphthalein	8.3 – 10.0
Litmus	5.0 – 8.0
Methyl red	4.2 – 6.3

- A titration between a strong acid (hydrochloric acid) and a weak base (aqueous ammonia), produces a salt, ammonium chloride which undergoes hydrolysis to form an acidic solution. Hence end point, the solution has a pH lower than seven. Methyl orange, litmus and methyl red would be ideal choices. (methyl range is commonly used)
- A titration between a weak acid (ethanoic acid) and a strong base, (sodium hydroxide) produces sodium ethanoate which hydrolyses in water to form an alkaline solution, with pH greater than seven. Phenolphthalein is the indicator of choice.
- A titration between a strong acid and a strong base forms a salt that does not undergo hydrolysis. pH of the solution at endpoint is seven and any indicator can be used for the titration.

pH CURVES

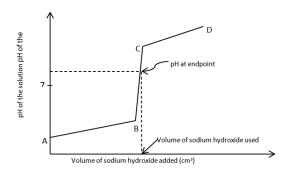
Titration of a strong acid against a strong alkali (hydrochloric *acid and* sodium hydroxide)



Explanation

- Initially, pH is low. Because hydrochloric acid is a strong acid the fully ionizes to give a high concentration of hydrogen ions.
- There is a gradual increase in pH between AB. This is because the acid is still in excess. The hydrogen ions gradually neutralized by the hydroxide ions from the alkali
- There is a rapid increase in pH between BC because the end point has been reached. A small amount of sodium hydroxide causes a big increase in pH.
- The pH continues to increase further between CD, due to addition of excess sodium hydroxide.
- The pH at endpoint is 7 because the salt formed (sodium chloride) does not undergo hydrolysis

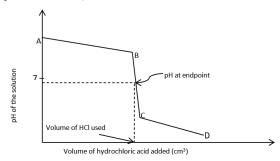
Titration of a weak acid against a strong alkali (ethanoic acid sodium hydroxide



Explanation

- Initially the pH is not very low. Because ethanoic acid is a weak acid that partially ionizes to give a lower concentration of hydrogen ions
- The pH increase gradually along AB as the alkali is added because of the gradual neutralization of the excess hydrogen ions by hydroxide ions. A buffer solution is formed that does not allow pH to change rapidly.
- pH increases rapidly along BC because the end point has been reached.
 Small amount of sodium hydroxide causes a big change in pH.
- The pH increase along CD because of excess sodium hydroxide added.
- The pH at end point is greater than 7 because of salt hydrolysis to form an alkaline solution

Titration of a weak alkali against a strong acid (aqueous ammonia and hydrochloric)s



Explanation

- Initially at A, the pH is not very high. Because aqueous ammonia is a weak base that partially ionizes to give fewer hydroxide concentration in the solution.
- The pH then decreases gradually along AB. This is because of addition of the hydrogen ions that neutralizes the hydroxide ions. The alkali is still in excess and together with the salt formed form a buffer solution that resists a rapid change in pH.
- The pH then decreases rapidly along BC when a small amount of the acid is added because the endpoint is reached.
- Along CD pH decreases gradually because of addition of excess acid
- The pH at endpoint is less than seven because the salt formed undergoes hydrolysis to produce hydrogen ions that make the solution acidic.

TOPIC 4.0 CHEMICAL KINETICS

GENERAL OBJECTIVE:

By the end of this topic, the learner should be able to appreciate that different reactions occur at different rates and explain why they do so.

LESSON 4.1 SIMPLE RATE EQUATIONS

By the end of this lesson, you should be able to:

- Explain the concept of chemical reaction.
- Explain the law of mass action and its application.
- Explain order of a reaction and rate constant.
- Define the different terms used in kinetics.
- Relate mechanisms of reactions to kinetics.

INTRODUCTION

- Chemical kinetics is a branch of chemistry that deals with the measurement of reaction velocities/rates and determination of mechanisms by which reactants are converted into products.
- The knowledge of chemical kinetics is useful when altering the rates of chemical reaction is needed. For instance, manufacturers of fertilizers aim at speeding up the formation of ammonia from nitrogen and hydrogen whereas a car manufacturer wishes to slow down the rate at which iron rust.

Rates of reaction

Reaction rate is the speed at which a chemical **reaction** proceeds. It is often expressed in terms of either the concentration (amount per unit volume) of a product that is formed in a unit of time or the concentration of a reactant that is consumed in a unit of time.

Consider the reaction

$$A \rightarrow product(p)$$
....(I)

The rate of the reaction or reaction velocity may be defined as the rate of disappearance of the reactant (A) or the rate of appearance or formation of the product (P) with respect to time.

Thus rate =
$$-\frac{dA}{dt} = \frac{dP}{dt} = K[A]$$

Where, K, is the rate constant.

In general, for a reaction

$$aA + bB \rightarrow cC + dD$$
(II)

The rate of reaction is given as

Rate =
$$-\frac{1}{a}\frac{dA}{dt} = -\frac{1}{b}\frac{dB}{dt} = +\frac{1}{c}\frac{dC}{dt} = +\frac{1}{d}\frac{dD}{dt}$$

Since the reaction depends on the concentration of the reactants, the rate equation for the reaction in (II) can be expressed in a rate equation represented as

Rate =
$$K[A]^x[B]^y$$
.

Definitions terms in a rate law

- i) [A] is the molar concentration of reactant A
- ii) **x** is the order of reaction with respect to A
- iii) **y** is the order of reaction with respect to B.
- iv) The algebraic sum (**x** + **y**) is the overall order of the reaction. i.e. the order of the reaction is the sum of power dependence of the rate on the concentration of each reactant.
- v) **K** is the **rate constant**, or the specific **rate constant**. It is the proportionality **constant** in the **equation** that expresses the relationship between the **rate** of a **chemical** reaction and the concentrations of the reacting substances.

Stoichiometry of a reaction is the quantitative relationships of the amount of products and reactants in a given reaction

The values of x and y are often 0 or 1 or 2 and rarely 0, 3, fraction, or negative numbers.

These values x and y are experimentally determined values and cannot be predicted until one has carried out the experiment. The order of the reaction has nothing to do with the stoichiometry of the equation for the reaction.

For example, a simple reaction between bromated (V) ions, bromide ions and hydrogen ions to give bromine is represented by the equation:

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

This has a complex rate equation from kinetic measurements as expressed below:

$$-\frac{d[BrO_3^-]}{dt} = K[BrO_3^-][Br^-][H^+]^2$$

Determining the order of reaction

Method 1. **Initial rate method**. The order of a reaction can be found by comparing the initial rates of two more or reactions at known initial concentrations.

Example 1

The following results obtained for a reaction between A and B; can be used to determine the order of reaction with respect to A and with respect to B and the rate constant.

Run	Concentration (moldm ⁻³)		Initial rate (moldm ⁻³)
	A	В	*******
(a)	0.50	1.0	2.0
(b)	0.50	2.0	8.0
(c)	0.50	3.0	18.0
(d)	1.0	3.0	36.0
(e)	2.0	3.0	72.0

Let the rate equation = $K[A]^x[B]^y$

To obtain x, which compare reactions in which the concentrations of B are constant but those of A vary such as (d) and (e):

$$\frac{Rate(e)}{Rate(d)} = \frac{72}{36} = \frac{K[2.0]^{x}[0.3]^{y}}{K[1.0]^{x}[0.3]^{y}}$$

To obtain y, which compare reactions in which the concentrations of A are constant but those of B vary such as (b) and (a):

$$\frac{Rate(b)}{Rate(a)} = \frac{8.0}{32.06} = \frac{K[0.50]^{x}[2.0]^{y}}{K[0.50]^{x}[1.0]^{y}}$$

Calculating the rate constant, K,

We substitute for x and y in the and any of the experimental results above, in the rate equation e.g. (a)

$$2 = K [0.5]^{1}x [1.0]^{2}$$

 $K = 4.0 dm^{6} mol^{-2}s^{-1}$

Activity

1. Tabulated are values of initial rates for the reaction

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

Experiment	[A] ₀ (moldm ⁻³)	[B] ₀ (moldm ⁻³)	Initial rate (moldm ⁻³ min ⁻¹)
1	0.150	0.25	1.4 x 10 ⁻⁵
2	0.150	0.50	5.6 x 10 ⁻⁵
3	0.075	0.50	2.8 x 10 ⁻⁵
4	0.075	0.25	7.8 x 10 ⁻⁵

a) Find the order of reaction with respect to A, the order of reaction with respect to B, and the overall order of the reaction.

- b) Find the value of the rate constant
- c) Find the initial rate of the reaction when $[A]_0 = 0.120$ moldm⁻³ and $[B]_0 = 0.22$ moldm⁻³.

Activity 2

The rate equation for a certain reaction is:

Rate = $K[P][Q]^2[R]$

- a) State what would happen to the rate of reaction if
 - i) the concentration of P and Q is kept constant, but that of R is doubled.
 - ii) the concentration of all species are halved
 - iii) the concentration of all species are doubled
- b) the following were obtained in a study of reaction between peroxodisulphate and iodide ions

Expt. No.	[S ₂ O ₈) ²] Moldm ⁻³	[I'] Moldm ⁻³	Rate Moldm ⁻³ s
1	0.024	0.024	9.60 x 10 ⁻⁶
2	0.048	0.024	1.92 x 10 ⁻⁶
3	0.048	0.012	9.60 x 10 ⁻⁶

- i) Write the rate equation
- ii) Calculate the rate constant for the reaction and state its units

iii)

LESSON 4.2: REACTIONS OF VARIOUS ORDERS

SPECIFIC OBJECTIVES.

By the end of this lesson, you should be able to;

- describe the experimental procedure to determine orders of reaction.
- explain the concept of half-life.

INTRODUCTION

1. FIRST-ORDER REACTION

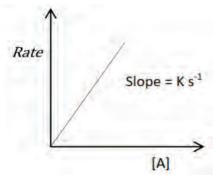
A reaction is said to be first order if the rate is proportional to the first power of concentration of reactants on which the reaction kinetics depends. That is, the rate law for the first order reaction is given by

Rate =
$$K[A]$$

Identification of a first-order reaction

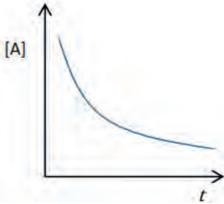
The first-order reaction can be identified from the shapes of the following graphs.

All these graphs that show that the rate of reaction is proportional to the concentration of the reactant in the chemical reaction.



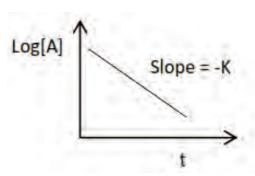
- i) Rate of reaction against concentration

 A straight line with a positive gradient shows that the rate is proportional concentration of the reactant and that the reaction is thus first order.
- ii) The concentration of the reactant against time.



Hyperbola shows that the rate of reaction is proportional to the concentration of the reactant and thus the first-order reaction

iii) For a first-order reaction, a plot logarithm of concentration against time gives a straight line with a negative gradient.



A typical example of a reaction that follows a first-order reaction mechanism is a radioactive disintegration process.

Definitions

Radioactive decay (also known as nuclear decay, radioactivity, radioactive disintegration, or nuclear disintegration) is the process by which an unstable atomic nucleus loses energy by radiation.

The integrated rate law for the first-order reaction

Consider the first-order reaction

 $A \rightarrow P$

If the initial concentration [A] of reactant (A) at the time, t=0, is **a** moldm⁻³ and the concentration of the product, P, after time t is **x** moldm⁻³; then concentration of A at time, t, will be (a-x) moldm⁻³.

Then, the rate of reaction as the rate of formation of the product is represented as

$$\frac{dx}{dt} = k[a - x]$$

Or, separating variables,

$$\frac{dx}{(a-x)} = kdt$$

To get relationship between concentration and time, integrate both sides, i.e.

$$\int \frac{dx}{(a-x)} = \int kdt$$
$$-In(a-x) = kt + C$$

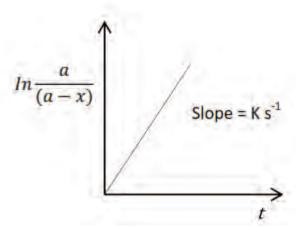
At t = 0, x = 0, thus, C = -Ina

Substituting for C, we derive the relationship:

$$Ina - In(a - x) = kt$$

$$In\frac{a}{a - x} = kt$$

The plot of $In\frac{a}{a-x}$ against time, t, gives a straight line and the slope of this graph is equal to ks^{-1} .



Half-life of the first order reactions

The half-life of the reaction is the time taken by a reactant to reduce to half of its initial concentration.

The expression for the half-life of a first-order reaction is obtained from the integrated rate law: i.e.

$$In\frac{a}{a-x} = kt$$

At
$$t = t_{\frac{1}{2}}$$
, $(a - x) = \frac{a}{2}$,

Where $t_{\frac{1}{2}}$ is half-life Then,

$$In\frac{a}{\frac{a}{2}} = kt\frac{1}{2}$$

And thus,

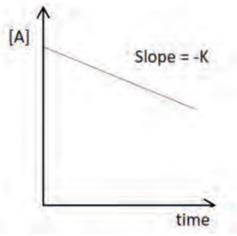
$$t^{1/2} = \frac{ln2}{k}$$

Note that, Inx = 2.303logx

This shows that in the first-order reaction, the half-life is independent of the initial concentration of the reactants. The time necessary for the reactants to decrease to any other given fraction can be derived in a similar manner.

2. Zero-order reactions

In a zero-order reaction, the rate is independent of the concentration of the reactants. A plot of the concentration [A] of the reactant against time has the form below:



The rate equation for a zero-order reaction:

Rate =
$$K[A]^0$$
 or Rate = $K s^{-1}$

Example, the reaction between iodine and propanone is a zero-order with respect to iodine.

$$CH_3COCH_3(aq) + I_2$$
 acid $CH_3COCH_2I(aq) + HI(aq)$

Pseudo-order reaction

A **pseudo order reaction** is a reaction that is truly **higher-order** but can be approximated to a **lower order** under special circumstances.

For instance, an elementary reaction between two reactants A and B is normally expected to be a second-order; for example, hydrolysis of an ester and inversion of sucrose.

$$CH_{3}COOC_{2}H_{5} + H_{2}O \xrightarrow{H^{+}} CH_{3}COOH + CH_{3}CH_{2}OH$$

$$C_{12}H_{22}O_{11} + H_{2}O \xrightarrow{H^{+}} C_{6}H_{12}O_{6} + C_{6}H_{12}O_{6}$$
Glucose fructose

However, if one of the reactant B is present at a very much greater concentration than that of A or else only acts as a catalyst, the concentration of B is considered constant ad the rate law becomes

Rate =
$$K'[A]$$

Such a reaction is said to be pseudo-first order since the rate is proportional to the concentration of A raised to the first power. Nevertheless, it must be remembered that the new constant (K') is not a true constant because it also depends on the concentration of B. Since water is usually found in excess, the reactions are given above are in practice found to be pseudo-first-order.

Note that:

- 1) For a zero-order reaction, any change in concentration of the reactant does not affect the rate of reaction.
- 2) For a first-order reaction increasing the concentration of the reactant two or three times also increase the rate two or three times.

Activity

- a) State what is meant by the term order of a reaction
- b) Methylethanoate is hydrolyzed by water in the presence of an acid according to the following reaction:

$$CH_3COOCH_3 + H_2O(l) / \hookrightarrow / CH_3CH_2OH + CH_3OH$$

- i) State the molecularity of the reaction
- ii) State the conditions under which the reaction can be the overall first order
- c) The table below shows some kinetic data for the following reaction:

Expt. No.	[A) Moldm ⁻³	[B] Moldm ⁻³	Rate Moldm ⁻³ s ⁻¹
1	0.20	0.20	1.2 x 10 ⁻⁸
2	0.20	0.60	1.2 x 10 ⁻⁸
3	0.40	0.60	4.8x 10 ⁻⁸

- i) Write the overall order of reaction
- ii) Calculate the rate constant and give its units.

LESSON 4.3: MEASURING THE RATES OF REACTIONS

By the end of this lesson, you should be able to;

- apply the knowledge of rate equations in sketching and interpreting graphs.
- discuss the relationship between a mechanism of reaction and molecularity.

- carry out designed experiments to generate kinetic data for determining order of reaction, rate of reaction and rate constants.
- explain the theories of collision.
- use theories of reaction to explain factors that affect rates of reaction

INTRODUCTION

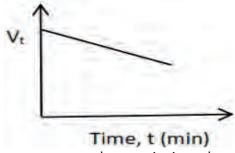
The rate of a chemical reaction can be obtained by following some property which alters with the extent of the reaction. By analyzing the reaction mixture at suitable intervals, it's possible to determine the concentration of both the reactant and/or the product at different times and hence obtaining the rate (i.e. the rate at which the concentration of a particular substance changes with time).

In practice, the rates may be measured by observing the rate of change of physical properties such as refractive index, volume, color, and if the reaction is sufficiently slow, its rate may be found by frequent withdrawal of small portion of the reacting mixture and analyze then chemically at intervals.

Example: Iodination of propanone

An experiment to determine the order reaction with respect to iodine in the reaction of iodine with propanone in presence of an acid catalyst.

- 1. A fixed volume of standard Iodine solution is added to an excess of propanone solution in a flask.
- 2. To this mixture is added a fixed volume of dilute sulphuric acid and a stop clock started immediately.
- 3. At intervals of time say (every 10 minutes for 50 minutes), a specified portion is pipetted from the mixture and into a flask containing sodium hydrogen carbonate which stops the reaction by neutralizing the acid catalyst.
- 4. The resultant mixture is titrated with standard sodium thiosulphate using a starch indicator.
- 5. The volume (V_t) of thiosulphate used on the portion of the mixture after a specified time (t) is proportional to the amount of iodine remaining in the mixture.
- 6. The initial amount of iodine (V_0) is obtained by titrating a similar portion of the original mixture with sodium thiosulphate solution.
- 7. A plot of the graph of V_t against time gives a straight line as shown below showing that the order of reaction with respect to iodine is zero.



NB. The gradient gives the rate constant whose units is molcm⁻³ s⁻¹.

Activated complex

With the exception of radioactive disintegration all elementary reaction occurs via a transition state, for example, substitution reaction is expected to proceed as below

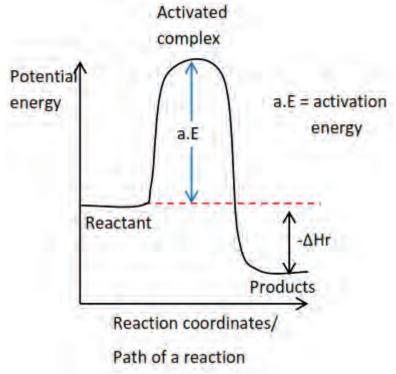
$$A + BC \quad \longleftrightarrow \quad [A....B.....C] \quad \longleftrightarrow \quad AB + C$$

In order to form the transition state, the reactants must first acquire activation energy i.e. This is the minimum energy required for the reaction to take place. Being energy-rich, the transition species is unstable and cannot be isolated and is usually referred to as the activation complex. This may decompose either to give the product or original reactants. The energy variation during the above process may be represented by the figures below:

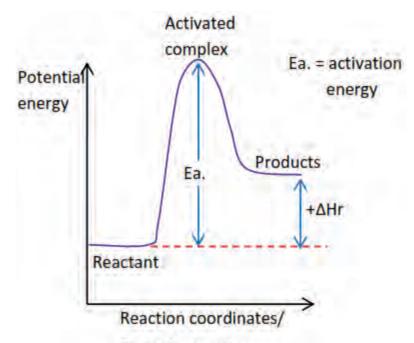
Definition

An **activated complex** is short lived intermediate involving unstable arrangement of atoms that results in the maximum **energy** point along the reaction path.

The energy diagram for the reaction for an exothermic reaction



The energy diagram for the reaction for an endothermic reaction



Path of a reaction

The difference between the energy of the reactants and the product is the enthalpy of the reaction (ΔH_r) which is negative for exothermic reaction (i.e. energy given out during the reaction and the reaction mixture heats up) or positive for endothermic reaction (i.e. energy is required for the reaction to take place.)

Definition

The **molecularity** of a reaction is defined as the number of molecules or ions that participate in the rate-determining step.

The **activation energy** of a **chemical** reaction is the difference between the energy of the **activated complex** and the **energy** of the reactants.

Factors that affect the rate of reaction

The main factors which influence reaction rate are

- i) concentration of the reactant
- ii) temperature
- iii) Pressure
- iv) presence of light
- v) the size of the particles for solid reactants.
- vi) Catalyst

1. Particle size

The smaller the particle sizes the faster the reaction in the solid state because of increased surface area for contact. e.g.

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

The reaction is faster when CaCO₃ is in powder form than big chips.

2. Concentration

The higher the concentration of reactants; the faster is the rate of reaction due to the increase in the rate of collision among the reacting molecules.

3. Pressure

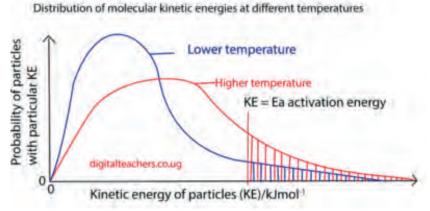
Pressure increases the rate of reaction when the reactants are in the gaseous phase because it increases the proximity and the rate of collision of the reacting molecules.

4. Temperature

Temperature increases the rate of reaction because

- Particles gain kinetic energy which increases the rate collision
- it increases the fraction of molecules with energy equal or higher than the activation energy that enables the reaction to take place in case collision take place between molecules.

The graph below shows the distribution of kinetic energies of molecules of a gas at temperatures T_1 and T_2 ; T_2 being higher than T_1 .



The number of molecules with energy equal to or greater then E_a increases rapidly with temperature as shown by the shaded area under graph above.

5. Light

Some reactions are catalyzed by light such as photosynthesis and formation of silver from silver salts that take place when a photographic film is exposed to light. The higher the light intensity, the higher the rate of reaction will be.

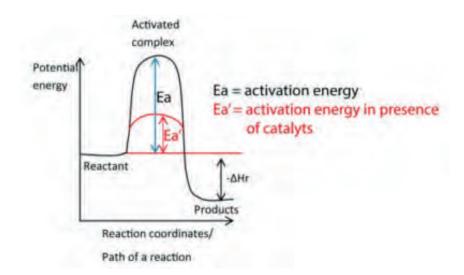
6. Surface area

Increasing surface area of the reactant increases the rate of reaction because it brings the reacting substances into more intimate contact to facilitate their interaction.

7. Catalyst

Increase the rate of reaction by lowering the activation energy

The energy diagram for the reaction for exothermic reaction in the absence and presence of a catalyst.



TOPIC 5.0 ELECTROCHEMISTRY

GENERAL OBJECTIVE:

By the end of this topic, the learner should be able to outline the effect of electric current on substances and the ability of the substances to generate electricity.

LESSON 5.1 ELECTROCHEMICAL CELLS

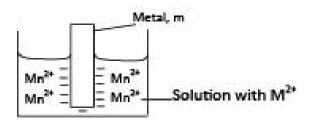
SPECIFIC OBJECTIVES.

By the end of this lesson, you should be able to;

- explain the concept of electrode potential.
- describe the electrochemical series.
- use the electrochemical series to explain the absolute and relative electrode potential.
- describe the structure and functioning of standard hydrogen electrode.

INTRODUCTION

When a strip of metal is placed in a solution of its ions, the metal atoms tend to ionize; cations dissolve in solutions while electrons remain on the metal surface. For instance, a divalent metal, M, ionizes as follows



The attraction of the metal rod (containing negative charge) and the solution (containing positive charges) causes a potential difference called **electrode potential**.

The metal dipped into it's a solution containing metal ions is called electrode half-cell represented symbolically as M^{n+}/M . For example, a half-cell of zinc rod dipped in zinc ion solution is symbolized as Zn^{2+}/Zn

Electrode potential is a potential difference that is set up between a metal and its solution containing metal ions.

Factors affecting the magnitude of the potential difference

- 1. **The concentration of metal ions already in solution**. Since the ionization equation (1) is a reversible reaction, the higher the concentration of metal ions in solution, the further to the left will be the state of equilibrium and hence the smaller the electrode potential.
- 2. **Temperature.** Increasing temperature increases the ionization of metal atoms and thus increases the electrode potential.
- 3. **Pressure: applicable to gas systems**, the higher the pressure the higher the electrode potential because increased pressure increases the gas concentration at gas-liquid junction.
- 4. **Position of metal in electrochemical series.** Metals above hydrogen in electrochemical series, have ionization reactions that lie more to the right than left, thus, the metal tends to be negatively charged with respect to their solutions. Thus, have negative electrode potentials.

Metals below hydrogen in electrochemical series, their ionization reaction lie more to the left and their electrode potentials are positive.

Standard electrode potential (SEP)

This is the electrode potential of a metal dipped in a solution containing one mole of metal ions in a dm³/litre of solution at 298K and 1 atmosphere. It is denoted by E⁰.

Factors affecting standard electrode potential

Electrode potential involves formation of hydrated ions. It is a sum of atomization energy (which is endothermic) + ionization energy (which is endothermic) + ionic hydration energy (which is exothermic).

When atomization and/or ionization energy is high, the standard electrode potential becomes more positive.

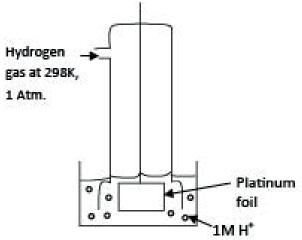
On the other hand, when the hydration energy is higher than the sum of ionization and atomization energy, standard electrode potential is negative.

Short-hand Notation for an electrode half cells

A metal rod dipped in a solution of metal ions constitutes a half cell. The accepted short form of writing an electrode is to write is to write 'oxidized form/reduced form' of metal. For example, the zinc half-cell is written as Zn²⁺/Zn and copper electrode as Cu²⁺/Cu.

Standard Hydrogen electrode

It consists of hydrogen gas at 298K and pressure of 1 atmospheres bubbling over a strip of platinized foil (i.e. platinum coated) in a solution which is 1M with respect to H⁺ ions



The shorthand notation for a hydrogen electrode is

$$H^+$$
, $M/\frac{1}{2}$ H_2 , 1 atm. Or $H^+/\frac{1}{2}$ H_2 .

And electrode reaction is

$$H+(aq) + e \rightarrow \frac{1}{2} H_2(g)$$

A potential develops on the surface of the platinum; by convention, it is assigned an arbitrary value of zero volts.

Hydrogen electrode is use as a reference electrode and the electrode potential of all other electrodes are measured relative to this.

LESSON 5.2: Measurement of electrode potential of metal

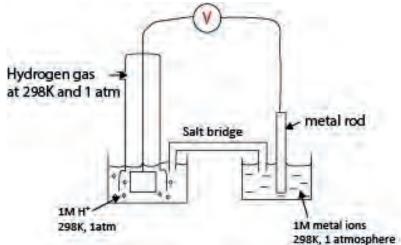
SPECIFIC OBJECTIVES:

By the end of this lesson, you should be able to;

- describe the measurement of standard electrode potential.
- explain the term reduction potential.
- apply reduction potential to metal-metal ion convention cells.
- construct an electrochemical cell.
- write the cell notation.
- calculate the e.m.f of a cell and use it to predict spontaneity of reactions.

INTRODUCTION

A standard metal electrode is combined with a standard hydrogen electrode as shown in Fig.4.3 below



The two compartments in the figure are connected by a **salt bridge**. This contains an electrolyte such as potassium chloride, which conducts electricity but does not allow mixing of two solutions in half cells. The measurement on the high resistance voltmeter is the standard electrode of the metal since that of hydrogen half-cell is zero.

Definition

Standard electrode potential is the electrode potential value of an electrode measure with respect to a standard hydrogen electrode of 0 volts. When an electrode is immersed or dipped into a solution of 1M concentration of its ions at a standard temperature of 298K and pressure of 1 atmosphere.

Some electrode and their standard electrode potentials are given below:

Electrode	Electrode reaction E ^o /	volts
Zn ²⁺ /Zn	$Zn^{2+}(aq) + 2e \rightarrow Zn(s)$	-0.76
Cu ²⁴ /Cu	$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$	+0.34
Fe ²⁺ /Fe	$Fe^{2+}(aq) + 2e \rightarrow Fe(s)$	-0.44
Ag*/Ag	$Ag^{+}(aq) + e \rightarrow Ag(s)$	+0.80

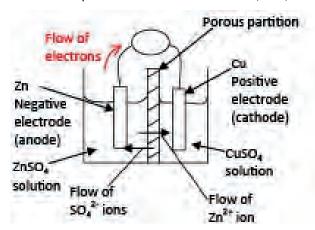
Galvanic or Voltaic cells or electrochemical cells

This is a type of cell in which a chemical reaction results in production of an electric current.

By combining two suitable electrodes (half cells) a cell of a particular emf may be obtained. One electrode acts as electron supplier and the other as electron acceptor.

The Daniel cell

It consists of the zinc electrode dipped into 1M zinc sulphate solution and copper electrode dipped into 1M copper sulphate solution, the two solution separated by a porous partition. The cell develops an electromotive force (emf) of 1.10V.



Half call reaction

At zinc electrode (anode)

Oxidation occurs and the electrode dissolves.

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

At the copper electrode

Reduction occurs (cathode)

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

Overall equation

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

Cell notation

The Daniel cell can be represented as

 $Zn(s)/ZnSO_4$ (aq)//CuSO₄ (aq)/Cu(s)

Or simply

 $Zn(s)/Zn^{2+} (aq)//Cu^{2+} (aq)/Cu(s)$

The single vertical line (/) indicates a phase boundary and double vertical lines (//) indicate a porous partition between the solutions.

E.m.f of a cell

The e.m.f of the above cell is given by $E = E_{Cu} - E_{zn}$

Rules regarding electrode potentials

1. If the direction of an electrode reaction is reversed, the sign of its electrode potential must also be reversed.

$$Zn^{2+}(aq) + 2e \rightarrow Zn(s)$$
 $E^0 = -0.76V$

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e$$
 E0 = +0.76V

a) If an electrode reaction equation is multiplied by a positive factor. The electrode potential must **not** be multiplied by that factor. It remains unchanged.

$$Zn^{2+}(aq) + 2e \rightarrow Zn(s)$$
 $E^0 = -0.76V$
 $2Zn^{2+}(aq) + 4e \rightarrow 2Zn(s)$ $E^0 = -0.76V$
Not 1.52V

Generally, the e.m.f of a cell is defined as follow

$$E^{0}_{cell} = E^{0}_{R.H.E} - E^{0}_{L.H.E}$$

NB. For a positive cell e.m.f, R.H.E is for the half cell with most positive electrode potential.

Example 1

Calculate the standard e.m.f of Zn/Zn²⁺//Cu from the data given below. Write down the half-cell reactions and cell reaction.

Electrode	Eº/V
Zn^{2+}/Zn	-0.76
Cu ²⁺ /Cu	+0.34
Answer	
$E^0_{cell} =$	$E^0_{R,H,E}-E^0_{L,H,E}$
=	0.34 - (-0.76) = +1.10V

Electrode reactions

At R.H.E (cathode)

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

L.H.E (anode)

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

Cell reaction

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

Implication of the e.m.f of a cell

For electrode; since, standard electrode potentials are reduction potentials, a negative value for E⁰ implies that the reduction reaction is non-spontaneous while a positive value implies that the reduction reaction is spontaneous.

For a cell a negative value of E⁰_{Cell} indicates that the cell reaction as written is non-spontaneous and instead is spontaneous in the reverse direction.

Therefore, the value of standard electrode potential may be used to predict the direction of spontaneous chemical reaction. Then when writing down or constructing a cell given two electrodes together with their standard electrode potentials, the electrode with the less negative E^o (if both are negative or electrode with more positive value if both are positive) must be the right hand electrode of the cell and the other the left hand electrode.

Activity

- a) Construct a cell using Li⁺/Li and Mg²⁺/Mg electrodes, given that E^0 Li⁺/Li = -3.04V and E^0 Mg²⁺/Mg = -2.37V.
- *b)* Calculate the E^ocell.
- c) Give the cell reaction

LESSON 5.3: STANDARD ELECTRODE POTENTIAL AND STANDARD FREE ENERGY CHANGE

SPECIFIC OBJECTIVES

By the end of this lesson, you should be able to;

- use Gibb's free energy expression to predict feasibility of reactions.
- describe the construction of Daniel cell.
- explain the functioning of a battery.
- explain the conversion of one form of energy to another.

There is a relationship between electrochemistry and thermochemistry. In the electrode reaction

$$Mn+ (aq) + ne \longrightarrow M(s)$$

If the standard free energy change, ΔG^0 then the value of the standard electrode potential, E^o , at the same temperature is given by

$$\Delta G^0 = -nFE^0$$

Where n is the number of electrons transferred in the electrode reaction and F is the Faraday constant.

For example, $E^0 = +0.34V$ at 298K for the reaction

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

The value of ΔG⁰ is given by

$$\Delta G^0 = -2 \times 96500 \times (-0.34) = 65.6 \text{kJmol}^{-1}$$
.

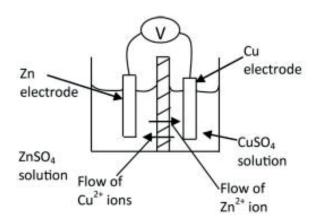
Liquid junction potential

Is a potential difference set up across a phase boundary between two solutions in a cell. It tends to oppose the cell potential i.e. it reduces it and hence the observed cell emf is less than the actual emf of the cell

Causes of liquid junction potential

It is caused by the differential diffusion of charges across the porous partition between the two solutions of the cell. For example, in the Daniel cell, the Zn²⁺ ions diffuse into the CuSO₄ solution and Cu²⁺ diffuses into the ZnSO₄ solution.

The speed of migration of Zn²⁺ and Cu²⁺ cations across the phase boundary is different due to a number of factors. Some of which are either the ionic size and/or the extent to which they are hydrated. Due to this, a p.d. is set up across the boundary called Liquid Junction Potential.



This liquid junction potential may be eliminated by connecting the solutions in the two half cells by means of a salt bridge which is a glass tube containing a saturated solution of either KCl or NH_4NO_3 .

NB. In the cell diagram/notation, the double lines either represent a porous partition or a salt bridge.

Types of electrodes

- 1. The metal/metalloid e.g. Zn²⁺/Zn
- 2. The gas electrode e.g. Pt, $H+/\frac{1}{2}H_2$
- 3. The metal/insoluble electrode: this type of metal coated with one of its insoluble salt surrounded by a solution containing the anion of the salt e.g. Hg/Hg₂Cl₂, KCl(aq) or Hg/Hg₂Cl₂, Cl⁻ This electrode is commonly known as a calomel electrode.
- 4. Ag/AgCl(s), Cl⁻

Possible electrode reactions

As R.H.E (reduction) AgCl (s) $+ e \rightarrow Ag(s) + Cl^{-}(aq)$ As L.H.E (oxidation) Ag(s) $+ Cl^{-}(aq) \rightarrow AgCl(s) + e$

 Hg/Hg_2Cl_2 , KCl(aq) or Hg/Hg_2Cl_2 , Cl^- This electrode is commonly known as a calomel electrode.

Possible electrode reactions

As R.H.E (reduction) $Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-(aq)$ As L.H.E (oxidation) $Hg(s) + 2Cl^-(aq) - 2e \rightarrow Hg_2Cl_2(s)$

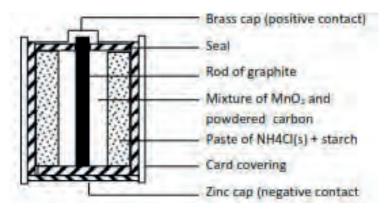
The two electrodes Ag/AgCl(s), Cl⁻ and Hg/Hg₂Cl₂, KCl(aq) have stable potential and are not easily affected by oxidants or reducing agents, and because of their high stability, they are sometimes used as reference electrodes since hydrogen electrode in practice is easily poisoned by oxidants and reducing agents.

Oxidation—reducing (redox) electrodes

This type comprises a reduced species and oxidized species in the same solution, e.g. Pt/Fe^{3+} , Fe^{2+} or Pt/Cr^{3+} , Cr^{2+} .

Dry cells

These were invented to overcome the difficulty of electrolytic solution leaking out of cell such as Daniel cell. In dry cell, the electrolyte is made into a paste. An example is shown below



This type of cell is used in radio, flashlight and clocks as it is portable.

The initial electrode processes are

Anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e$

Cathode: $2NH_4^+(aq) + 2e \rightarrow 2NH_3(g) + 2H_2(g)$

The lead-acid accumulator

The cell stores or accumulates electric charges. It consists of two lead plates dipping into a 30% solution of sulphuric acid. Both plate becomes covered with an insoluble film of lead II sulphate

First, the cell must be charged. A direct current is passed through the cell. The processes which take place are:

Charge

Positive plate

 $PbSO_4(s) + 2e \rightarrow Pb(s) + SO_4^{2-}(aq)$

Negative plate

The plates are now different and therefore have different potentials, so that, when they are connected, an electric current will flow between them. When the cell supplies an electric current, i.e. discharge the process which take place are:

Negative plate

 $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e$

Positive plates

 $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e \rightarrow PbSO_4(s) + 2H_2O(l)$

NB: the plate which is positive during the charge becomes negative during the discharge

INORGANIC CHEMISTRY

TOPIC: BONDING AND STRUCTURE

Lesson 2. 1 Types of bonding and structure.

Lesson Outcome:

By the end of this lesson, you should be able to appreciate the knowledge of bonding and structure to understand how compounds are formed by chemical means.

Introduction:

In this lesson you will understand the different types of bonding and structure, their properties and use this knowledge to explain the formation of compounds by reading attentively to the conversation between three Learners Job, Peter and Mary.

Materials you need: periodic table, internet, images, pen, book, pencil.

Mary: What are the different types of bonding and structure and how are they formed?

Job: Different types of bonding exists, these includes, covalent bond, ionic bond (electrovalent bond), metallic bonding, Hydrogen bond, and dative (coordinate) bonding.

Discussion. On different types of bonding.

Peter: Covalent bond

These are bonds formed by equal sharing of two or more electrons between two atoms in a molecule.

Each atom contributes equal numbers of electrons so that the atomic orbital overlap. The shared electrons must be unpaired with opposite spin.

Covalent bonds are usually formed between non-metal atoms due to their high electronegativity. E.g. Ammonia, Chlorine, carbon dioxide, methane etc.

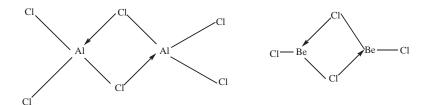
Mary: Co-ordinate/ Dative bond

This is weak covalent bond formed between an electron rich atom and electron deficient atom/ion.

The atom with lone pairs of electrons donates an electron pair therefore it is called donor atom and the atom receiving the electrons is acceptor.

Examples include:

Hydroxonium, ammonium and dimerised AlCl₃ and BeCl₂ i.e. in the vapour phase Aluminum Chloride and Beryllium chloride exist as



Job: Ionic bonding

Ionic bond is bond formed by electron transfer from electropositive element to another electronegative atom.

The electropositive atom loses electrons to become positively charged while the electronegative atom gains the electrons to become negatively charged.

Mary: Metallic bond

This is an electrostatic attraction between the delocalized electrons of the metal atoms and positive nucleus.

The strength of the metallic bond increases with increase in the number of delocalized electrons

Activity 2.1 The table below shows the melting points of elements in period 3 of the periodic table

г					I	ı		
L	Element	Na	Mg	Al	Si	P	S	Cl
	At. no.	11	12	13	14	15	16	17
	Melting							
	point(°C)	98	650	660	1410	44	119	-101

- (a) Plot a graph of melting point against atomic number
- (b) Explain the shape of graph

Teacher: Copy the table above and answer the questions that follow.

Peter: Finally, Hydrogen bonding

It is a permanent bond formed by dipole-dipole attraction between the hydrogen atom and a highly electronegative atom in a molecule with at least a lone pair of electron

Compounds of Nitrogen, Oxygen and Fluorine form hydrogen bonds

Follow up activity.

- (a) Distinguish between electrovalent and covalent bonding.
- (b) State four applications of hydrogen bonding.
- (c) Research on the structure of compounds.

TOPIC: COMPOUNDS OF GROUP VII ELEMENTS

Lesson 1.3. Compounds of group VII elements.

Lesson Outcome: A learner should be able to explain how different compounds of group VII elements are formed.

Introduction: Group VII elements form variety of compounds. These includes Hydrides, Chlorides, Oxo-acids and inter-halogens., **Kato** and **Hope.** are going to discuss the compounds. You will require a pen and paper, chemistry note book and periodic table.

Hope: How are the compounds of group VII elements formed?

Kato: Compounds of Halogens include, Hydrides/ Halogen acids.

Let us Study the table below carefully.

	HF	HCI	HBr	HI
B.E (KJmol ⁻	556	431	336	229
B.p.t (°C)	+19.9	-85	-66.7	-35.4

Kato, reads the values in the table and asks the questions below.

- i) Describe the trend in boiling point, and bond energy among the hydrides?
- ii) Explain your observation?

Hope explains;

The **boiling point** increases from HCl to HI. This is because they are simple molecules held by van der -Waals whose magnitude increases with molecular mass.

However, HF has extremely high boiling point because the molecules associate by hydrogen bonding due small ionic radius of the fluoride ions.

Bond energy, decreases from HF to HI due to:

- Increased atomic radius which increases the bond length
- Decrease in electronegativity down the group thus the bonds become less polar.

Kato: Oxo- acids / ions

All halogens except fluorine form oxo-ions and oxo-acids e.g. HOCl, HClO₂ , HClO₃ and HClO₄

Question. Draw and name the structures of the above oxo- acids.

3. Chloric (V) acid

This is a powerful oxidizing agent that only occurs in aqueous solution. Its salts are more stable and can be obtained by passing chlorine gas through hot Conc. Alkali.

$$3Cl_2(g) + 6OH^-(ag)$$
 — \rightarrow $ClO_3^-(ag) + 5Cl^-(ag) + 3H_2O(l)$

The Chlorate(V) and Chloride are separated by fractional crystallization.

Hope: Interhalogen compounds

These are compounds formed between halogens with the molecular formula AB, AB₃, AB₅ and AB₇where A- is a less electronegative atom with a vacant orbital and a higher oxidation state while B- is more electronegative.

Examples include: ICl⁻ - Iodine monochloride, ClF₃- Chlorine trifluoride.

Question: Explain the shapes of the following inter-halogen compounds:

- (i) lodine pentafluoride.
- (ii) Chlorine trifluoride.

Follow up activity.

Note: Teacher gives a task to the learners.

To, Explain the following observations:

- (a) When hydrochloric acid is exposed in air, it turns brown.
- (b) A colourless solution of acidified hydrogen peroxide turns brown on addition of acidified potassium iodide.
- (c) Describe how sodium chloride is manufactured

Research on the qualitative test for Cl^{-,} Br⁻ and l⁻ lons. In each case suggest the reagent used and write an ionic equation for the reaction.

TOPIC: CHEMISTRY OF d-BLOCK ELEMENTS.

Lesson 4.1 Physical properties of d-block elements.

Lesson Outcome:

By the end of this lesson, you should be able to describe the trend in the physical properties of the d-block elements and interpret the graph of variation of physical properties.

Introduction:

From the electronic configuration, a transition metal is defined as that element having a partially filled 3d subshell therefore Zinc is not regarded as transition metal.

Inquiry question:

How do the physical properties among the d-block elements across the period.

In activity 1. You are given data on variation of atomic radius across the transitional elements below; write the values in your chemistry note book.

Element	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn
At.										
Radius	1.44	1.32	1.22	1.17	1.17	1.16	1.16	1.15	1.17	1.25
(°A)										

Attempt the given questions.

- i) Describe the trend in atomic radius across the transitional elements?
- ii) Explain your observation?

Expected correct responses.

The atomic radius decreases from scandium to nickel and it slightly increases from nickel to Zinc.

As atomic number increases, the nuclear charge increases. However, the electrons are being added to inner 3d-subshell therefore these electrons are poorly shielded from the nuclear charge hence the nuclear attraction for the outer for the most electron increases resulting into increase in atomic radius/ metallic radius.

The decrease in radius coupled with increasing atomic mass causes an increase in the density and decrease in atomic volume in passing from Scandium to Nickel.

Activity 2. The table below shows the electronegativity values for elements in d-block of the periodic table

Element	Sc	Ti	V	Cr	Mn	Fe	Со	Cu	Zn
At. No.	21	22	23	24	25	26	27	29	30
Electronegativity	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.9	1.6

- (a) Plot a graph of electronegativity against atomic number
- (b) Explain the trend of your graph in (a)

Glossary

Electronegativity is the tendency of an element to attract bonding electrons towards itself in a covalent compound.

TOPIC: CHEMISTRY OF d-BLOCK ELEMENTS

Lesson 5.1 General characteristics of d-block elements.

Lesson Outcome:

By the end of the lesson, you should be able to discuss the general characteristics of d- block elements.

Introduction: In this lesson we shall discuss the general characteristics of d-block elements. Follow the conversation between Mugaga and Diana below.

Mugaga: What are the general characteristics of d-block elements?

Diana: The general characteristics of d- block elements include;

- ability to form coloured compounds.
- they form complexes.
- catalytic activity.
- they are Paramagnetic.
- they have various oxidation states.

Mugaga: Variable oxidation states

The elements exist in variable oxidation states in variety of the compounds due to availability of the 3d-electrons which can participate in bond formation by either ionic or covalent

The commonest stable oxidation states are in bold as shown in the table

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
								+1	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3		
	+4	+4	+4	+4					
		+5	+5	+5					
			+6	+6	+6				
				+7					

Activity 1.

- (a) Define the following terms;
 - i) Oxidation state
 - ii) Oxidising agent
- (b) Determine the oxidation state of the transition metals in the following complex.
- (i) K₂Cr₂O₇

(iii) [Co (NH₃)₅SO₄]Br

(ii) MnO₄²-

(iv) [CuCl₂(CH₃NH₂)₂]

Diana: Para magnetism

A substance that can be drawn into a strong magnetic field is known as paramagnetic substance.

Transition metals are paramagnetic due to the presence of unpaired 3d-electrons. Every spinning electron acts as a tiny magnet. However, in an orbital with 2 paired electrons, the magnetic moment of one electron cancels out.

Para magnetism increases with increase in the number of unpaired 3d-electrons.

Mugaga: Formation of Coloured Compounds

The 3d-electrons in isolated metal atom are degenerate. i.e. Energetically alike. However, in presence of ligands, the orbitals overlap differently and spit in to two levels of different of energy. This excites electrons from a lower to higher level of energy. The frequency of light absorbed from this energy transition is from the visible region of the spectrum hence this appears as colour.

Note; Scandium and Zinc form colourless compounds therefore they are regarded as non-transition metals.

Diana: Catalytic activity

Transition elements and their compounds act as catalysts with several chemical processes

Homogeneous catalysis (where the catalyst are in the same phase with the reactants), due to variable oxidation state transition metals/ ions form with the activated complex thus providing an alternative reaction path way of lower reaction energy e.g.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \xrightarrow{Fe^{2+}(aq)} 2SO_4^{2-}(aq) + I_2(aq)$$

Heterogeneous catalysis (where the catalyst and reactants are in different phases), finely divided solid transition metals/ compound provide an active interface for adsorption of the reactant where they are bound to the surface by vander- Waals forces.

Examples include; V₂O₅- contact process, Iron- Haber process etc.

Mugaga: Complex formation

Transition metals form complexes due to:

- Small and highly charged ions
- Presence of vacant 3d-orbitals to accommodate lone pairs of electrons from the ligards

A ligand is anion or molecule with lone pairs of electrons linked to the central metal ion by a dative bond

Co-ordination number is the number of atoms of ligands molecules that form dative bonds in the complex ion.

A metal complex or co-ordination compound is a chemical system composed of electron donor and electron acceptor. Examples of complex include,

- [Cu(NH₃)₄]²⁺Tetraamminecopper(II)ion
- [Cr(H₂O)₄(NH₃)₂]³⁺ diamminetetraaquachromium(III)ion
- [Pt(NH₃)₂NO₂Cl]²⁺ chloronitrodiammineplatinum(IV) ion
- [Co(NH₃)₅SO₄]Br Sulphatopentaammine cobalt(III)bromide





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