NATIONAL OPEN UNIVERSITY OF NIGERIA

FACULTY OF SCIENCE

COURSE CODE: CHM 101

COURSE TITLE: INTRODUCTORY INORGANIC CHEMISRTY

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COURSE GUIDE

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INTRODUCTION

Inorganic Chemistry is the study of chemical elements and their compounds excluding compounds of carbon; but compounds of carbon and oxygen, Sulphur and metals are generally included in inorganic chemistry.

An element is a substance which cannot be resolved into two or more simpler substances following any known chemical process. Combination 0f two or more elements chemically form a new substance called compounds. Examples, water (formed from hydrogen and oxygen), common salt (formed from sodium and chlorine), carbon dioxide (from carbon and oxygen). Since scientist systematize the knowledge gained through observation and experiments. Development of periodic table and periodic law is an example of such attempt that has brought order in studying an expansive branch of chemistry covering over a hundred element. It is therefore pertinent to start the study of inorganic chemistry with the focus on the periodic table.

CHM 101 – Introductory inorganic chemistry is a two (2) credit hour course of seventeen (17) units. The course is designed to equip the student with in-depth knowledge of the periodic classification of element, properties of element according to groups and periods.

The course is designed to deal with periodic table and periodic law, electronic configuration, atomic radii, ionization energy, affinity of electrons, electronegativity, hydrogen, its reaction and compounds, Alkali and Alkaline earth metals compounds, physical and chemical properties etc.

This course guide gives the student a brief overview of the course content, course duration, and course materials.

WHAT YOU WILL LEARN IN THIS COURSE

The student will learn about the periodic table, how it came to be, and the periodic law. Scientist that contributed to the development of periodic table. Hydrogen, chemical properties and reactions. Alkali and Alkaline earth metals, their physical and chemical properties. Reactions and uses.

COURSE AIMS

The aim of this course is tailored towards teaching the students to understand periodic classification of elements, various contributors to the development of periodic table. Modern periodic law, electronic configuration and rules governing its atomic radii, ionization energy, affinity of electrons, electronegativity, Hydrogen, its properties, its bonding, manufacture, ionic salt, Alkali and Alkaline earth metals, their general physical and chemical properties, compounds and reactions.

COURSE OBJECTIVES

To make sure that this course achieves its aim, the stratified course objectives is shown below. The entire objectives are specific and peculiar to the course objectives.

The course objectives are stated below

i. To understand the scope and the basic principle of introductory inorganic chemistry
ii. To understand the elemental arrangement in the periodic table, electronic configuration of element and periodic law.
iii. To understand the work of scientist that led to the development of the periodic table, properties and reactions of elements according to positions in the periodic table, atomic radius.
iv. To understand hydrogen, its manufacture, reactions, its ionic salts-like hydrides, bonding, alkali and alkaline earth metals, their compound and reactivity.

WORKING THROUGH THIS COURSE

This contains some packages that will be given to the students at the beginning of the semester. It includes the course material. You will be required to participate fully in the continuous assessment and the final written examination in three areas such as TMA, MCQ and FBQ etc. The seventeen units of the course packaged for you in modules are summarized below

COURSE MATERIALS

1. Course Guide
2. Study Units

STUDY UNITS

The following are the three modules and the seventeen units contained in this course.

In module 1, introduction to periodic classification, attempt and contribution of J.W Dobereiner, Ade Chancourtois, John Newlands etc. Unit 2 discussed modern periodic law and nomenclature of elements having Z > 100; Unit 3 deals with the rules of filling orbitals, configuration of elements, ion and division of elements into blocks.

Atomic radii, covalent radius, periodicity, periodicity in ionization energy etc. were discussed in unit 4 and 5 while unit 6 and 7 discussed factors affecting electron affinity, Pauling electronegativity, Maulliken-Jafffe electronegativity and Alfred Rochow electronegativity.

Module 2 contains units 8, 9, 10 and 11 and contains extensive discussion of hydrogen, its position in the periodic table, its isotopes, manufacture, properties, uses, ionic or salt-like hydrides and metallic hydride, Hydrogen bonding, its effect on boiling and melting point, water solubility and polarizing power of hydrogen ion.

Unit 12 of module 3 took a look at the general physical and chemical properties of alkali and alkaline earth metal, their uses. Unit 13 discussed the compounds of alkali metals, oxides of hydrogen. Unit 14 explained solvation of alkaline metal ions, their complexation behavior and anomalous nature of lithium. Unit 15 and 16 dwelt on alkaline earth metals and their properties reactivity, occurrence, extraction, lattice energy, hydration energy and thermal stability of oxysalts. The course ends with unit 17 of module 3 by explaining complexation behaviour of alkaline earth metals and anomalous nature of Beryllium.

TEXTBOOKS AND REFERENCES

There are several books and other materials that treated Inorganic Chemistry 101. A good number of them are written down in the references.

The internet provides a lot of useful information concerning the course, therefore, the student is encouraged to use the internet and NOUN e-library were possible.

ASSESSMENT

There are two aspects of assessment for this course; the tutor-marked assignment (TMA) and end of course examination.

TMAs shall constitute the continuous assessment component of the course. They will be marked by the tutor and shall account for 30% of the total course score. Each learner shall be examined for four TMAs before the end of course examination.

The end of course examination shall constitute 70% of the total course score.

SUMMARY

This course is necessary as an introductory Inorganic Chemistry course. It opens up and introduces the student into the wider knowledge of the Chemistry of all the elements as classified in the periodic table, the historical development of the periodic table, the special place of Mendeleev in the development of modern periodic table and periodic law. Chemical and physical properties of elements as influenced by their position in the periodic table (Groups and Periods), their compounds, extraction, manufacture and uses.

We wish you an outstanding success in this course and others as you climb the ladder of knowledge. We hope that as you study hard to pass your examinations excellently, you will also allow the knowledge you acquire to have a positive influence on the society and environment.

MAIN COURSE

MODULE 1

MODULE 1
UNIT 1: THE PERIODIC TABLE

1.0 INTRODUCTION

You are aware that scientists, from the very beginning have attempted to systematize the knowledge they gain through their observations and experiments. Development of the periodic law and the periodic table of the elements is one of such attempt. This has brought order in the study of the vast chemistry of more than a hundred elements known now.

It is therefore quite natural that you should begin your study of inorganic chemistry with the study of the periodic table. In this unit, you will be starting from the very beginning, that is, with the very first attempt made at classification of the elements.
As early as 1815 Prout advanced the hypothesis that all elements were formed by the coalescence of hydrogen atoms, on inaccurate evidence that all atomic masses were whole numbers but it was Berzelius who showed that 'atomic mass' of chlorine was not 35 nor 36 but 35.5 far from a whole number. The discovery of isotope proved that chlorine was a mixture of containing two different kinds of atoms of mass 35 and 37.

By the mid-nineteenth century, more than 60 elements were known and many more were being discovered. The rate of discovery of the new elements was so fast that the chemists started wondering "where it would all lead to". Has nature provided a limit to the number of elements? And if so, how would one know about it? During this period, it was also realized that certain groups of elements exhibited similar physical and chemical properties. Was it a mere coincidence or did a relationship exist among theproperties of the elements? Attempts reply such probing questions ultimately resulted in the development of the periodic table.

2.0 INTENDED LEARNING OUTCOMES (ILOs)

After studying this unit, you should be able to:

1. List accurately at least two scientists who attempted to classify the elements into periods.
2. Write with at least 70% accuracy, brief accounts of the attempts made by the two scientists and the result of these attempts.
3. State Mendeleev's periodic law.

4. State the property used by Mendeleev to classify the elements in his periodic table.
5. Demonstrate an understanding of Mendeleev's law by applying it to predict properties of undiscovered elements.

3.0 MAIN CONTENT

3.1 THE BEGINNING OF CLASSIFICATION

One of the earliest attempts to classify elements was to divide them into metals and non-metals. Metallic elements we all know have certain properties which include

1. Having lustrous shinning appearance, such as iron
2. Malleability, meaning they can be beaten into thin sheets such as is done when buckets are being produced
3. Metallic elements can so be drawn into wire such as is done when making electric wire. This property is known as ductility.
4. They can also conduct heat and electricity. If you hold a piece of metal in your hand and put on end into fire or in contact with any hot object, your hand will feel the heat as it travels from the point of contact with heat through the metal to your hand. Similarly, if you hold one end of the metal through which an electric current is passed, you will be jolted by the current which travel through the metal to your hand.
5. Metallic elements also form basic oxides

In contrast to metallic elements, non-metallic elements have no characteristic appearance. They are brittle that is they break easily. They are poor conductors of electricity and heat. They form acidic oxides.

As more elements were discovered and knowledge of physical and chemical properties were refined, it became clear that within these two divisions of elements, there existed families of elements whose properties varied systematically from each other. Furthermore, certain elements, the metalloids possessed properties intermediate between the two divisions. Thereore were made to search for other classifications.

3.2 Attempts Made by J W Dobereiner

In 1829 JW Dobereiner observed that there exist certain groups of three elements which the called TRIADS. He also observed that elements in triad not only had similar properties, but also the atomic weight of the middle element was approximately an average of the atomic weights of the other two elements of the triad.

A few examples cited by him were: Li, Na, K, Ca, Sr, Ba, S, Se, Te and Cl. Br, I, Al though, Doberieiner's relationship seems to work only fora few elements, He was the first to point out a systematic relationship among the elements.
This was followed by Cannizzaro's unambiguous atomic mass with the consequent allotment of valencies to atoms as a measure of combining power.

In-text Question
State Prout's (1815) hypothesis of the elements explain how the error was corrected.

Anwser

In 1815, Prout advanced the hypothesis that all elements were formed by the coalescence of hydrogen atoms but on the inaccurate evidence that all atomic masses were whole numbers.

It was Berzelius who showed that 'atomic mass' of chlorine was not 35 nor 36 but 35.5 far from a whole number. The discovery of isotope proved that chlorine was a mixture containing two different kinds of atoms of mass 35 and 37.

3.3 Attempts Made by A. Dechancourtois

In 1862, A. DeChanourtois arranged the elements that were known at that time in order of increasing atomic weight on a line which spiralled around a cylinder from bottom to top.

3.4 Attempts Made by John Newlands

In 1864, John Newlands, an English Chemist reported his "LAW OF OCTAVES" He suggested that if the elements were arranged in order of increasing atomic weight, every eighth element would have properties similar to the first element. It brought the lithium-sodium-potassium triad together but failed to allow bigger octave if dealing with heavier elements. For example, He arranged the elements in the following manner.

Table 1: John Newland's arrangement of the element

Element	Li	Be	B	c	N	0	F
AtWt	7	9	11	12	14	16	19
Element	Na	Mg	Al	Si	P	S	Cl
AtWt	23	24	27	29	31	32	35.5
Element	K	Ca	Ti	Cr			
AtWt	39	40	48	32			

Thus we see K resembles Na and Li, Ca resembles Mg and Be, Al resembles B, Si resembles C and so on. He called it the "Law of octaves" because he says the cycle of repetition shown by the elements is like that shown by octaves of music where every eight note resembles the first in octaves of music.

Newlands "Law of octaves" was rejected for two reasons. Firstly, it did not hold good for elements heavier than Ca. Secondly, he believed that there existed some mystical connection between music and chemistry.

3.5 The Work of Lothar Meyer

Lothar Meyer and Dmitri Mendeleev whom you will read about next played key role in the development of the periodic law as it is known today.

In 1869, Lothar Meyer reported that when physical properties like atomic volume, boiling point etc. were plotted against atomic weight, a periodically repeating curve was obtained in each case. Figure 1 is a graph showing the variation in atomic volume with atomic number.
Lothar Meyer calculated the atomic volumes of the known elements, that is the volume in cm^3 occupied by 1mole of the elements in the solid state
Atomic volume = Mass of one Mol⁄Density
(Lothar Meyer also obtained semi curve by plotting atomic volume versus atomic weight)
The atomic volume behaviour is p e r i o d i c. It goes through circles, dropping from a sharp maximum to a minimum and then sharply rising again. Each of the cycles is called a period. The location of element on the peak or in the troughs has an important correlation with their chemical reactivity. The elements of the peaks (example alkali metals) are the most reactive. Those in the troughs (example noble metals) are characteristically less reactive.

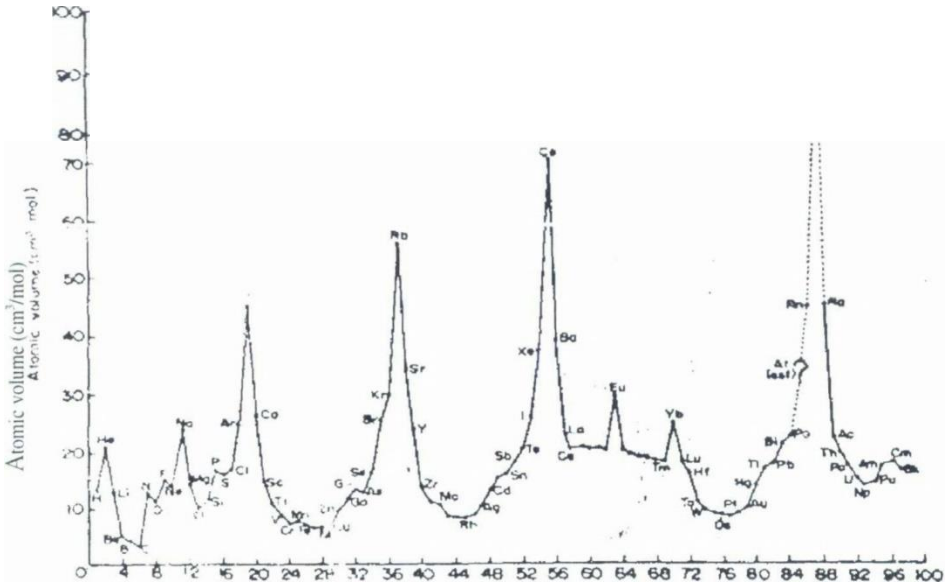

Figure 1. Periodic dependenceof atomic volume on atomic number

3.6. Mendeleev's Periodic Law

In contrast to Lothar Meyer, Mendeleev used chemical properties likevalence and formulae of hydrides, chloride, and oxides of the elements to illustrate his periodic law. According to Mendeleev's periodic law, if the elements are arranged sequentially in the order of increasing atomic weight, a periodic repetition, that is, periodicity in properties is observed. Mendeleev arranged elements in horizontal rows and vertical columns in order of increasing atomic weight so that the elements having similar properties were kept in the same vertical column.

Table 2. Mendeleev periodic table of against each element is the value of atomic weight

Series	Group I - R_1O	Group II - RO	Group III - R_2O_3	Group IV RH_4 RO_2	Group V RH_3 R_2O_6	Group VI RH_2 IO_2	Group VII RH R_1O_1	Group VIII - RO_4
1	H=1							
2	Li=7	Bc=9.4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27.3	Si=28	P=31	S=32	Cl=35.5	
4	K=39	Ca=40	Sc=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59 Ni=59
5	Cu=63	Zn=65	Ga=68	Ge=72	As=75	Sc=78	Bi=80	
6	Rb=85	Sr=87	Yt=88	Zr=90	Nb=94	Mo=96	Fm=100	Ru=104, Rh=104 Pd=106,
7	Ag=108	Cd=112	In=113	Sn=118	Sb=122	Te=125	I=127	
8	Cs=133	Ba=137	Da=138	Ce=148	-	-	-	--
9	-	-	-	-	-	-	-	--
10	-	-	Er=178	La=180	Ta=182	W=184		Os=195, Ls=195, Pi=198
11	Au=199	Hg=200	Ti=204	Pb=207	Bi=208			
12	-	-		Th=231	-	U=240	-	--

Though Newlands and Lothar Meyer also contributed in developing the periodic laws, the main credit goes to Mendeleev because of the following reasons:

a. He included along with his table, a detailed analysis of the properties of all known elements and correlated a broad range of physical and chemical properties with atomic weights.

b. He kept his primary goal of arranging similar elements in the same group quite clear. Therefore, he was bold enough in reversing the order of certaine elements. For example, iodine with lower atomic weight than that of tellurium (group VI) was placed in group VII along with fluorine, chlorine and bromine because of similarities in properties.

c. He also corrected the atomic weight of certain elements to include the min proper groups. For example, he corrected the atomic weight of beryllium (from 13.5 to 9) and indium (from 76 to 114) without doing any actual measurement. His competence was proved correct as Be and La with equivalent weight of 4.5 and 38 respectively are actually bivalent and trivalent.

d. Keeping to his primary goal of arranging similar elements in the same vertical column (group), he realized that some of the elements were still undiscovered and therefore left their places vacant in the table and predicted their properties. He predicted the existence in nature of over ten new elements and predicted properties of three of them, example eka-boron (scandium), eka aluminium (gallium) and eka silicon (germanium) from the properties of known elements surrounding them. When these elements were eventually discovered, Mendeleev prediction proved to be amazingly accurate. This you can see for yourself by comparing the prediction and observed properties of eka-alurninium (gallium) and eka silicon (germanium) given in table 2. The validity of Mendeleev periodic law was dramatically and conclusively proven by

the discovery of three out of the more than ten elements predicted by Mendeleev. The first to be discovered was eka-aluminiurn which was discovered by Lecoq de Boisbaudran in 1875.

Table 3. Comparison of predicted and observed properties of eka Aluminum (gallium) and eka Silicon (germanium)

Property	Predicted by Mendeleev for eka-aluminum	Observed for gallium	Predicted by Mendeleev for ekasilicon	Observed for germanium
Atweight	68	69.72	72	72.59
Density (kgm^{-3})	6.0 x l03	5.9×10^3	$5.5 \times l0^3$	5.3×10^3
Melting point/k	Low	302.8	High	1220k
Reaction with acids &alkalines	Slow	Slow	Slow	Reacts with concentrated acids & alkaline
Formula of oxide	E_2O_3	Ga_2O_3	-	-
Density of oxide (kgm^{-3})	5.5×10^3	$5.8 \times l0^3$	-	-
Formula for chloride	ECl_3	$GaCl_3$	$EsCl_4$	$GeCl_4$
Boiling point of chloride (k)	Volatile	474	373	357

Lecoq de Boisbaudran called the element gallium and said its density was 4.7×10^3 kgm^{-3}. Mendeleev on hearing this wrote to Lecoq de Boisbaudran telling him that everything he said about the new element was correct except its density. On further position of the metal, lecoq de Biosbandran discovered that Mendeleev was right that the density of gallium was 5.8xlO3 kg just like it had been predicted by Mendeleev. (Table 3)

Further proof of the law came via the works of Lars Fredrick Nilson who discovered Scandium and Winkler who discovered germanium. Both elements were found to have properties corresponding to those of earlier predicted for them by Mendeleev.

The development of the periodic law is an excellent example where careful observation, critic analys of available data without any pre-conceived notions and scientific foresight led to the discovery of a fundamental law of nature. Thus when Mendeleev arranged elements in order of increasing atomic weights, he critically analyzed the properties of the then known elements. He discovered that the properties of any element are an average of the properties of its neighbours in the periodic table. On this basis, he predicted the properties of undiscovered elements representing the gaps in the table. The many gaps in the table which Mendeleeff correctly predicted would eventually be filled by the discovery of more elements. No gaps remain to be filled, therefore the properties of many of these element are in close agreement with those predicted by Mendeleeff. In modern periodic table, the ordering of the element is based on atomic numbers rather than atomic masses. This accommodated

the discovery of the noble gasses, 14 rare earths (the first inner transition series called the lanthanides) and 11 man-made elements (part of the second inner transition series called the actinides)

In-text Question

Question
State the point that makes Mendeleev's periodic law stronger than Lother Meyer's

Answer
Mendeleev periodic used chemical properties like valence and formulae of hydrides, chlorides and oxides of elements to explain the periodic law as against Lother Meyers plot of some physical properties such as volume, boiling point against atomic weight.

4.0 SELF-ASSESSMENT EXERCISES

1. Give the names of the scientist whose work contributed to the development of the periodic table?

2. The law of octave was developed by_____

Answers

1. John Newlands

2. J.W. Dobereiner, Adechancourtis, John Newlands, Luther Meyer and Mendeleev

5.0 CONCLUSION

In conclusion, the Scientists tradition of recording and system knowledge gained through observations and experiments has enabled us to learn about the fundamental laws governing the arrangement of elements. Mendeleev prediction proved to be amazingly accurate. This you can see for yourself by comparing the prediction and observed properties of eka-alurninium (gallium) and eka silicon (germanium).

6.0 SUMMARY

In summary, we have learned the following in this unit, these are:

1. Scientists have always tried to systemize the knowledge they gain.
2. That the effort to reveal the secrets of the periodic table were led by the scientist J W Dobreiner, A de chanourtois, John Newlands, Lothar Meyer and Dmitir Mendeleev.
3. That the works of Dmitir Mendeleev formed the basis of the modern Periodic law.
4. That according to Mendeleev, the properties of any element are an average of the properties of its neighbours in the periodic table.

CLASS ACTIVITY (THE TUTOR SHOULD DIRECT)

1. (a) What property did Mendeleev use to classify the element in his periodic table?
   (b) Enumerate four defects in the Mendeleev's periodic table
2. Assuming that the element Ca had not been discovered, predict using the properties of the Known element surrounding Ca its own properties such as its atomic weight and density.

7.0 REFERENCES AND FURTHER READING

1. J. G Wilson, A. B. Newell (1971) General and Inorganic Chemistry (2nd edition) Published by Cambridge University Pres

2. F. A Cotton, G. Wilkinson and P. L. Gayus (1995) Basic Inorganic Chemistry. (3nd edition) John Wiley and Sons Published

3. Gary L. Miessler, Paul J. Fischer and Donald A. Tour (2014) Inorganic Chemistry. 5th edition. Pearson Publishers. ISBN 10:0-321-81105-4

4. J. D Lee (2016) Concise Inorganic Chemistry. (5th edition) John Wiley Publishers

MODULE 1

UNIT 2: MODERN PERIODIC LAW

1.0 INTRODUCTION

In the first unit, you learned about efforts made by several scientists to systematize the knowledge they gained through their observations and experiments. The effort of these scientists resulted in the formation of the periodic table and the periodic law. You learned about the works of such great pioneers as J. N Dobereiner, A de Chancoutois, John Newlands, Lothar Meyer and Dmitir Mendeleev.

The periodic table of today has many similarities with that formed by Mendeleev, but differs from the Mendeleev table in some significant ways which we shall see in the next unit. Also in the past, element were named by their discoverers. In some cases, such a practice has led to disputes between scientists who have discovered the same elements working independently in different parts of the world.

This has prompted the international union of pure and applied chemists' to device a method for naming newly discovered elements

2.0 INTENDED LEARNING OUTCOMES (ILOs)

At the end of this unit, you should be able to:

1. State the modem periodic law.
2. Explain the relative positions of K and Ar, Co and Ni and Te and I on the periodic table.
3. State the relationship between the atomic number and the Periodic classification of elements
4. Apply IUPAC nomenclature rules in naming new elements having Z>100

3.0 MAIN CONTENT

3.1 MODERN PERIODIC LAW

In the previous section, you studied how D. Mendeleev classified elements and formed his periodic table. You must have noticed that there were anomalies in Mendeleev's original periodic table. There was for example no place for lanthanides and actinides and in some instances, elements of higher atomic weight were placed before those of lower atomic weights example Co before Ni and Te before I.

He could not predict the existence of noble gases, nor could he properly place hydrogen. Between 1869-1907Mendeleev tried to improve his table. However, the most significant improvement of his

periodic table came through the discovery of the concept of atomic number in 1913 by Henry Moseley, who suggested that the atomic number of an element is a more fundamental property than its atomic weight. Mendeleev's periodic law was therefore accordingly modified. This is now known as the **MODERN PERIODIC LAW** and can be stated as "the properties of elements are periodic functions of their atomic numbers"

Arrangement of the elements in order of their increasing atomic number removes most of the anomalies of Mendeleev's periodic table. The positions of K and Ar, Co and Ni, Te and I do not remain anomalous any longer since atomic number not weight is used in arranging the elements.

As isotopes of an element have the same atomic number, they can all be placed at one and the same place in the periodic table. We know that the atomic number cannot be fractional. It increases by the integer from one element to the next. It has thus placed a limit on the number of elements. Today, 109 elements (from 1 to 109) have been discovered. And any more elements that may be discovered in future will be beyond 109.

Table 4. Shows the modem periodic table in the form devised by Mendeleev

Periods	A I B						A VII B	A VIII B
1	1 **H** 1.008	A II B	A III B	A IV B	A V B	A VI B	1 **H** 1.008	2 **He** 4.003
2	3 **Li** 6.941	4 **Be** 9.012	5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
3	11 **Na** 22.99	12 **Mg** 24.31	13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
4	19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.80	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85 27 **Co** 58.71 28 **Ni** 58.93
	29 **Cu** 63.54	30 **Zn** 65.37	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.91	36 **Kr** 83.80
5	37 **Rb** 85.74	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** 98.91	44 **Ru** 101.07 45 **Rh** 102.91 46 **Pd** 106.4
	47 **Ag** 107.87	48 **Cd** 112.40	49 **In** 114.82	50 **Sn** 118.96	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.30
6	55 **Cs** 132.91	56 **Ba** 137.54	57 **La*** 138.91	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	75 **Re** 186.2	76 **Os** 190.2 77 **Ir** 192.2 78 **Pt** 195.09
	79 **Au** 197.97	80 **Hg** 200.59	81 **Ti** 204.37	82 **Pb** 207.19	83 **Bi** 208.98	84 **Po** 120	85 **At** 120	86 **Rn** 222

7	87 **Fr** 223	88 **Ra** 226.03	89 **Ac**** 227.03	104 **Unq**	105 **Unp**	106 **Unh**	107 **Uns**	108 **Uno**	109 **Une**

*Lanthanides

58 **Ce** 140 .12	59 **Pr** 140 .91	60 **Nd** 144 .24	61 **Pm** 146 .92	62 **Sm** 150 .35	63 **Eu** 151 .96	64 **Gd** 157 .25	65 **Tb** 158 .92	66 **Dy** 162 .50	67 **Ho** 164 .93	68 **Er** 167 .26	69 **Tm** 168 .93	70 **Yb** 173 .04	71 **Lu** 174 .97

**Actinides

90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** 237.05	94 **Pu** 239.05	95 **Am** 241.06	96 **Cm** 247.07	97 **Bk** 249.08	98 **Cf** 251.08	99 **Es** 254.09	100 **Fm** 257.10	101 **Md** 258.10	102 **No** 255.0	103 **Lr** 257.0

3.2 Long Form of the Periodic Table

You have now seen that in the modern form of Mendeleev periodic table, elements are arranged in seven horizontal rows and eight vertical columns. Normal and transition elements belonging to A and B sub group of a group were placed in one and the same column of the table.

For example, Sc and Ga both in group IIIA and B and Ti and Ge both in group IVA and B. In the long form of the periodic table (see Table 4) elements are arranged in eighteen vertical columns by keeping the Elements belonging to A and B sub groups in separate columns. Note that in the new arrangement, Sc is in group IIIB whereas Ga is now placed in group IIIA.

You would have also noticed that the groupVIIIB of Mendeleev's periodic table contains three triads Fe, Co, Ni, (4th period), Ru, Rh, Pd (5th period) and O, S, Ir, Pr (1st period). In the long form of the table, each element of the triad is kept in a separate column. So the group VIIIB occupies three columns of the table. You can see therefore that, the long form of periodic table is an extension of the modern periodic table

Table 5: Long form of the periodic table

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VI	7 VIIB	8	9 VIII	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
<- sBlock ->									<------*f*-block elements ---→								
1 **H** 1.008																	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31				<------	*f*-block elements ---→						13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.80	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.71	29 **Cu** 63.54	30 **Zn** 65.37	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.91	36 **Kr** 83.80
37 **Rb** 85.74	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** 98.91	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.4	47 **Ag** 107.87	48 **Cd** 112.40	49 **In** 114.82	50 **Sn** 118.96	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.30
55 **Cs** 132.91	56 **Ba** 137.54	57 **La*** 138.91	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.09	79 **Au** 197.97	80 **Hg** 200.59	81 **Ti** 204.37	82 **Pb** 207.19	83 **Bi** 208.98	84 **Po** 120	85 **At** 120	86 **Rn** 222
87 **Fr** 223	88 **Ra** 226.03	89 **Ac**** 227.03	104 **Unq**	105 **Unp**	106 **Unh**	107 **Uns**	108 **Une**	109 **Une**									

<----------*f*- block elements---------->

58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** 146.92	62 **Sm** 150.35	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.92	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97

90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** 237.05	94 **Pu** 239.05	95 **Am** 241.06	96 **Cm** 247.07	97 **Bk** 249.08	98 **Cf** 251.08	99 **Es** 254.09	100 **Fm** 257.10	101 **Md** 258.10	102 **No** 255.0	103 **Lr** 257.0

Originally, Mendeleev gave A and B designation to the groups, containing normal and transition elements, respectively. However, in his Periodic table, this division into A and B group is often done arbitrarily. In different books for the elements of III to VIII groups, this designation of A and B groups is often reversed. To avoid this controversy, International Union of Pure and Applied Chemistry [IUPAC] has adopted Arabic numerals 1, 2, 3 ...18 as the newest group designation in the form of the periodic table. In this system therefore, the alkali and non-alkaline earth metals constitute group 1 and 2, transition elements of Sc to Zn families become groups 3, 4, 5..... 12 and finally the P block elements become groups 13, 14 ... 18 of the table.

In-text Question

Question
Suggesst one major factor that assisted in explaining the Mendeleev's periodic table.

Answer
The most significant improvement of Mendeleev periodic table came through the discovery of the concept of atomic number in 1913 by Henry Moseley, who suggested that the atomic number of an element is a more fundamental property than its atomic weight.

3.3 Nomenclature of Elements Having Z >100

It has been a historical practice to allow the discoverer of the elements to assign the element's name. In recent times, this has led to some controversy because elements with very high atomic number are so unstable that only minute quantities of them, sometimes only one or two atoms are prepared before scientists claim credit for their discovery. This has led to the questions of the reliability of the data and whether the said new element has in fact been discovered.

For example, both American and Soviet scientists claimed credit for discovering element 104. The Americans named it rutherfordium and the Soviet scientist named it Kurchotovium. To avoid this problem, the IUPAC has made an official recommendation that until a new element discovery has been proved, a systematic nomenclature be applied according to the following IUPAC nomenclature rules;

1. The names be derived directly from the atomic number of the element using the following numerical root.

0	1	2	3	4	5	6	7	8	9
Nil	Un	Bi	Tri	quad	pent	hex	Sept	Oct	Enn

2. The root be put together in the order of the digit which make up the atomic number and be terminated by "ium and ending occurring in the names of the 1 metallic elements as these are the final "n"of enn be dropped when it occurs before 'nil' and'i' of 'bi' and 'tri' be dropped when it occurs before 'ium'.

3. The symbol of the element be composed of the initial letters of the numerical roots which make up the names.

Table 6. Gives the systematic names and symbols of elements having Z=101 to 106 derived by application of IUPAC nomenclature rules

Atomic Number	**Systematic Names**	**Symbol**	**Trivial Name**
101	Unnilunium	Unu	Mendelevium
102	Unnilbium	Unb	Nobelium
103	Unniltrium	Unt	Lawrencium
104	Unnilquadium	Unq	
105	Unnilpentium	Unp	
106	Unnilhexium	Unh	

To further enhance our understanding of the rules, let us work out the name of the element 101. We start with the 1st 1 of the 101
You have un,
Then 0 you have nil
Then 1 again you have un
You end it with 'ium'
The name of element 101 is therefore un + nil + un +ium, that 1s unnilunium.

In-text Question

Question
State the controversy that arose due to the discovering of element 104.

Answer
Both American and Soviet scientists claimed credit for discovering element 104. The Americans named it rutherfordium and the Soviet scientist named it Kurchotovium.

4.0 SELF-ESSESSMENT EXERCISE (S)

1. Which group of elements appears in the modern periodic table but did not appear in Mendeleev's original table? Why?
2. What is the name of an element with atomic number 104?

Answer

1. Group18 containing noble gases appears in the modern periodic table, but it did not appear in Mendeleev’s original table because noble gases were not discovered at that time.

   The **reason is that** in the periodic table, elements are arranged in the order of increasing atomic number.

2. You start with first of 104,
   You have un
   Then 0 you nave nil

Then 4, you have quad

The name of the element 104 is therefore is un + nil + quad + ium, that is 1s unnilquadium

5.0 CONCLUSION

In concluding, we can say that the periodic table in its current form is the result of years of painstaking research backed by consensus of opinions of leading scientists on the form it should take. You have now seen that in the modern form of Mendeleev periodic table, elements are arranged in seven horizontal rows and eight vertical columns. Normal and transition elements belonging to A and B sub group of a group were placed in one and the same column of the table. Periodic table, this division into A and B group is often done arbitrarily. In different books for the elements of III to VIII groups, this designation of A and B groups is often reversed.

6.0 SUMMARY

In this unit we have learned that

1. The periodic law first proposed by Dmitri Mendeleev had to be modified.
2. The modification came as a result of the recovery of the concept of the' atomic number' in 1913 by Hendry Moseley.
3. The introduction of the concept of atomic number further clarified the arrangement of the elements in the periodic. Table and removal any ambiguities which were observed.
4. The atomic number rather than the atomic weight is the most important determinant of the properties of an element.
5. As a result of a consensus reached by IUPAC the recommendation of any newly discovered element must follow IUPAC nomenclature rules.

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. What will be then name of an element whose atomic number is 110? Explain how you got your answer.
2. How would you use the modern periodic law to remove the anomalies with regards to the positions of ILK an Ar in Mendeleev's periodic table?

7.0 REFERENCES AND FURTHER READING

1. J. G Wilson, A. B. Newell (1971) General and Inorganic Chemistry (2nd edition) Published by Cambridge University Pres

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3. Gary L. Miessler, Paul J. Fischer and Donald A. Tour (2014) Inorganic Chemistry. 5th edition. Pearson Publishers. ISBN 10:0-321-81105-4

4. J. D Lee (2016) Concise Inorganic Chemistry. (5th edition)Wiley Publishers

5. **MODERN PERIODIC LAW**
https://www.youtube.com/watch?v=QjRN0rkt-gg

6. **Nomenclature of Elements Having Z >100**
https://www.youtube.com/watch?v=8MxXNcKtCII

MODULE 1

UNIT 3 ELECTRONIC CONFIGURATION

1.0 INTRODUCTION

In the last unit, you learned about the periodic table. The periodic law gives rise to the periodic arrangement of the element according to their atomic numbers, which indeed means according to the number of electrons in their orbital. In the next unit you will be studying the distributions of the electrons within the atom (the electronic configuration), and how they govern the properties of the elements.

The electronic configurations of isolated atoms of elements are usually verified experimentally by a detailed analysis of atomic spectra. In this unit, we are not discussing these methods. Instead we are going to discuss the process of filling in of electrons in the various atomic orbitals.

2.0 INTENDED LEARNING OUTCOMES (ILOs)

1. State the principle involved in determining which electron goes into which atomic orbital
2. Fill out correctly electrons in a given atom once given the number.
3. List the four blocks of elements on the periodic table and determine to which block an element belongs if given the electronic configuration.

3.0 MAIN CONTENT

3.1 ELECTRONIC CONFIGURATION OF ATOMS
Rules governing the filling of electrons in orbital

The electronic configuration of atoms can be predicted with the help of AUFBAU or the building up process. In the aufbau process, it is assumed that there exists asset of empty hydrogen like orbital around the nucleus of an atom. The electronic configuration of the atom in the ground state is then derived by adding electrons one at a time to the orbitals of the lowest energy in the sequence shown by arrows in figure 2

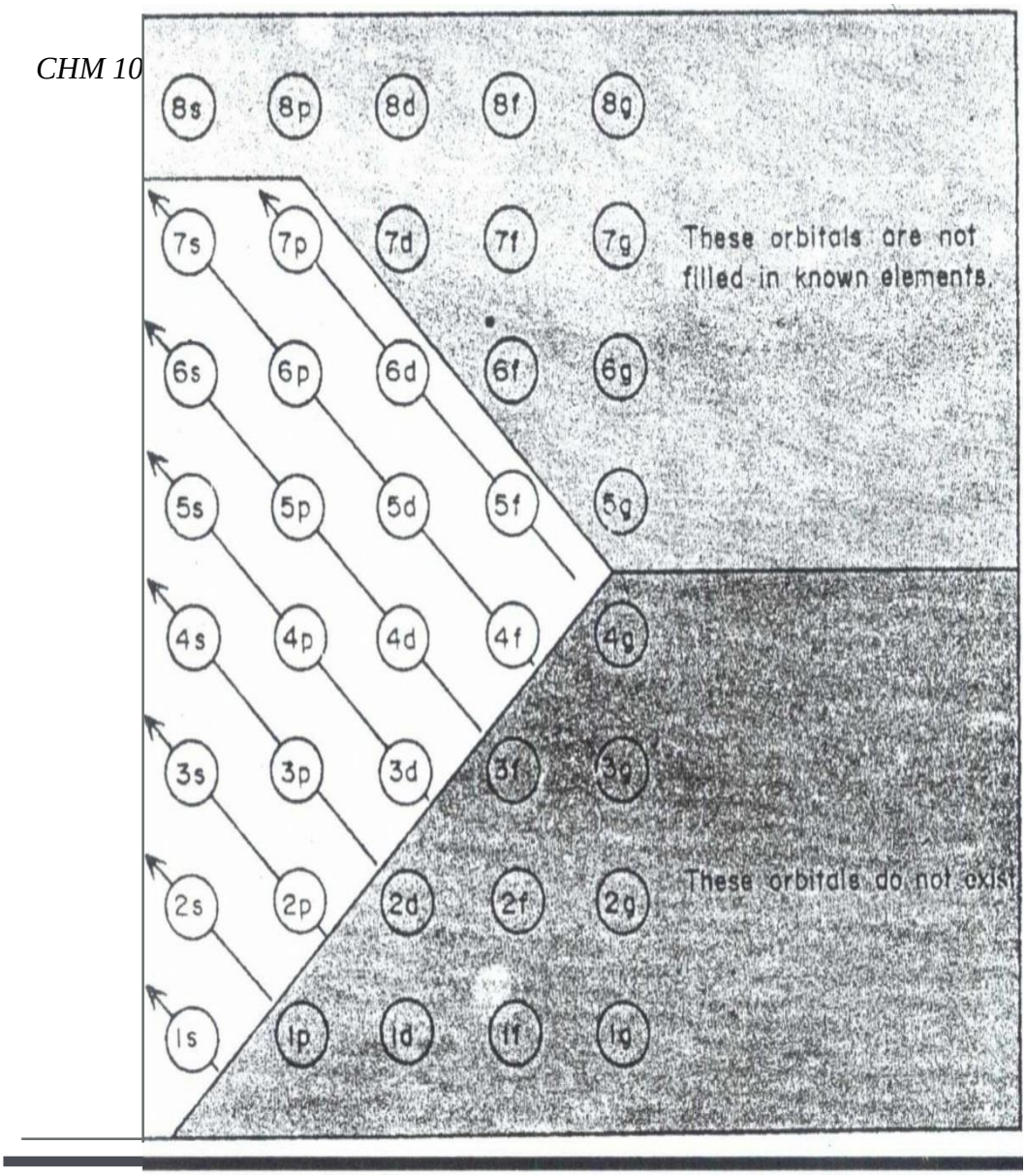

Fig 2: Order or filling of atomic orbitals in poly electronic atoms

The order in which the orbitals are filled as shown in figure 2, is governed by the n+1 rule. According to this rule, in the building up of electronic configuration of the elements, the sub-shell with the value of n+l fills first. This rule reminds us that the energy of sub shells of multi electron atoms depends upon the value of both the quantum numbers n and 1, but mainly on the value of n. For example, to determine whichof the sub shells 5s or4p fills first. We follow the rule thus: for the 5s sub shell the value n+1 =5 +0=5; for 4p sub shell also the value of n+1 =4+ 1 =5, but the 4p sub shell has the lower. Value of the principal quantum number n and therefore it fills first. Filling of electrons in orbitalsis also governed by Paulis Exclusion Principle and Hund's Rule.

The Pauli Exclusion Principle states that no two electrons in the same atom can have the same values for all the four quantum numbers while hund's rule states that electrons occupy each levels singly before electron pairing takes place.

According to the Exclusion Principle, no two electrons in the same atom can have the same value of n, l and mi, they will differ in their m, values. In order words, an orbital can have at the most two electrons of opposite spin. Since there is only 1s -orbital for any given value of n, it can contain only two electrons. However, the three p orbitals for any given value of n can contain six electrons, the five d orbitals, for any given value of n can hold a total of ten electrons and the seven f orbitals can have

fourteen electrons. Permitted combinations of all the four quantum numbers for the electrons in different orbitals are given below in table 7

Hund's Rule

Table 7. Permitted combinations of quantum numbers for S.P, d and f orbitals

M	***T***	***m_1***	***m_1***	**Common name**	**Number of Electron**
1	0	0	±1/2	1_r	2
2	0	0	±1/2	2_r	2
2	1	-1	±1/2	2_p	6
		0	±1/2		
		+1	±1/2		
3	0	0	±1/2	3_r	2
3	1	-1	±1/2	3_p	6
		0	±1/2		
		+1	±1/2		
3	2	-2	±1/2	3_d	10
		-1	±1/2		
		0	±1/2		
		+1	±1/2		
		+2	±1/2		
4	0	0	±1/2	4_s	2
4	1	-1	±1/2	4_p	6
		0	±1/2		
		+1	±1/2		
4	2	-2	±1/2	4_d	10
		-1	±1/2		
		0	±1/2		
		+1	±1/2		
		+2	±1/2		
4	3	-3	±1/2	4_f	14
		-2	±1/2		
		-1	±1/2		
		0	±1/2		
		+1	±1/2		
		+2	±1/2		
		+3	±1/2		
5		0			

Hunds rule of maximum multiplicity states that, as far as possible in a given atom in the state, electrons in the same sub shell will occupy different orbitals and will have parallel spins. That means that when electrons are added to orbitals of the same energy such as three p orbitals or five d orbitals, one electron will enter each of the available orbital, two electrons in separate orbitals feel less repulsion than two electrons paired in the same orbitals. For example, carbon in the ground State has the configuration $1S^2 2S^2 2Px^1 2Py^1$ rather than $1S^2 2S^2 2Px^2$. so far you have studied the rules governing the filling of

electrons in the orbitals of atoms. We shall now consider the electrons configurations of all the elements in the periodic table, these are given in table 8

Table 8. Ground state electronic configuration of gaseous atoms

Z	**Symbol**	**Configuration as Core plus outermost orbital**
1	H	$\|S^1$
2	He	$\|S^2$, or He |
3	Li	[He]$2S^1$
4	Be	[He]$2S^2$
5	B	[He]$2S^2 2p^1$
6	C	[He]$2S^2 2p^2$
7	N	[He]$2S^2 2p^3$
8	O	[He]$2S^2 2p^4$
9	F	[He]$2S^2 2p^5$
10	Ne	[He]$2S^2 2p^6$ or [Ne]
11	Na	[Ne]$3S^1$
12	Mg	[Ne]$3S^2$
13	Al	[Ne]$3S^2 3P^1$
14	Si	[Ne]$3S^2 3P^2$
15	P	[Ne]$3S^2 3P^3$
16	S	[Ne]$3S^2 3P^4$
17	Cl	[Ne]$3S^2 3P^5$
18	Ar	[Ne]$3S^2 3P^6$ or [Ar]
19	K	[Ar]$4S^1$
20	Ca	[Ar]$4S^2$
21	Sc	[Ar]$3d^1 4s^1$
22	Ti	[Ar]$3d^2 4s^2$
23	V	[Ar]$3d^3 4s^2$
24	Cr	[Ar]$3d^4 4s^2$
25	Mn	[Ar]$3d^5 4s^1$
26	Fe	[Ar]$3d^6 4s^2$
27	Co	[Ar]$3d^7 4s^2$
28	Ni	[Ar]$3d^8 4s^2$
29	Cu	[Ar]$3d^{10} 4s^1$
30	Zn	[Ar]$3d^{10} 4s^2$
31	Ga	[Ar]$3d^{10} 4s^1 4p^1$
32	Ge	[Ar]$3d^{10} 4s^1 4p^2$
33	As	[Ar]$3d^{10} 4s^1 4p^3$
34	Se	[Ar]$3d^{10} 4s^1 4p^4$
35	Br	[Ar]$3d^{10} 4s^1 4p^5$
36	Kr	[Ar]$3d^{10} 4s^1 4p^6$ or Kr
37	Rb	[Kr]$5S^1$
38	Sr	[Kr]$5S^2$

39	Y	[Kr] $4d^1 5S^2$
40	Zr	[Kr] $4d^2 5S^2$
41	Nb	[Kr] $4d^4 5S^1$
42	Mo	[Kr] $4d^5 5S^1$
43	Tc	[Kr] $4d^6 5S^2$
44	Ru	[Kr] $4d^7 5S^1$
45	Rh	[Kr] $4d^8 5S^1$
46	Pd	[Kr] $4d^{10}$
47	Ag	[Kr] $4d^{10} 5S^1$
48	Cd	[Kr] $4d^{10} 5S^2$
49	In	[Kr] $4d^{10} 5S^2 5p^1$
50	Sn	[Kr] $4d^{10} 5S^2 5p^2$
51	Sb	[Kr] $4d^{10} 5S^2 5p^3$
52	Te	[Kr] $4d^{10} 5S^2 5p^4$
53	I	[Kr] $4d^{10} 5S^2 5p^5$
54	Xe	[Kr] $4d^{10} 5S^2 5p^6$ or [Xe]
55	Cs	[Xe]$6S^1$
56	Ba	[Xe]$6S^2$
57	La	[Xe] $5d^1 6S^2$
58	Ce	[Xe] $4f^1 5d^2 6S^2$
59	Pr	[Xe] $4f^5 6S^2$
60	Nd	[Xe] $4f^5 6S^2$
61	Pm	[Xe] $4f^5 6S^2$
62	Sm	[Xe] $4f^5 6S^2$
63	Eu	[Xe] $4f^5 6S^2$
64	Gd	[Xe] $4f^1 5d^1 6S^2$
65	Tb	[Xe] $4f^5 6S$
66	Dy	[Xe] $4f^5 6S^2$
67	Ho	[Xe] $4f^{51} 6S^2$
68	Er	[Xe] $4f^{52} 6S^2$
69	Tm	[Xe] $4f3^5 6S^2$
70	Yb	[Xe] $4f^{54} 6S^2$
71	Lu	[Xe] $4f^4 5d^1 6S^2$
72	Hf	[Xe] $4f^4 5d^2 6S^2$
73	Ta	[Xe] $4f^4 5d^3 6S^2$
74	W	[Xe] $4f^4 5d^4 6S^2$
75	Re	[Xe] $4f^4 5d^5 6S^2$
76	Os	[Xe] $4f^4 5d^6 6S^2$
77	Ir	[Xe] $4f^4 5d^7 6S^2$
78	Pt	[Xe] $4f^4 5d^8 6S^1$
79	Au	[Xe] $4f^4 5d^{10} 6S^1$
80	Hg	[Xe] $4f^4 5d^{10} 6S^2$
81	Ti	[Xe] $4f^4 5d^{10} 6S^2 6P^1$
82	Pb	[Xe] $4f^4 5d^{10} 6S^2 6P^2$
83	Bl	[Xe] $4f^4 5d^{10} 6S^2 6P^3$
84	Po	[Xe] $4f^4 5d^{10} 6S^2 6P^4$
85	At	[Xe] $4f^4 5d^{10} 6S^2 6P^5$

86	Rn	[Xe] $4f^{4}5d^{10}6S^{2}6P^{6}$ or [Rn]
87	Fr	[Rn]$7S^{1}$
88	Ra	[Rn]$7S^{2}$
89	Ac	[Rn] $6f^{5}7S^{2}$
90	Th	[Rn] $6f^{5}7S^{2}$
91	Pa	[Rn] $5f^{4}6d^{1}7S^{2}$
92	U	[Rn] $5f^{4}6d^{1}7S^{2}$
93	Np	[Rn] $5f^{4}6d^{1}7S^{2}$
94	Pu	[Rn] $5f^{5}7S^{2}$
95	Am	[Rn] $5f^{5}7S^{2}$
96	Cm	[Rn] $5f^{4}6d^{1}7S^{2}$
97	Bk	[Rn] $5f^{59}7S^{2}$
98	Cf	[Rn] $5f^{510}7S^{2}$
99	Es	[Rn] $5f^{511}7S^{2}$
100	Fm	[Rn] $5f^{512}7S^{2}$
101	Md	[Rn] $5f^{513}7S^{2}$
102	No	[Rn] $5f^{514}7S^{2}$
103	Lr	[Rn] $5f^{414}6d^{1}7S^{2}$
104	Unq	[Rn] $5f^{414}6d^{2}7S^{2}$
105	Unp	[Rn] $5f^{414}6d^{3}7S^{2}$
106	Unh	[Rn] $5f^{414}6d^{4}7S^{1}$
107	Uns	[Rn] $5f^{414}6d^{5}7S^{2}$
108	Uno	[Rn] $5f^{414}6d^{6}7S^{2}$
109	Une	[Rn] $5f^{414}6d^{7}7S^{2}$

3.2 Electronic Configuration of all the Elements in the Periodic Table

Period 1

T**his contains only hydrogen and helium and it is** the smallest of all the periods of the table. Hydrogen (Z=1) and helium (Z = 2) are the two elements belonging to the period. The electronic configuration of hydrogen and helium are $1S^{1}$ and $1S^{1}$ respectively. Thus the 1S orbital which is the only orbital coresponding to 1 is completely filled. The $2S^{2}$ configuration of helium is usually represented by [He], so any time you see [He] electron configuration it represents $1S^{2}$.

Period 2

This period contains elements from lithium (Z=3) to neon (Z=10). In lithium and beryllium, the filling of 2S orbital takes place, then in the next six elements from boron to neon, the 2p orbitals are filled. Neon thus has the electronic configuration of [He] $2S^{2}2P^{6}$ which as was done in the case of He, is represented by [Ne]. (An electronic configuration of [Ne] means $1S^{2}2S^{2}2P^{6}$. At this stage, the shell having n=2 is complete.

Period 3

This is similar to period 2, this period also consists of 8 elements from sodium (Z=11) to argon (Z=18), these elements 3S and 3p orbitals are successively filled in the sequence just as was done in period 2, thus argon has the electronic configuration [Ne] $2S^{2}2P^{6}$ represented as [Ar] although the third

principal shell (n = 3) can accommodate 10 more electron in 3d orbitals, filling of 4s orbital takes place first because of its lower energy but it does not immediately expand from 8 to 18 until scandium is reached

Period 4

This period 18 elements from potassium (Z=19) to krypton (Z=36). In K and Ca, the first two elements of this period, the successive electrons go into the 4s orbitals giving them the configuration [Ar] 4S1 and [Ar] $4S^2$ respectively. Then in the following 10 elements (Sc, Ti, V, Cr Mn, Fe, Co, Ni, Cu and Zn) filling of hither to unoccupied 3d orbitals takes place. Thus the electronic configuration of zinc becomes [Ar] $3d^{10}4S^2$

Occasionally an electron from 4s orbitals is shifted out of turn to the 3d orbitals due to higher stabilityof half-filled and completely filled orbitals, for example, Cr (Z=24) and Cu (Z=29) have the configuration [Ar] $3d^5 4S^1$ and [Ar] $3d^{10}4S^1$ instead of the· expected [Ar] $3d^{10}4S^2$ and [Ar] $3d^9 4S^2$ respectively. After the 3d level is filled, in the next six elements of this period, that is Ga, Ge, As, Se, Br and Kr, the 4p orbitals are gradually filled and Kr has the electronic [Ar] $3d^{10}4S^2 4P^6$ represented as [Kr].

Period 5

The next 18 elements from rubidium (Z=37) to Xenon (Z=54) belong to this period. In building up of the atoms of these elements, 5S 4d and 5p orbital are successively filled just as the 4s 3d, Cd, 4p are filled in the elements of period 4. In Rb (Z=37) and Sr (Z=38), the 5S orbital is filled. After that in elements fromy (Z=39) to Cd (Z=48) filling of 4d orbitals takes place. You can see from table 8 that once again there are minor irregularities in the distribution of electron between 4d and 5S orbitals. For example, Mo (Z=42) and Ag (Z=47) have respectively [Kr] $4d^5 5S^1$ and [Kr] $4d^{10}5S^1$ configurations similar to those of Cr and Cu respectively. Anomalous electronic configuration of Nb, Ru, Rh and Pd cannot be explained in simple terms. You have to therefore, remember them as exceptions. Now in the next six elements, that is I, Sn, Sb, Te, I and Xe filling of S P orbitals take place and thus Xe (Z=54 attains [Kr] $4d^{10}5S^2 5P^6$ configuration

Period 6

This period contains 32 elements from caesium (Z=55) to radon (Z=86) in which the 6S, 4f, 5d and 6p orbitals are filled. The first two elements of this period have configurations analogous to those of corresponding member of the lower periods, thus caesium (Z=55) and barium (Z=56) have [Xe] $6S^1$ and [Xe] $6S^2$ configuration respectively. According to aufbau principle in the next element La (Z = 57), the additional electron should enter 4f orbital. Instead it goes to the 5d orbitals and La has the configuration [Xe] $5d^1 6S^2$, but why? The extra electron in the building up of La atom goes to 5d orbital instead of 4f orbital because in La atom, the 5d and 4f orbitals have almost the same energy and hence, the electron is free to enter any of these two orbitals.

In the next 14 elements from cerium (Z=58) to lutecium (Z=7l), the 4f orbital is successively filled pertaining to [Xe] $4f^1 5d^1 6S^2$ and [Xe] $4f^{14}4d^1 6S^2$ configuration, respectively, but you should remember, it is only Ce (Z=58) Gd (Z=64) and Lu (Z=71) that 5d orbitals have one electron while in all the remaining Lanthanides the 5d orbitals remain vacant after Lutecium, successive electrons occupy 5d orbitals and the electronic configuration builds up from [Xe] $4f^{14}4d^2 6S^2$ for hafnium to [Xe] $4f^{14}4d^{10}6S^2$ for mercury the homologue of zinc and cadmium.

Again a minor departure from a steady increase in the number of d electrons occurs. For example, gold has [Xe] $4f^{14}4d^{9}6S^{2}$, and as you can see, has to do with the greater stability of half-filled/fully filled orbitals. Finally, the period is completed with successive occupation of the 6p orbitals from thallium, [Xe] $4f^{14}5d^{10}6S^{2}6p^{1}$ to radon, [Xe] $4f^{14}5d^{10}6S^{2}6p^{6}$.

Period 7

This period is still in complete and contains 23 elements from francium (Z=87) to unnitennium (Z =109). In these elements electrons are Filled in 7s, 5f and 6d orbitals. Francium ([Ru] $7S^{1}$), radium ([Ru] $7S^{2}$) and antinium ([Ru] $6d^{1}7S^{2}$) have electronic configurations analogous to those of caecium, barium and lanthanum respectively. Thorium has the configuration [Ru] 6d27S2. Therefore, in the 13 elements from protactinium (Z=91) to lawrencium (Z=103) filling of Sf orbitals takes place successively. However, out of these only Pa (Z=91), U (Z=92), Np (Z=93), Cm (Z=96) and Lr (Z=103) have an electron in 6d orbitals. In the rest of the elements, the 6d orbitals remain vacant, thus the electronic configuration of Lr (Z=103) is [Ru] $4f^{14}6d^{2}7S^{2}$
The next six known elements of this period are members of 6d transition series which have the configurations [Ru] $4F^{14}5d^{2}6p^{2}7S^{2}$ to [Ru] $4f^{14}6d^{7}7S^{2}$

Having examined the electronic configuration of elements in the periodic table, you can see from table 8 that the elements occupying the same group of the periodic table have the same valence-shell electronic configuration. In order words, the elements having the same valence shell electronic configuration recur periodically, that is after intervals of 2, 8, 8, 18, 18 and 32 in their atomic number. Therefore, periodicity in the properties of elements can easily be understood.

In-text Question

Question
State why Cr (Z=24) and Cu (Z=29) have the configuration [Ar] $3d^{5}4S^{1}$ and [Ar] $3d^{10}45^{1}$ instead of the· expected [Ar] $3d^{10}4S^{2}$ and [Ar] $3d^{9}4S^{2}$ respectively.

Answer

Occasionally an electron from 4s orbitals is shifted out of turn to the 3d orbitals due to higher stability of half-filled and completely filled orbitals

3.3 Electronic Configurationof Ions

So far, we have studied the electronic configuration of neutral atoms of elements. I am sure you will be interested in knowing the electronic configuration of ions that are obtained by removal of electrons from the elements. When the gaseous iron atom having [Ar] $3d^{6}4S^{2}$ ground state electronic configuration loose an electron, the Fe^{+} ion is formed. These ions have its minimum energy in the configuration [Ar] $3d^{7}$, although the iso-electronic manganese atom has the configuration [Ar] $3d^{5}4S^{2}$ in the ground state. Similarly, the ground state of the Fe^{2+} and Fe^{3+} ions are [Ar] $3d^{6}$ and [Ar] $3d^{5}$ respectively rather than [Ar] $3d^{5}4S^{1}$ and [Ar] $3d^{3}4S^{2}$ which are ground states of iso-electronic atoms of chromium and Vanadium respectively. Evidently the differences in nuclear charge between Fe^{+} and Mn, Fe^{2+} and Cr and Fe^{3+} and V are important in determining the orbital to be occupied by the electrons.

However, along the series of ions carrying the same charge, the electronic configuration often changes much more regularly than the electronic configuration of the corresponding atoms. Thus for dipositive

ions Sc^{3+} to Zn^{2+}, the ground state electronic configuration changes regularly from [Ar] $3d^1$ to [Ar] $3d^{10}$ for tripositive ions, there is a similar regular change from [Ar] for Sc^{3+} to [Ar] $3d^9$ for Zn^{3+}. For tripositve ions of lanthium elements, thereis a regular change from [Xe] $4f^1$ for Ce^{3+} to [Xe] $4f^{14}$ for Lu^{3+}. Since the chemistry of elements is essentially that of their ions, the regularities in configuration of ions are much more important than the irregularities in the electronic configuration of the neutral atoms.

3.4 Electronic Configuration and Division of Elements into Blocks

Elements of the periodic table have been divided into four blocks s, p, d and f depending upon the nature of the atomic orbitals into which the differentiating or the last electron enters.

The S-Block Elements-In these elements the differentiating electron enters the 'ns' orbital. Alkali and alkaline earth metals of groups (IA) and 2 (llA) belong to this block. As you know the valence shell electronic configuration of these groups are ns^1 and ns^2 respectively. We also know that each period of the periodic table begins with alkali metals. All the elements in thi s block are metals.

The p-Block Elements- In the elements belonging to this block, the p-orbitals are successively filled. Thus the elements of the group 13 (1llA), 14(IVA), 15(VA), 16(VIA), 17(Vl1A) and 18(zero) are members of this block, since in the atoms of these elements, the differentiating electron enters the np orbitals. The ns orbital in the atoms of these elements are already completely filled so they have the valence shell electronic configuration ns^2np^{1-6}

Note that the elements of s-and p-blocks are also known as normal representative or main group elements.

The d-Block Elements- The elements in which the differentiating electron enters the $(n-1)^d$ orbitals are called d-block elements. These elements are placed in the middle of the periodic table between the s^- and p^- block elements. The electronic configuration of the atoms of the elements of this block can be represented by $(n-1)d^{1-10}$ ns^{0-12} These elements which are also called transition elements are divided into four series corresponding to the filling of 3d- 4d- 5d- or 6d- orbitals while the 3d, 4d, and 5d series consist of 10 elements each, the 6d series is incomplete and has only seven elements viz: Ac (Z=89) and from Unq 9 (Z=104) to Une (Z=109). The element from Sc(Z=21) to Zn(Z=30),Y(Z=39) to Cd(Z=48), La(Z=57) and from Hf(Z=72) to Hg (Z =80) are the members of 3d, 4d, and 5d series respectively.
Note: That D-Block elements are also known as transition elements.

The f-Block Elements- The elements in which the extra electron enters (n-2) f orbitals are called the f-block elements. The atoms of these elements have the general configuration $(n-2)\ f^{1-14}(n-l)\ d^{0-1}ns^2$. These elements belong to two series depending upon the filling of4f and 5f orbitals. Elements from Ce (Z = 58) to Lu (Z = 71) are the members of the 4f series, while those from the (Z=90) to Lr (Z=103) belong to the 5f series. Elements of 4f series which follow lanthanium in the periodic table are known as LANTHANIDES whereas those of 5f series following actinium are called ACTINIDES. All these elements are collectively referred to as INNER-TRANSITION elements because of filling of electrons in an inner (n-2) f sub shell.
Note that f-block elements are also known as inner transition elements.

In-text Question

Question
Explain Hunds rule of maximum multiplicity

Answer
Hunds rule of maximum multiplicity states that, as far as possible in a given atom in the state, electrons in the same sub shell will occupy different orbitals and will have parallel spins. That means that when electrons are added to orbitals of the same energy such as three p orbitals or five d orbitals, one electron will enter each of the available orbital, two electrons in separate orbitals feel less repulsion than two electrons paired in the same orbitals.

4.0 SELF-ASSESSMENT EXERCISES

1. What principles or rules are violated in the following electronic configuration? Write the names of the principle or rule in the space provided along side each configuration.

(i) $1S^2 2S^3$
(ii) $1S^2 2S^2 2Px^2\ 2py^1$
(i) $1S^2 2Px^2$

2. Write the electronic configuration of the atoms whose atomic numbersare:

(i) 21
(ii) 24
(iii)29

Answers

1 (i) Exclusion principle
(ii) Hund's rule
(iii) aufbau principle

2 (i) $1S^2 2S^2 2p^6 3S^2 3p^6 3d^{14} S^2$
or $[Ar]3d^1 4S^2$
(ii) $1S^2 2S^2 2p^6 3S^2 3p^6 3d^5 4S^1$
or $[Ar]3d^5 4S^1$
(iii) $1S^2 2S^2 2p^6 3S^2 3p^6 3d^{10} 4S^1$
or $[Ar]\ 3d^{10} 4S^1$

5.0 CONCLUSION

In conclusion, we have seen that the order in which electrons occupy atomic orbitals is governed by certain rules and principles. These rules determine how many and which electrons occupy valence shells. It is the valence shells that determine the kind of reaction an atom will be involved in. It is therefore very important that the order of filling of orbitals is properly understood. Having examined the electronic configuration of elements in the periodic table, you can see from table 8 that the elements occupying the same group of the periodic table have the same valence-shell electronic configuration. In order words, the elements having the same valence shell electronic configuration recur periodically, that is after intervals of 2, 8, 8, 18, 18 and 32 in their atomic number. Therefore, periodicity in the properties of elements can easily be understood.

6.0 SUMMARY

In summary, we have studied the following in this unit

1. That the filling in of electrons into their orbitals is governed by
   a) The aufbau principle which assumes that there exist a set of empty hydrogen like orbitals into which electrons can be added
   b) The n+l rule, which states that in building up electronic configuration of the elements the sub shell with the lowest value of n=1 fills first.
   c) The Pauli Exclusion principles which states that no two electrons in the same atom can have the same value of all four quantum numbers.
   d) The Hund's rule which states that as far as possible in a given atom in the ground state, electrons in the same sub shell will occupy different orbitals and will have parallel spins.
2. That the electronic configuration of ions changed regularly.
3. That the elements in the periodic table are divided into four blocks viz: S-P-D- and F Blocks.

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. Explain Pauli's exclusion principle

2. Distinguish LANTHANIDES and ACTINIDES.

7.0 REFERENCES AND FURTHER READINGS

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   https://www.youtube.com/watch?v=oCajIGPK-WM
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   https://www.youtube.com/watch?v=hJ0WwAGSjlc

MODULE 1
UNIT 4: ATOMIC RADII

1.0 INTRODUCTION

In units 1-3 we studied the development of the periodic law and the periodic table. We learned about the properties of elements being periodic function of their atomic numbers. We learned how electrons are arranged in their orbitals. Arrangements that give rise to similarities and differences in the properties of elements whose valence electrons appear in the same group and those whose valence electrons are in different groups respectively. These differences in the properties arise due to differences in atomic properties. Such as size of the atoms as measured in terms of radii.

In this unit, you will be studying about different types of atomic radii, factors affecting atomic radii and periodicity in atomic radii.

2.0 INTENDED LEARNING OUTCOMES (ILOs)

By the time you have studied this unit, you should be able to:

1. Define accurately"Atomic radii"
2. Distinguished between various forms of atomic radii
3. List and explain with 80% accuracy the two factors affecting atomic radii
4. Explain using examples periodicity in atomic radii.

3.0 MAIN CONTENT

3.1 MEASUREMENT OF ATOMIC RADII

Atomic radii are the measure of the size of the atom. Atomic radii are important because other atomic properties like ionization energy, electron affinity and electronegativity are related to them. The wave mechanical picture of an atom depicts an atom as composed of a compact nucleus surrounded by an electron cloud. This electron cloud does not have a definite boundary surface like that of a ball. There is a definite but very small probability of finding an electron at an infinite distance from the nucleus of the atom. However, this does not mean that the atom. is indefinitely large, therefore we have to find

away to define the size of an atom. Accordingly, the radius of an atom can be defined as the distance from the centre of the nucleus to the point where the electron density is virtually zero.

Now that we have defined the size of an atom, we have to tackle the problem of measuring that size. We are immediately confronted with the problem of defining and accurately measuring the size we mean. Thus, if we are measuring the size of an atom when it is occupying a lattice site of the crystal, the value will be different from one when it is colliding with another atom in the gaseous state. Further more, the size of a neutral atom will be different from the one when it is present as a cation or anion. Consequently, we can not have one set of atomic radii applicable under all conditions. It therefore becomes necessary to specify the bonding conditions under which the size is being measured. Pertaining to the four major types of bonding, the atomic radii to be measured are:

1. Covalent radius
2. Crystal or Metallic radius
3. Vander Waals radius
4. Ionic radius

3.2 Covalent Radius

It is possible to determine the distance between the nuclei of bonded atoms by employing Spectroscopic or X-ray and electron diffraction techniques.

The covalent or atomic radii are additive that is the bond distance in C-Cl is almost the same as that obtained by adding together the atomic radius of carbon and chlorine

Covalent radius can be defined as one half of the distance between the nuclei of two like atoms bonded together by a single covalent bond.
For simplicity simplicity homonuclear diatomic molecules will be examined first, Homonuclear means that there is only one type of nucleus, that is one element present and diatomic means that the molecules are composed of two atoms.

If in a homonuclear diatomic molecule of A_2 type (eg F_2, Cl_2, Br_2, 1_2) r_{A-A} is bond length or inter nucleus distance and r_A is the covalent radius of the atom A, then $r_A = 1/2\ r_{A-A}$. The internuclear distance r_{C-C} between two carbon atoms in diamond is 154pm so the covalent radius of carbon, is equal to77pm. Similarly, the r_{Cl-Cl} for solid l_2 is 198 pm, r_{Cl} is therefore 99pm.

In the heteronuclear, diatomic molecule of AB type, if the bonding is purely covalent, then the bond length rA-B is equal to the sum of covalent radii of A and B that is $r_{A-B}=r_A+r_B$. Thus covalent radii are additive. It is possible to calculate the radius of one of the atoms in a heteronuclear diatomic molecule of AB type. If we know the internuclear distance r_{A-B} and radius of the other atom. For example, the Si-C bond length in carborundum is 193 pm and covalent radius of C is 77, so you can calculate the covalent radius of Si as follows:

r_{Si} - C= r_{Si}+ r_C or r_{Si}=r_{Si}-C - r_C or r_{Si}=193-77=116pm

As stated earlier, the above relatio holds well only ifthe bond between the atoms A and B is purely covalent. If there is a difference inthe electronegativities of the bonded atoms, it causes shortening of the bonds. Schoemaker and Stevenson have proposed the following relationship between the shortening of the bond and the electronegativity difference of the atoms;

$r_{A-B} = r_A + r_B - 0.07\ (X_A - X_B)^2$

Here X_A and X_B are the electronegativities of A and B respectively. Multiplicity of the bond also causes a shortening of the bond. Usually a double bond is about 0.86 times and a triple bond about 0.78 times the single bond length for the second period elements. Covalent radii of the elements are listed in table 9.

In-text Question

Question
Explain the wave picture of the atom.

Answer
The wave mechanical picture of an atom depicts an atom as composed of a compact nucleus surrounded by an electron cloud. This electron cloud does not have a definite boundary surface like that of a ball. There is a definite but very small probability of finding an electron at an infinite distance from the nucleus of the atom.

Table 9. *Covalent and Vander Waals radii of elements*

1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*		*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*
IA	*IIA*	*IIIB*	*IVB*	*VB*	*VI*	*VIIB*	*VIIIB*				*IB*	*IIB*	*IIIA*	*IVA*	*VA*	*VIA*	*VIIA*	*VIIIA*
H 37 120																		**He** 120
Li 123	**Be 89**												**B**	**C**	**N**	**O**	**F**	**Ne**
Na 156	**Mg 136**												**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
K 103	**Ca 174**	**Sc 144**	**Ti** 132	**V** 122	**Cr 118**	**Mn 117**	**Fe 117**	**Co 116**	**Ni 115**		**Cu 117**	**Zn 125**	**Ga 125**	**Ge 122**	**As 121 200**	**Se 117 200**	**Br 114 195**	**Kr 189**
Rb 216	**Sr 191**	**Y 162**	**Zr 145**	**Nb 134**	**Mo 130**	**Tc 127**	**Ru 125**	**Rh 125**	**Pd 128**		**Ag 134**	**Cd 144**	**In 144**	**Sn 140**	**Sb 141 220**	**Te 137 220**	**I 133 215**	**Xe 210**
Cs 235	**Ba 198**	**La* 169**	**Hf 144**	**Ta 134**	**W 130**	**Re 128**	**Os** 126	**Ir 127**	**Pt 130**		**Au 134**	**Hg 147**	**Ti 155**	**Pb 154**	**Bi 148**	**Po 146**	**At -**	**Rn 215**

Ce 168	**Pr** 165	**Nd** 164	**Pm** -	**Sm** 166	**Eu** 185	**Gd** 161	**Tb** 159	**Dy** 159	**Ho** 158	**Er** 157	**Tm** 156	**Yb** 170	**Lu** 156

3.3 Van Der Waal's Radius

In the solid state, non-metallic elements usually exist as aggregates of molecules. The bonding within a non metal molecule is largely covalent. However, individual molecules are held together by weak forces known as Vander Waals forces. Half of the distance between the nuclei of two atoms belonging to two adjacent molecules in a crystal lattice is called Vander Waal's radius. Table 9. Lists the values of Van der Waals radii of some elements. Figure 3. Illustrate the difference between the covalent and vander Waals radii of chlorine

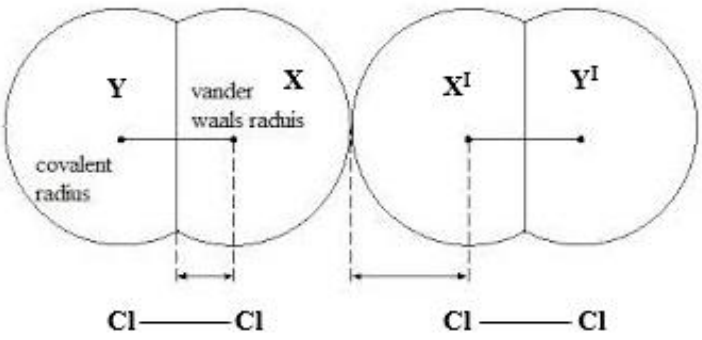

Fig 3. Covalent and vander Waals radii of solids chlorine

It is evident from the figure that half of the distance between the nuclei X and X^1 of the two non-bonded neighbouring chlorine atoms of adjacent molecule A and B is the Vander Waal's radii of chlorine atom. On the other hand, half of the distance between the two nuclei X and Y in the same molecule is the covalent radius of chlorine atom. Thus Van der Waal's radii represent the distance of the closest approach of an atom to another atom it is in contact with, but not covalently bond to it. Values of Vander Waals radii are larger than those of covalent radii because vander Waals forces are much weaker than the forces operating between atoms in a covalently bonded molecule.

3.4 Metallic or Crystal Radius

Metallic or crystal radius is used to describe the size of metal atoms which are usually assumed to be loosely packed spheres in the metallic crystal. The metal atoms are supposed to touch one another in the crystal. Metallic radius is defined as one-half of the distance between the nuclei of two adjacent metal atoms in the close packed crystal lattice, for example the internuclear distance between two adjacent Na atom in a crystal of sodium metal is 382 pm so metallic radius of Na metal is 382 that is 191pm.

The metallic radius depends to some extent on the crystal structure of the metal. Most metals adopt a hexagonal close packed (hcp) or cubic close packed (ccp) or body centered cubic (bcc) lattice (see figure 4)

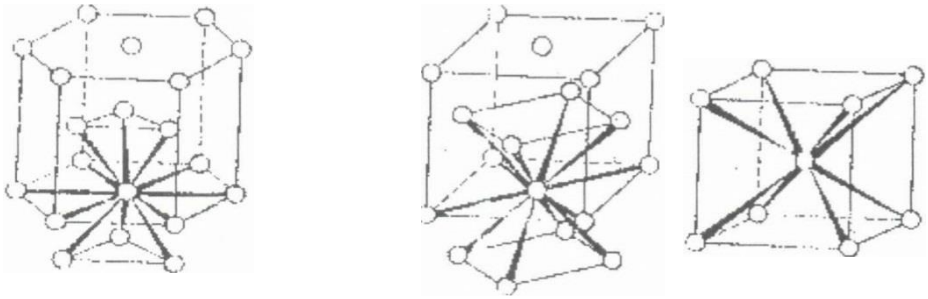

Fig. 4. Types of metallattices (a) hexagonal; (b) cubicclosepacked (c) body-centredcubic

Table 10. Metalic and ionic radii of elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
IA	IIA	IIIB	IVB	VB	VI	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
H 208(-1)																	**He**
Li 155 60(+1)	**Be 112** 31(+2)											**B**	**C**	**N**	**O**	**F**	**Ne**
Na 190 95(+1)	**Mg 160** 65(+2)											**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
K 235 133**(+)**	**Ca 197** 99**(+2)**	**Sc 164** 81(+3)	**Ti 147** 76(+) 68(+)	**V 135 84(+) 66(+)**	**Cr 130 84(+) 69(+)**	**Mn 135 80(+) 66(+3)**	**Fe 126 76(+2) 64(+3)**	**Co 125 72(+2) 63(+3)**	**Ni 125 72(+2) 62(+3)**	**Cu 128 69(+1) 96(+2)**	**Zn 137** 74(+2)	**Ga 141** 113(+1) 62(+3)	**Ge 141** 113(+1) 62(+3)	**As 129** 47(+5) 198(-2)	**Se 140** 47(+6) 198(-2**)**	**Br 114** 39(+7) 195(-1)	**Kr**
Rb 248 148**(+1)**	**Sr 215** 113**(+2)**	**Y 178** 93(+3)	**Zr 160 80(+4)**	**Nb 146 70(+5)**	**Mo 139** 68(+4) 62(+6)	**Tc 136**	**Ru 134** 69(+3) 67(+4)	**Rh 134** 86(+2)	**Pd 137 96(+2)**	**Ag 144** 126(+1)	**Cd 154** 97(+2)	**In 166** 132(+1) 81(+3)	**Sn 162** 112(+2) 71(+4)	**Sb 159** 62(+5) 245(-3)	**Te 160** 56(+6) 211(-2)	**I** 50(+7) 216(-1)	**Xe**
Cs 267 169(+1)	**Ba 222 135(+2)**	**La* 188** 115(+3)	**Hf 160 81(+4)**	**Ta 149 73(+5)**	**W 141 68(+4) 64(+6)**	**Re 137**	**Os 135 69(+4)**	**Ir 134 66(+4)**	**Pt 139 96(+2)**	**Au 146 137(+1)**	**Hg 157** 110(+2)	**Ti 171** 140(+1) 95(+3)	**Pb 175 120(+3) 84(+4)**	**Bi 170 120(+3) 74(+5)**	**Po 176**	**At**	**Rn**

In both these structure, a given metal atom has twelve nearest neighbours. However, a significant number of metals adopt a body centred cubic lattice (BCC) in which the number of nearest neighbours is eight. The number of nearest neighbours of a metal atom in a lattice is known as the coordination number of the metal. Experimental studies on a number of metals having more than one crystal lattice have shown that the radius of a metal in an eight coordinate lattice is about 0.97 of the radius of the same metal in a twelve coordinate environment. These bonds, eight or twelve per metal atom. On the other hand, the metallic crystal lattices are stronger than the Vander Waals forces.

Table 10. Gives a set of twelve coordinate radii for metal atoms. Compare these with the covalent radii or Vander Waals radii in table 9. The metallic radii are generally larger than the corresponding covalent radii. Although both involve a sharing of electrons this is because the average bond order of an individual metal-metal bond is considerably less than one and therefore the individual bond is weaker and longer than the covalent. This does not mean that the overall bonding is weak as there is a large number of hese bonds, eight or twelve per metal atom. On the other hand, the metallic crystal lattices are stronger than the Van der waals forces.

3.5 Ionic Radius

Ionic radius is defined as the distance between the nucleus of anion and the point up to which the nucleus has influence on the electron cloud. In order words, it may also be defined as the distance of the closest approach from the centre of ion by another ion. Ionic radius is usually evaluated from the distance determined experimentally between the centres of nearest neighbors. Thus if we wish to estimate the ionic radius of Na^+ we may measure the internuclear distance between Na^+ and Cl^- ions in the NaCl crystal lattice. This distance is the sum of radii of Na^+ and Cl^- ions. From the electron density maps obtained by X-ray analysis, it has become possible, in some cases, to apportion the internuclear distance into ther adius of cation and anion. A small member of ionic crystals has thus been studied and the ionic radii of some of the elements have been determined. These radii have become the basis for assigning the ionic radii of most of the other elements.

Values for ionic radii cannot be measured absolutely, but are estimated. They are not completely accurate or reliable. Though it is possible to measure the interatomic distance between two different ions very accurately by X-ray crystallography.

Ionic radii are of two types, **cation radii** and **anion radii.** All common cations are smaller than all common anion except for rubidium and caesium cations (largest single atom cations). This is not too surprising since not only is there a loss of electron(s) from apartially filled outer shell on cation foarmaton, but there is also an increase in the over all positive charge on the ion.

Conversely, in anion formation the addition of an electron to an atom increases the size due to increase in inter-electronic repulsion in the valence-shell and decrease in effective nuclear charge. In general, there is a decrease in size of anions to covalent radii of corresponding atoms to cations thus in the series of isoelectronic species (eg. N^{3-}, O^{2-}, Ne, Na^+, Mg^{2+} and Al^{3+}). The greater the effective nuclear charge, the smaller is the radius of the species. In table 10; radii of some of the common ions have been listed.

3.6 Factors Affecting the Atomic Radii

So far, we have defined and explained types of atomic radii. We shall now turn our attention to two of the factors that affect them.

1. (**Principal QuantumNumber (n): The principal quantum n has integral values of 1, 2, 3, 4, etc.** As the principal quantum number increases, the outer electrons get farther away from

the nucleus and hence the atomic radius generally increases, been with largest value of n has the most energy, therefore it requires the least input of energy to ionize it.

2. **Effective Nuclear Charge (Z*):** The magnitude of the effective nuclear charge determines the magnitude of the force of attraction exerted by the nucleus on the outer most electrons. The greater the magnitude of effective nuclear charge, the greater is the force exerted by the nucleus on the outermost electron. Hence theelectron cloud of the outer most shell is pulled inward nearer to the nucleus and consequently its distance from the nucleus. That is, atomic radius decreases. Effective nuclear charge Z* is the amount of positive charge felt by the outer electrons in an atom. It is always less than the actual charger Z of the nucleus of the atom. This is because electrons in inner shells partially shield the electrons in the outer shell from nuclear attraction. The effective nuclear charge felt by the outer electron depends upon the actual nuclear charge and the number and type of inner screening electrons. It can be calculated by subtracting he screening or shielding constant, S from the atomic number Z Thus Z* =Z-S.

You can estimate the value of screening constant, S, with the help of **Slater's** rules in the following manner:

1. Write out the electronic configuration of the element in the following order and groupings; (ls) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p) (5d) (5f) ((6s, 6p) etc.

2. Electrons in any group higher in this sequence than the electron under consideration contribute nothing to s. For example, in Ti atom (electronic configuration IS2 2S2 2p6 3S2 3p6 3d2 4S2). The two electrons in 4S orbital will contribute nothing towards the screening for an electron in3d orbital.

3. Then for an electron in an ns or np orbitals
   (a) All other electrons in the (ns, np) group contribute S=0.35 each except for the electron in is which contribute S=0.30
   (b) All electron sin (n-1) shells contribute S=0.85 each
   (c) All elctrons in (n-2) or lower shells contribute S=1.00 each

4. For an electron in an nd or nf orbrtal
   (a) All electrons in the same group that is nd or nf contribute S= 0.35each.
   (b) Those in the groups lying lower in the sequence than the nd or nf group contribute S=1.00 each.

In order to demonstrate the application of Slater's rules, we shall now calculate the Z*for an electron in N, K and Zn atoms.

1. Electronic configuration of N= $IS^2\ 2S^2\ 2p^3$
   Grouping (IS^2) ($2S^2\ 2p^3$)
   Value of screening constant for an electron in 2p orbital will be
   S= (4x0.35) + (2x0.85) =3.10. Hence
   Z*=Z-S=7-3.10=3.90

2. Electronic configuration of K=$1S^2 2S^2 2p^6 3S^2 3p^6 4s^1$
   Grouping of orbitals will be (IS^2) ($2S^2 2p^6$) ($3S^2\ 3p^6$) ($4s^1$)
   Value of screening constant for an electron in 4s orbitals will be
   S=90.85 x8) + (Ix10) =16.80. Hence effective nuclear charge
   Z*=Z- S=19-16.80= 2.20

3. Electronic configuration of Zn= $1S^2 2S^2 2p^6 3S^2 3p^6 3d^{10} 4S^2$
   Grouping of the orbitals gives $(1S^2)$ $(2S^2 2p^6)$ $(3S^2 3p^6)$ $(3d^{10})$ $(4S^2)$
   Value of screening constant for S for an electron in 4S orbital will be S= (0.35x1) + (0.85 x18) + (1x10) = 25.65 hence the effective nuclear charge felt by 4S electron will be Z* = Z- S = 30-25.65=4.35

If we consider a 3d electron m Zn the grouping is as above, but the effective nuclear charge felt by the 3d electron will be Z* =Z- S=30- [(9 x0.35) = (18 x1)] =8.85. Thus you can see an electron in 3d orbitals in Zn is more strongly old by the nucleus than that in 4S orbital

Table 11 contains a list of values of nuclear charge for electron in valence shell in the first thirty elements calculated by Slater's rules. You can see from the table that there is a steady increase in Slater's Z* across rows of the periodic table. Effective nuclear charge felt by electrons also depends on the oxidation state of an atom in a compound. The higher the oxidation state of the atom, the higher will be the effective nuclear charge felt by the electrons and therefore, smaller will be the atomic radius. Thus the ionic radius of Fe^{3+} ion will be smaller than that of the Fe^{2+} ion. Similarly, covalent radius of bromine in BrCl, will be then that in BrCl.

Table 11: Effectiveness of nuclear charge for first 30 elements

Period	**Element**	**Z**	**S**	**Z***
1	H	1	0	1.0
2	He	2	0.3	1.70
	Li	3	1.70	1.30
	Be	4	2.05	1.95
	B	5	2.40	2.60
	C	6	2.75	3.25
	N	7	3.10	3.90
	O	8	3.45	4.55
	F	9	3.80	5.20
	Ne	10	4.15	5.85
3	Na	11	8.80	2.20
	Mg	12	9.15	2.85
	Al	13	9.50	3.50
	Si	14	9.85	4.15
	P	15	10.20	4.80
	S	16	10.55	5.45
	Cl	17	10.90	6.10
	Ar	18	11.25	6.75
4	K	19	18.80	2.20
	Ca	20	17.13	2.85
	Sc	21	18.0	3.0
	Ti	22	18.85	3.15
	V	23	19.70	3.30
	Cr	24	20.55	3.45
	Mn	25	21.40	3.60
	Fe	26	22.25	3.75
	Co	27	23.10	3.90
	Ni	28	23.95	4.05
	Cu	29	24.80	4.20
	Zn	30	25.65	4.35

3.7 Periodicity in Atomic Radii

Now that we know the various types of atomic radii and the factors that affect them, we will consider the periodicity in them. Before doing that however, we would like to emphasize that trends observed in one type of radii (example covalent radii) are generally found in the other type of radii also (example ionic and metallic radii). Two general periodic trends are found for all types of atomic radii. These are the atomic radii decreases along a period and generally increase down a group in the long form of the periodic table (see fig 4). These changes in the atomic radii can be related to the charges in effective nuclear charge and the principal quantum number in the periodic table.

If you examine table 11 you will find out that there is a steady increase (by 0.65 units) in the value of Z* from alkali metals to halogens for the elements of period 2 and 3, but there is no change in the

value of n because the electrons fill the same principal shell. As a result of this there is a steady decrease in the covalent radius from 123 and 165pm for Li and Na to 64 and 99pm for F and Cl respectively.

In comparison to the above, the decrease in covalent radii across the transition series is much smaller. As you know, electrons are successfully filled in the (n-l) d orbitals across a transition series and hence screen the size determining ns electrons from the nuclear charge more effectively. Therefore, across a transition series, there is only small increase in effective nuclear charge (by 0.15units), therefore only a small increase in effective nuclear charge decrease in atomic radius from one element to another take splace.

In 3d series, covalent radius decreases from 144pm for Sc to115pm for Ni. Then in copper and zinc due to completion of 3d sub shell, the electronic charge density in this sub shell becomes very high which increases the inter electronic repulsion. As a result, covalent radii of Cu and Zn increases lightly to 117 and 125pm respectively. Thus across the ten elements of the first transition series, there is an over all decrease in covalent radius by 19pm which is much less than that across seven normal elements of period 2 (59pm) and period 3(57pm). But due to this, the covalent radii of elements from Ga to Kr following Zn becomes much smaller than that expected by simple extrapolation of the values for elements of period 2 and 3 for example, the covalent radii of Al and Ga are equal where as the covalent radii of elements Ge, As, Se, Br are only slightly larger than those of corresponding elements (Si, P, and Cl) of period 3.The rate of decrease in the size across the Lanthanide series is even less than that across the first transition series.

In the Lanthanide elements, filling of (n-2)f orbitals take place, while simultaneously the nuclear charge increases. The electrons in the (n-2)f orbital shield then s electrons, (which largely determine the size, from the increase in nuclear charge) almost completely (S=1.00). As a result of this, there is only a small decrease in the atomic radius from one element to another. But there are 14 elements in the series. There is a total of contraction of 13pm across the series from Ca (Z=57) to Lu (Z =71). This is known as **lanthanide contraction**, because of which the atom s of elements (Hf to Hg) following Lu are usually smaller than they would be if the lanthanide had not been built up before them. Lanthanide contraction almost exactly cancel out the effect of the last shell added in the sixth period and therefore, the transition elements or 4d and 5d series have almost the same atomic radii.

On descending any group of the periodic table, the number of electron in the valence shell remains constant but the number of shells around nucleus increases monotonically, so that the effective nuclear charge felt by valence electrons stays nearly the same. So with increase in principal quantum number (n) of the valence shell, an increase in atomic radii is generally observed down any group of the periodic table. For example, as shown in figure 3, there is an increase in atomic radii of alkali and alkaline earth metals as we proceed downward in the group.

However as pointed out earlier, with the inclusion of 3d transition elements in period 4 increase in the radii of elements from Ga to Br is smaller than expected. Similarly, because of inclusion of Lanthanide elements in period 6, atoms of the transition elements of this period (Hf to Hg) are almost of the same size as atoms above than in period 5 (Zr to Cd). After that, only a small increase in size of elements of period 6 (Tc to Al) as compared to the size of elements above them in period 5 (In to I) is observed.

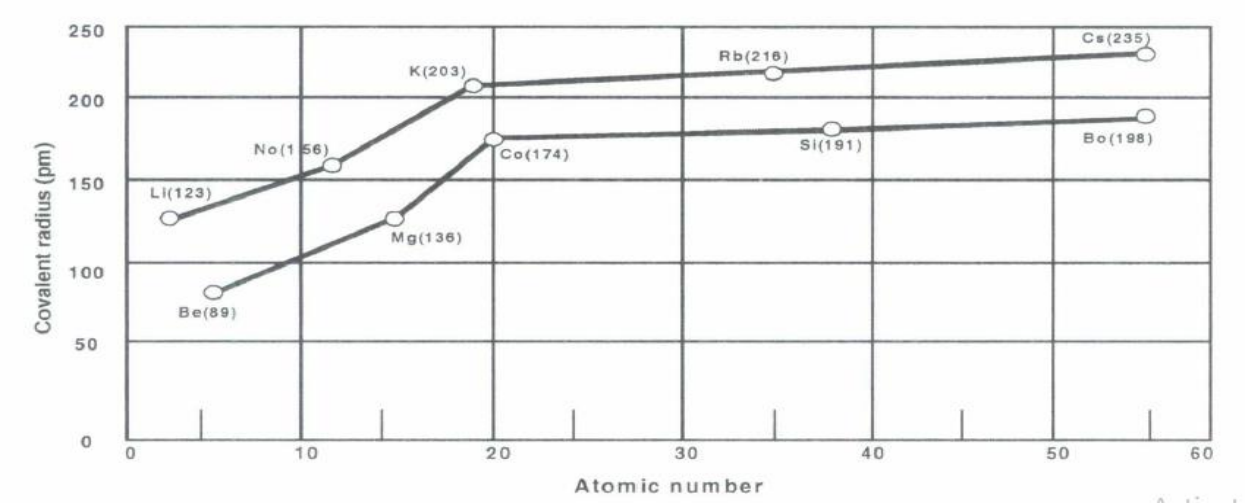

Fig 5. Plot of covalent radius against atomic number

In-text Question

Question
Explain the effect of completely filled d-orbital in Cu and Zn.

Answer
In copper and zinc due to completion of 3d sub shell, the electronic charge density in this sub shell becomes very high which increases the inter electronic repulsion. Therefore, covalent radii of Cu and Zn increases lightly to 117 and 125pm respectively. Thus across the ten elements of the first transition series, there is an over all decrease in covalent radius

4.0 SELF-ASSESSMENT EXERCISES

1. Assuming that the atoms are touching each other, what would be the internuclear distance between two fluorine atoms in F_2?

2. Arrange the following isoelectronic species in order of decreasing atomic radius. Na^+, Mg^{2+}, Al^{3+}, Si^{4+}, N^{3-}, O^{2-}, F^-, Ne

Answers

1. The distance between two fluorine atoms in F2 molecule will be twice the covalent radius of fluorine atom.

2. $N^{3-} > O^{2-} > F^- > Ne > Na^+ > Mg^{2+} > Al^{3+} > Si^{4+}$

5.0 CONCLUSION

Having gone through this unit, we can conclude that knowledge of the size of an atom is indeed very essential. It is through the knowledge of the atomic radii that we can predict accurately their action of the atom. Conversely, in anion formation the addition of an electron to an atom increases the size due

to increase in inter-electronic repulsion in the valence-shell and decrease in effective nuclear charge. The bonding within a non metal molecule is largely covalent. However, individual molecules are held together by weak forces known as Vander Waals forces

6.0 SUMMARY

In this unit, you have studied the following:

1. The definition of atomic radii.
2. The various types of atomic radii viz: covalent, van der Waals metallic and ionic radii
3. Factors affecting radii that is the principal quantum number and the effective nuclear charge Z*
4. Periodicity in atomic radii nuclear chargeZ*
5. Periodicity in atomic radii

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. a) How doe's atomic size varies in a group and in a period? Give reasons for the variation.
   b) Arrange H_2, H^+ and H^- in order of increasing atomic radius

2. What are iso-electronic ions? How does their size vary with the change of atomic number?

7.0 REFERENCE AND FURTHER READING

1. J. G Wilson, A. B. Newell (1971) General and Inorganic Chemistry (2nd edition) Published by Cambridge University Pres

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6. **COVALENT RADIUS**
   https://www.youtube.com/watch?v=A24TJLH_z_w

7. **Metallic or Crystal Radius**
   https://www.youtube.com/watch?v=oH_BI1Yjtm**4**

8. **Ionic Radius**
   https://www.youtube.com/watch?v=vfr4qnLxaTg

9. **Factors Affecting the Atomic Radii**
   https://www.youtube.com/watch?v=oopbV8e1pzM

MODULE 1

UNIT 5: IONIZATION ENERGY

1.0 INTRODUCTION

When elements react, they do so by gaming, losing or sharing of electrons. This process of gaining, losing or sharing of electronsis usually accompanied byenergy changes. You know that the electrons to be shared, gained or lost are bound to the nucleus of its atom by an electrostatic force of attraction. In order to remove an electron from an atom, its force of attraction has to be over come. This can be done by supplying energy. The energy required to remove the least strongly bond electron from an isolated gaseous atom in its ground state is known as the ionization energy. This process can be represented by the following equation:

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

Since more than one electron may be removed from an atom, the energy required for the above process is called the first ionization energy. The second ionization energy is the energy required to remove an electron from aunivalent cation that process is represented by this reaction.

$M^{+}_{(g)} \longrightarrow M^{2+}_{(g)} + e$

The second ionization energy is much larger than the first ionization energy. This is because in this case an electron is being removed from a positively charged cation. Similarly, you can define third, fourth and higher ionization energies. **The energy needed to remove an electron completely from an atom of an element is known as the first ionization energy, the second ionization energy is the energy needed to remove completely the second electron from a singly charged ion, and so on.**

$K_{(g)} \longrightarrow K^{+}_{(g)} + e^{-1}$ 1st ionization energy +418KJmol^{-1}

$K_{(g)} \longrightarrow K^{2+}_{(g)} + e^{-1}$ 2nd ionization energy +3070KJ mol^{-1}

Notice the large difference between the two values, due to the fact that it is difficult to ionize an electron when the atom already bears a positive charge. The SI unit of ionization energy which we will use throughout this course is KILOJOULE per mole. **The ionization energies for group the Group 2 elements show that the first ionization energy is almost double the value for the corresponding Group 1 element, but in general the first ionization energy decreases in a regular way on descending the main groups.**

In this unit, you will be studying the factors that affect ionization energy, periodicity in ionization across the periods, trends in ionization energy, down the groups and trends in successive ionization energy.

2.0 INTENDED LEARNING OUTCOMES (ILOs)

By the time you have studied this unit, you should be able to:

1. Define ionization energy
2. Differentiate between first, second, subsequent ionization energies
3. List the factors that affect ionization energies
4. Explain trends in ionization energies across period down the groups

3.0 MAIN CONTENT

3.1 FACTORS AFFECTING IONIZATION ENERGIES

The ionization energy (I) of an outer valence electron is related to the effective nuclear charge felt by the electron and its average distance from the nucleus as stated in the equation below

$$I = \frac{Z^* e^2}{2} (1/r)av$$

Where Z* is the effective nuclear charge, e is the charge on electron and (1/r)av is the average value of the electron from the nucleus, thus the higher effective charge felt by the electron, the higher will be the ionization energy. Also the further the electron is from the nucleus, the lower will be the ionization energy and vice versa.

In addition to the above, the ionization energy also depends upon the relative stabilities of the sub shell from which the electron is removed. As we have seen before, completely filled and half-filled sub shells are comparatively more stable, so removal of an electron from them requires more energy. The valence shell electronic configurations of noble gases are exceptionally stable and therefore their ionization energies are the highest in their respective period.

Factors affecting ionization energies are (i) The size of the atom (2) The charge on the nucleus (3) How effectively the inner electron shells screen the nuclear harge (4) The type of electron involved (s, p, d and f)

3.2 Periodicity in Ionization Energy across Periods

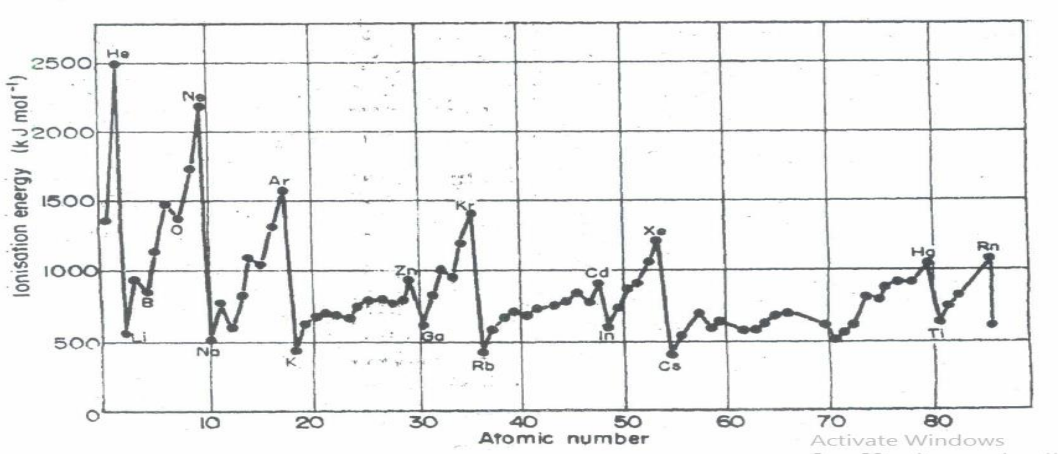
In the previous sub-section, we defined and identified factors which affect ionization energies. In the next sub-sections, we shall examine the variation in ionization energy across the periods and down, the group in the periodic table, values of ionization energies of elements are given in table 12

Table 12: Ionization energies of elements in $KJmol^{-1}$

IA	IIA	IIIB	IVB	VB	VI	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
H 1312																	**He 2372**
Li 520	**Be 900**											**B 800**	**C 1086**	**N 1403**	**O 1314**	**F 1681**	**Ne 2081**
Na 495	**Mg 738**											**Al 577**	**Si 787**	**P 1060**	**S 1000**	**Cl 1255**	**Ar 1520**
K 418	**Ca 590**	**Sc 633**	**Ti 659**	**V 650**	**Cr 653**	**Mn 717**	**Fe 762**	**Co 759**	**Ni 736**	**Cu 745**	**Zn 905**	**Ga 141 579**	**Ge 260**	**As 946**	**Se 941**	**Br 1142**	**Kr 1350**
Rb 403	**Sr 549**	**Y 615**	**Zr 659**	**Nb 664**	**Mo 688**	**Tc 697**	**Ru 711**	**Rh 720**	**Pd 804**	**Ag 731**	**Cd 867**	**In 558**	**Sn 707**	**Sb 833**	**Te 869**	**I 1007**	**Xe 1170**
Cs 374	**Ba 502**	**La 541**	**Hf 674**	**Ta 745**	**W 770**	**Re 761**	**Os 837**	**Ir 879**	**Pt 870**	**Au 890**	**Hg 1006**	**Ti 589**	**Pb 715**	**Bi 703**	**Po 813**	**At 912**	**Rn 1037**

Ce	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**

The variation in ionization energy in a particular group or period is best shown by a graph showing ionization energies against atomic number. Fig 6 shows the plot of first ionization energies of the elements of the first six periods against their atomic numbers. As is evident from the figure, the first ionization energy generally increases from alkali metals to noble gases across any row of the periodic table. But the increase is not perfectly regular.
Fig 6:



You have seen from an earlier section that across any row of the periodic table the effective nuclear charge steadily increases and the atomic radii decreases. These two effects reinforce each other to increase the ionization energies across a period. Thus the ionization energies of the alkali metals are the lowest and those of the noble gases are the highest in their respective periods. However as pointed out earlier the increase is not smooth and some anomalies are observed. For example, in the elements of period 2, in spite of increase in Z* and decrease in r, the first ionization energies of B and O are lower than those of Be and N respectively. However, these anomalies in the trend in ionization energy can be explained by electronic structures of these elements.

In the case of beryllium, the electron is removed from the filled 2S sub shell whereas in boron, the electron is removed from the singly occupied 2p sub shell. The 2p sub shell is higher in energy than the 2S, so the 2p electron of boron is more easily removed than the 2S electron of beryllium. When we come to nitrogen, we will find out that we have a half filled 2p sub shell (electronic configuration $IS^2 2S^2 3P^3$) while in oxygen the 2p sub shell is occupied by four electrons. The fourth electron in this 2p sub shell is in an orbital already occupied by another electron, so it experiences considerable repulsion. As a result, this electron is more easily removed than one of the electrons from a singly occupied orbital in nitrogen atom. Thus the ionization energy of oxygen becomes less than that of nitrogen.

Similar anomalies are observed in elements of period 3 where the first ionization energies of magnesium and phosphorous are higher than those of aluminium and sulphur respectively. We have earlier seen that across the transition series, the increase in effective nuclear charge and consequent decrease in atomic radius is small. Therefore, increase in the first ionization energies is also small. However, following the transition elements, the first ionization energy drops abruptly in gallium, indium and thallium. This again is due to the removal of an electron from a singly occupy n p orbitals which are of relatively higher energy than the ns orbital of Zn, Cd and Hg

In-text Question

Question
Establish why large difference exist in the two ionization energies of the reaction below.

$K_{(g)} \longrightarrow K^{+}_{(g)} + e^{-1}$ 1st ionization energy +418KJmol^{-1}

$K_{(g)} \longrightarrow K^{2+}_{(g)} + e^{-1}$ 2nd ionization energy +3070KJ mol^{-1}

Answer
This occurs as a result of the fact that it is difficult to ionize an electron when the atom already bears a positive charge. This is because in this case an electron is being removed from a positively charged cation**. The electrostatic force of the nucleaus is stronger on the electron of the ion than on the electron of the atom.**

3.3 Trends in Ionization Energy down the Groups

We have learned from aprevious sub section that on moving down a group of S and p- block elements effective nuclear charge remains almost steady.

But there is a general increase in the atomic radius due to increase in the value of the principal quantum number n1, thus the dominant factor in determining the ionization energies of the elements on moving down the group is their atomic radius rather than the effective nuclear charge. Therefore, as expected, the first ionization energies decrease down the groups in the case of the main group elements in the periodic table. But in the case of transition elements opposite trends are observed. Thus, the first ionization energies of the corresponding elements of 3d and 4d series are almost similar but these are smaller than the first ionization energies of the elements of 5d series. Certainly the higher values of ionization energies of the 5d transition elements are consistent with the relatively smaller size of their atoms.

3.4 Trends in Successive Ionization Energies

We have already defined successive ionization energies that is first, second, third etc. Values of eight successive ionization energies of the first twenty elements are listed in Table 12. It is evident from the values in the table that the successive ionization energies of an element inevitably become larger because the removal of successive electron leaves a higher charge on the nucleus to hold the remaining electrons. It is also clear from the table that the difference between successive ionization energies of the same element is not constant. Big jumps occur when ever an electron from a sub shell of lower principal quantum number is removed for the first time. For example, for alkali metals the second ionization energies are much higher than the first. For alkaline earth, metal the third ionization energies are much larger than the second and for the halogen, the eighth ionization energies are much greater than the seventh. These how ever cannot be explained on the basis of increase in nuclear charge alone. The stabilities of closed shell configuration similar to those of the noble gases are more important in these cases.

So far in our study, we have seen that ionization energy generally increases across a period and decreases down the group in the periodic table. Accordingly, the tendencies to form cation that is metallic character decreases across a period and increases down the group. For example, in period 3 metallic character decreases from Na to Cl whereas in the elements of group 14, C is a non metal, Si and Ge are semi metals or metalloid whereas Sn and Pb are metals.

In-text Question

Question
Discuss why the first ionization energies decrease down the groups in the case of the main group element.

Answer
increase in the atomic radius due to increase in the value of the principal quantum number n1, thus the dominant factor in determining the ionization energies of the elements on moving down the group is their atomic radius rather than the effective nuclear charge. Therefore, as expected, the first ionization energies decrease down the groups in the case of the main group elements in the periodic table. But in the case of transition elements opposite trends are observed.

4.0 SELF- ASSESSMENT EXERCISES

1. Which of the atoms having the following electronic configurations will have the highest first ionization energy and why?

   (1) [Ne] $3S^2 3P^2$
   (2) [Ne] $3S^2 3P^3$
   (3) [Ne] $3S^2 3P^4$
   (4) [He] $2S^2 2P^3$
   (5) [Ar] $3d^{10} 4S^2 4P^3$

2. In order of increasing ionization energy for the atoms N, Ne, Na and P is;

Answers
1. The atom with [He] $2S^2 3p^3$ configuration will have the highest first ionization energy because this is the smallest atom having exactly half filled p sub shell.
2. Na< P<N<Ne

5.0 CONCLUSION

We can conclude this unit by observing that chemical reaction inevitably involves either a gain, a loss or sharing of electrons by atoms. It follows therefore that, whether a reaction takes place or not, the ease with which it can happen and how regularly it happens, depends very much on the factors which affect the formation of ions by the element. The valence shell electronic configurations of noble gases are exceptionally stable and therefore their ionization energies are the highest in their respective period. Factors affecting ionization energies are (i) The size of the atom (2) The charge on the nucleus (3) How effectively the inner electron shells screen the nuclear harge (4) The type of electron involved (s, p, d of f). We have earlier seen that across the transition series, the increase in effective nuclear charge and consequent decrease in atomic radius is small. Therefore, increase in the first ionization energies is also small. However, following the transition elements, the first ionization energy drops abruptly in gallium, indium and thallium.

6.0 SUMMARY

In this unit we have studied the following

1. The ability of an element to participate in a chemical reaction is governed by it sability to give up, gain or share its outer most electrons.
2. That this ability is measured in form of its ionization energy.
3. That the ionization energy can be defined as the energy required to remove the least strongly bond electron from an isolated gaseous atom in its ground state.
4. That the ionization energy is affected by such factors as the effective nuclear charge of the atom and the reactive stabilities of the sub-shell from which the electron is removed.

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. Why is the second ionization energy of sodium higher than that of magnesium?
2. Each member of the class should write an electronic configuration of any element with atomic number not more than 30.

7.0 REFERENCES AND FUTHER READING

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MODULE 1

UNIT 6: ELECTRON AFFINITY

1.0 INTRODUCTION

You will recall that in the last unit (unit 5) you studied the process of removal of electron from a neutral atom. You learned that the energy required to remove an electron from an isolated neutral atom in gaseous state is known as the ionization energy. In this unit, we are going to study the process of addition of an electron to the gaseous atom in its ground state. In effect what we are going to learn about is the reverse of the process of ionization which we studied earlier on. We shall be talking about electron affinity.

2.0 INTENDED LEARNING OUTCOMES (ILOs)

By the end of your study of this unit, you should be able to:
1. Define electron affinity
2. List the three factors affecting electron affinity
3. Discuss how electron affinityvaries across periods and groups.

3.0 MAIN CONTENT

Electron affinity of an atom is a measure of its ability to accept an electron to form an anion. It **is** defined as the energy released or absorbed when an electron is added to the gaseous atom in its ground state or an energy released when an extra electron is added to a neural gaseous atom. It can be represented by the following equation in which E_A represents electron affinity of X.

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

When one mole of chlorine atom picks up one mole of electron, 348 kilojoules of energy is released. So the electron affinity of chlorine is 348KJ/Mol.

Since energy is evolved, these term is having a negative sign, meaning that energy is given out when the atom accepts an electron.

In the reverse process of removal of an electron from the chloride ion to form a chloric atom obviously an equal amount of energy has to be supplied. So, the electron affinity can also be expressed as the ionization energy of the anion. Thus the electron affinity of chlorine atom is clearly the ionization energy of the chloride ion. Electron affinities are difficult to measure because the accurate values for all elements are not available. Values for some elements are given in table 13.

We learned in the preceding unit that energy is required to over come the attractive force of the nucleus before an electron is removed from an isolated neutral atom in a gaseous state. It follows therefore that the reverse process of the addition of an electron to the neutral atom should release energy. Thus, the electron affinities of most elements are negative. However, a few elements are known to have positive values for electron affinity which means that the electron must be forced unto the neutral atom to form an anion. For example, nitrogen, alkaline earth metals and noble gases have positive values. All second and higher electron affinities also have large positive values.

This is not surprising, since the second and the subsequent electrons must be forced on against the negative charge of the anion. For example:

$O^-_{(g)} + e \longrightarrow O^{2-}_{(g)}$ $\quad E_A = +701\ KJmol^{-1}$

$S^-_{(g)} + e \longrightarrow S^{2-}_{(g)}$ $\quad E_A = +565\ KJmol^{-1}$

Note that as it is conventionally acknowledged, a negative value means an exothermic process. That is the reaction $X_{(g)} + e \longrightarrow X^-_{(g)}$ is exothermic. Also by high electron affinity, it is meant that the electron affinity is large and negative.

Table 13: Electron Affinities of some elements in $Kgmol^{-1}$

1	2	13	14	15	16	17	18
H							
-73							
Li	Be	B	C	N		F	He
-60	+100	-27	-122	+9	O -141	SS-328	+54
Na	Mg	Al	Si	P	S	Cl	Ne
-53	+30	-44	-134	-72	-200	-348	+99
K	Ca	Ga	Ge	As	Se	Br	
-48	-	-30	-120	-77	-195	-325	
Rb	Sr	In	Sn	Sb	Te	I	
-47	-	-30	-121	-101	-190	-295	
Cs	Ba	Ti	Pb	Bi	Po	At	
-45	-	-30	-110	-110	-183	-270	

3.1 FACTORS AFFECTING ELECTRON AFFINITY

Factors affecting electron affinities are generally the same with those affecting ionization energies. These factors are:

1. **Atomic Radius:** When an electron adds on to any atom, the nucleus of the atom holds it by an electrostatic force of attraction which depends upon the effective nuclear charge and size of the atom. The smaller the size of the atom, the greater will be the force of attraction of the nucleus for the extra action added. Therefore, the higher will be the electron affinity of the atom thus, more energy will be released in picking up an electron.

2. **Effective Nuclear Charge:** The higher the effective nuclear charge, the greater the force of attraction exerted by the nucleus on the added electron and hence, higher will be the electron affinity of the atom.

3. **Electronic Configuration:** Electronic configuration of the atom also plays an important role in determining the magnitude and sign of electron affinity. Halogens can achieve a stable noble gas configuration by accepting just one electron. Therefore, they have large negative (exothermic) electron affinities. On the other hand, the noble gases with closed shell ns^2np^6 configuration, beryllium and magnesium with np^2 (stable due to filled sub shell) and nitrogen having ns^2np^3 (stable due to half-filled p sub shell) configurations strongly resist the addition of any electron. Therefore, the electron affinities of these elements are either zero or have small positive values.

3.2 Periodicity in Electron Affinity

We have so far defined electron affinity and have considered the factors that affect it. In this sub section we will learn how the electron affinity varies in the provided descriptions.

Trends across periods:

On moving from left to right in a period, the size of an atom decreases and effective nuclear charge increases. Both these factors favour an increase in the force of attraction exerted bythe nucleus on the extra electron.

Consequently, the electron affinity generally increases across a period though irregularly. Thus electron affinities of alkaline metals have small negative values indicating their reluctance to form an anion. On the other hand, electron affinities of halogens in a period have the highest negative values which reflect their ability to form anions most readily. As explained earlier, the electron affinities of noble gases, beryllium, magnesium and nitrogen have small positive values.

Trend across groups:

We know from the previous section that on moving down the group of s- and p- block elements in the periodic table, the effective nuclear charge remains almost steady, but there is a general increase in atomic radius due to increase in the value of the principal quantum number n. As a result, the electron affinity generally decreases down any group in the periodic table. This is evident from the values given listed in table 3.1values of electron affinities of second row non-metalsthat is B, C, N, 0, F are however against the general trend, being smaller than those of corresponding elements that is Al, Si, P, S, Cl of period 3. This is apparently an indirect result of the small size of the atoms of these elements that is B, C, N, 0, F. Thus, the crowding of electrons in the smaller outer shell of an atom of an element of period 2 makes mutual repulsion of electrons substantially greater than that in the relatively larger outer shell of an atom of an element of period 3. Therefore, even though an electron added to an atom of an element of period 2 is closer to the nucleus than one added to an atom of an element of period 3, the greater inter electronic repulsion in a smaller shell leads to a lower electron affinity.

In-text Questions

Question
Explain a feature of the periodic table on moving from left to right.

Answer
When moving from left to right in a period table, the size of an atom decreases and effective nuclear charge increases. Both factors favour an increase in the force of attraction exerted bythe nucleus on the extra electron.

Question

Discuss why nitrogen, alkaline earth metals and noble gases have positive values.

Answer
The electron affinities of most elements are negative but a few elements are known to have positive values for electron affinity which means that the electron must be forced unto the neutral atom to form an anion. For example, nitrogen, alkaline earth metals and noble gases have positive values. All second and higher electron affinities also have large positive values.

4.0 SELF-ASSESSMENT EXERCISES

1. List three factors that affect electron affinity?
2. Why does the electrons affinity generally decrease down a group?

Answers

1. Factors affecting electron affinity include:
   (1) Atomic radius
   (2) Effective nuclear charge
   (3) Electronic configuration

2. On moving down a group of s and p-block elements in the periodic table, the effective nuclear charge remain almost steady, but there is a general increase in atomic radius due to increase in the value of the principal quantum number n. s a result, the electron affinity generally decreases down the group.

5.0 CONCLUSION

In conclusion, we can say the electron affinity of an element determines how easy or difficult it is for that element to participate in a chemical reaction. The electron affinity can also be expressed as the ionization energy of the anion. Thus the electron affinity of chlorine atom is clearly the ionization energy of the chloride ion. The crowding of electrons in the smaller outer shell of an atom of an element of period 2 makes mutual repulsion of electrons substantially greater than that in the relatively larger outer shell of an atom of an element of period 3.

6.0 SUMMARY

In this unit, we have studied the following;

1. That the electron affinity of an element is the energy released or absorbed when an electron is added to a gaseous atom in its ground state
2. That it is affected by three factors viz: atomic radius, effective Nuclear charge and electronic configuration
3. That the electron affinity varies across periods and groups in the periodic table.

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. Explain why the second electron affinity values are always positive.
2. Explain the difference between electron affinity and electronegativity.

7.0 REFERENCE AND FURTHER READING

1. J. G Wilson, A. B. Newell (1971) General and Inorganic Chemistry (2nd edition) Published by Cambridge University Pres

2. F. A Cotton, G. Wilkinson and P. L. Gayus (1995) Basic Inorganic Chemistry. (3nd edition) John Wiley and Sons Published

3. Gary L. Miessler, Paul J. Fischer and Donald A. Tour (2014) Inorganic Chemistry. 5th edition. Pearson Publishers. ISBN 10:0-321-81105-4

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MODULE 1
UNIT 7: ELECTRONEGATIVITY

1. 0 INTRODUCTION

In units 5 and 6 you studied ionization energies and electron affinities of isolated gaseous atoms. These quantities are a measure of the tendency of isolated atoms to lose or gain electrons. In this unit, you are going to learn about electronegativity of an element. The electronegativity of an element is a measure of the power of an atom in a molecule to attract shared electrons to itself. Unlike ionization and electron affinity, it is not a directly measurable physical quantity but rather, a theoretical concept for which several numerical scales have been developed.

In this unit, we are going to discuss the three most important scales that have been developed for measuring electronegativity.

2.0 INTENDED LEARNING OUTCOMES (ILOs)

By the time you have finished studying this unit, you should be able to do the following:

1. Define the concept of electronegativity
2. Calculate, given all the necessary impact, the electronegativity of an element, using Pauling, Mulliken-Taffe and Alfred Rochow electronegativity scales.
3. Discuss with at least eighty percent accuracy periodicity in electronegativity.

3.0 MAIN CONTENT

3.1 PAULING ELECTRONEGATIVITY SCALE

As you know in homonuclear diatomic molecule like A_2 (A-A) and B_2 (B-B) the electron pair is equally shared between the atoms bonded together. In a heteronuclear diatomic molecule of the AB type however, the situation is quite different. In the process of formation of a bond between A and B, atom A slowly start stripping off its electrons thereby becoming a partially cationic species (it becomes partially positively charge). As the positively developes on A, its tendency to attract electron increases. Mean while a similar process also takes place on atom B, thus both atoms A and B start attracting the electron pair towards themselves. They continue doing so until the tendencies of both the atoms in the bonded state to attract the electron pair to wards themselves balance.

If one of the atoms say B, has higher tendency to attract the electron pair toward itself compared to that on the other atom say A, the electron pair will spend more time on B than A. Partial charges will thus be generated on A and B. This tendency of attracting the shared electron pair toward itself by an atom of a molecule has been termed the electronegativity of the element. The concept of electronegativity was first developed by Pauling. He defined it on the basis of the patterns desirable in the single bond energies of elements which were derived from the thermochemical data. Therefore, electronegativity of an atom is the tendency of the atom to attract electrons to itself when combined in a compound. The implication is that when a covalent bond is formed, the electrons used for bonding need not be shared equally by both atoms. If bonding electrons spend more time round one atom that atom will have a δ-charge and the other will atom will have δ+. He realized that bond energy, E_{A-B} between two unlike ions like atom A and B is greater than $\sqrt{E_{A-A}}\sqrt{E_{B-B}}$ where E_{A-A} and E_{B-B} are bond energies of A-A and B-B homonuclear bonds. He assigned the course of this excess bond energy $E_{A-B} - \sqrt{E_{A-A}}\sqrt{E_{B-B}}$ to the electrostatic attraction between partially charged atoms are separated due to differences in electron attracting tendencies of A & B that is the difference in the electronegativity of A and B. He was able to derive a relationship which can be stated as

$$\Delta X_{A-B} = \frac{\sqrt{E_{A-B} - \sqrt{E_{A-A}}\sqrt{E_{B-B}}}}{96.49}$$

Where X_A is the electronegativity of element A and X_B is that of element B. Knowing bond energies, it is possible to calculate the difference between the electro negativities of the two elements. This formula only gives the difference in the electronegativities of the two elements and not the absolute value assigned to a particular element. The largest electronegativity difference is that between fluorine the most electronegative element and calcium, the most electropositive element that came out to be 3.3. Pauling assigned arbitrarily a whole number value 4.0 for fluorine so that values of electronegativity of all elements remain positive. Table 14 shows values of electronegativity of different elements (bold faced) as calculated by Pauling using his formulae.

3.2 Mulliken-Jaffe Electronegativity Scale

Mulliken defined electronegativity as the mean value of first ionization energy and first electron affinity. Both quantities are given positive values if loss of electron involves absorption of energy and negative values if gain of electron involves release of energy.Thus electronegativity X_A of atom A is given by the following relationship.

$$X_A = \frac{(I)_A + (E_A)_A}{2}$$

According to this relationship, a very electronegative element has very high ionization energy. So it will be difficult to remove its electrons. It also has a very high electron affinity. Hence, a very stable species results when electrons are added. On the other hand, an element of low electronegativity will have a low ionization energy and low electron affinity. So it loses an electron readily and has little tendency to pick up electron. It is very difficult to measure electron affinity for all elements (as we learned in unit 6). Therefore, this method is not universally applicable. The electronegativity values on Mulliken Scale are about 2.8 times those of Pauling's values. The trends in the variation of electronegativity are however the same.

In-text Question

Question

Between AA and AB which one will have a stronger electronegativity?

Answer
The charge on AA is the same but that of AB are not, If B, has higher tendency to attract the electron pair toward itself compared to that on the other atom say A, the electron pair will spend more time on B than A. Partial charges will thus be generated on A and B. This tendency of attracting the shared electron pair toward itself by an atom of a molecule be stronger and has been termed the electronegativity of the element unlike the atoms of AA.

3.3 Alfred-Rochow Electronegativity Scale

According to Alfred Rochow, electronegativity is equated to the force of attraction between an atom and the electron separated by a distance equal to the covalent radius of the atom. The force of attraction is expressed according to coulomb's law as:

$$F = \frac{Z * e^2}{r^2}$$

Where Z* is Slater's effective nuclear charge ethe electronic charge and r-the covalent radius.

Electronegativity is a measure of the attraction that an atom has for electrons in abond it has formed with another atom. The ability of an atom to attract electrons depends upon the charge on the atom and the hybridization of the atom. An atom which has acquired a positive charge will tend to attract electrons to it more readily than will a neutral atom. In turn, a negatively charged atom will be less attractive to electron than a neutral atom. Hybridization also affects electronegativity because of lower energy and hence, greater electron attracting power of s-orbital. Thus hybrid orbitals having greater s• character possess higher electronegativity. An atom in sp hybridized state will be more electronegative than the same atom in Sp^2 hybridized state which will in turn be more electronegative than the same atom in SP^3 hybridized state. Thus the carbon atom in CH_4, C_2H_4 and C_2H_2 has different values of electronegativity.

So you can say that electronegativity is not a constant quantity. All the electronegativity scales give only average values of electronegativities of element in different bonding environments.

Table 14: Electronegativity values of element

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VI	7 VIIB	8	9 VIII	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIII A
H 2.1 2.2	<----------Paulins scale <-----Alfred-Rochos scale																He
Li 1.5 1.15	Be 1.5 1.50											B 2.0 2.0	C 2.5 2.5	N 3.0 3.05	O 3.5 3.5	F 4.0 4.1	Ne
Na 0.9 1.0	Mg 1.2 1.25					f-						Al 1.5 1.45	Si 1.8 1.74	P 2.1 2.05	S 2.5 2.45	Cl 3.0 2.85	Ar
K 0.8 0.9	Ca 1.0 1.05	Sc 1.3 1.2	Ti 1.5 1.3	V 1.6 1.45	Cr 1.6 1.55	Mn 1.5 1.6	Fe 1.8 1.65	Co 1.8 1.7	Ni 1.8 1.75	Cu 1.9 1.75	Zn 1.6 1.65	Ga 1.6 1.8	Ge 1.8 2.0	As 2.0 2.2	Se 2.4 2.5	Br 2.8 2.75	Kr
Rb 0.9 0.8	Sr 1.0 1.0	Y 1.2 1.1	Zr 1.4 1.2	Nb 1.6 1.25	Mo 1.8 1.3	Tc 1.9 1.35	Ru 2.2 1.44	Rh 2.2 1.45	Pd 2.2 1.35	Ag 1.9 1.4	Cd 1.7 1.46	In 1.7 1.5	Sn 1.8 1.7	Sb 1.9 1.8	Te 2.1 2.0	I 2.5 2.2	Xe
Cs 0.7 0.85	Ba 0.9 0.95	La 1.1 1.1	Hf 1.3 1.25	Ta 1.5 1.35	W 1.7 1.4	Re 1.9 1.45	Os 2.2 1.5	Ir 2.2 1.55	Pt 2.2 1.45	Au 2.4 1.4	Hg 1.9 1.45	Ti 1.8 1.45	Pb 1.8 1.55	Bi 1.9 1.65	Po 2.0 1.75	At 2.2 1.90	Rn
Fr 0.7	Ra 0.9	Ac 1.1	Unq	Unp	Unh	Uns	Une	Une									

All the electronegativity scales we studied give only relative values of electronegativities. These values are nevertheless useful in making quantitative comparisons between elements. Electronegativities can be used to predict the value of the bonding that a compound will have. The larger the difference between the electronegativities of the two elements, the more polar will be the bond between these elements. An electronegativity difference of about 107 correspond to a partial ionic character of about 50%. So, a bond can be considered predominantly ionic, if the difference in the electronegativities of the bonded is more than l.7. On the contrary, a difference in the range of 0.4 to 1.7 results in a covalent bond's partial ionic characters or polar covalent bond.

3.4 Periodicity in Electronegativity

Electronegativity values of elements show fairly discernible periodic trend through out the periodic table. The trend is similar to that of ionization energies. Thus as expected, electronegativity of elements increases sharply across a row of S and P-block element. This is as a result of the sharp increase in effective nuclear charge of these elements example from lithium to fluorine. However, across a series of transition elements, the increase in electronegativity is much smaller. This is because the additional electron is being added to an inner shell which provides relatively good shielding for the outer electron from the nucleus. On moving down a group of representative elements, for example in the lithium group, there is a general decrease in electronegativity. The decrease is relatively small except between the first two elements.

The much greater electronegativity of lithium row elements correlates well with their small size. As expected, the elements of period 4 from gallium onwards that is Ga, Ge, As, Se and Br have greater electronegativities than would be expected by extrapolation from values for the first two elements in the respective groups. This is due to the insertion of transition elements because of which the effective nuclear charge of these elements is greater than that, if the transition elements were not there. Similarly, the presence of the lanthanide elements is responsible for greater electronegativity of the elements of 5d series than would be expected by extrapolation from values of the element so f, 3d and 4d series.

4.0 SELF-ASSESSMENT EXERCISES

1. Name the least and most electronegativity elements in the periodic table

2. State a relationship between electronegativity and hybridization

Answers

1. Caesium and francium are the least electronegative element whereas fluorine is the most electronegative element in the periodic table

2. Hybridization affects electronegativity because of lower energy and hence, greater electron attracting power of s-orbital. Thus hybrid orbitals having greater S character possess higher electronegativity. An atom in sp hybridized state will be more electronegative than the same atom in Sp^2 hybridized state which will in turn be more electronegative than the same atom in SP^3 hybridized state.

5.0 CONCLUSION

Let us conclude this unit by pointing out that, studies of ionization energy and electron affinity show us the tendency of elements to loose or gain electron while going into a relationship. In this unit on the other hand, we studied the power of these elements while in a relationship with each other to attract to it the electrons in the bond between them. An atom in sp hybridized state will be more electronegative than the same atom in SP^2 hybridized state which will in turn be more electronegative than the same atom in SP^3 hybridized state. Thus the carbon atom in CH_4, C_2H_4 and C_2H_2 has different values of electronegativity.

6.0 SUMMARY

In summary we have learnt the following from this unit:

1. That electronegativity is the tendency of an atom to attract toward itself the shared electron pair of a bond in which it is involved
2. That electronegativity can be measured by using any of the three scale developed by either, Pauling, Mulliken or Alfred Rochow
3. That the measurements vary according to the method used in measuring it.
4. That the values of electronegativity vary across periods and groups of the periodic table.

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. Explain why the electronegativity values of noble gases are zero while those of halogens are the highest in each period.

7.0 REFERENCES AND FURTH ER READINGS

1. J. G Wilson, A. B. Newell (1971) General and Inorganic Chemistry (2^{nd} edition) Published by Cambridge University Pres

2. F. A Cotton, G. Wilkinson and P. L. Gayus (1995) Basic Inorganic Chemistry. (3^{nd} edition) John Wiley and Sons Published

3. Gary L. Miessler, Paul J. Fischer and Donald A. Tour (2014) Inorganic Chemistry. 5th edition. Pearson Publishers. ISBN 10:0-321-81105-4

4. J. D Lee (2016) Concise Inorganic Chemistry. (5^{th} edition)Wiley Publishers

5. **Pauling Electronegativity Scale**
   https://www.youtube.com/watch?v=uPH-qs5s5Ic

6. **Mulliken-Jaffe Electronegativity Scale**
   https://www.youtube.com/watch?v=tLqaJGl4FQA

7. **Alfred-Rochow Electronegativity Scale**
   https://www.youtube.com/watch?v=BXcLHVmOlGQ

8. **Periodicity in Electronegativity**
   https://www.youtube.com/watch?v=c9n2-gkVsaw

MODULE 2

UNIT 1: HYDROGEN

1.0 INTRODUCTION

In the past seven units you studied the development of the periodic table and periodicity in the properties of elements. I am sure that you noticed the fact that the very first element in the periodic table is hydrogen. The hydrogen atom consists of only one proton and one electron. Inspite of that, hydrogen forms more compounds than any other element. In addition, it is the most abundant of all the elements in the universe (73.9% by weight). It is also the principal element in the solar atmosphere. However, although hydrogen is very much in abundance (0.14% by weight) on earth, it exists only in the combined state. Turquet de Mayerne (1655) and Boyle (1672) collected an inflammable gas when reacting sulphuric acid with iron but Cavendish studied its properties and called it inflammable air but it was Lavoisier that gave it the name hydrogen. It occurs in the Free State in volcanic gases and outer part of sun. Most other stars are composed of hydrogen. The extreme high temperatures of the sun/stars (10^6-10^{70}C) LEADS TO NUCLEAR FUSION of hydrogen atoms to occur resulting in liberation of enormous amount of energy.

I am sure seeing how important hydrogen is and its peculiarity of being the first element in the periodic table, you will like to know more about hydrogen. In this unit you will be studying some important aspects of the chemistry of hydrogen. You will also be studying its position in the periodic table, its isotopes and other forms.

2.0 INTENDED LEARNING OUTCOMES (ILOs)

After studying this unit, you should be able to:

1. Justify the position of hydrogen in the periodic table
2. Describe isotopes of hydrogen
3. Differentiate between Ortho and Paraforms of hydrogen.

3.0 MAIN CONTENT

3.1 POSITION OF HYDROGEN IN THE PERIODIC TABLE

The position of hydrogen in the periodic table is of particular interest. Hydrogen is the first element of the periodic table, with an electronic configuration of $1S^1$ this electronic configuration is similar to

the outer electronic configuration of the alkali metals (ns^1). On the other hand, like halogens, it is one electron short of the corresponding inert gas helium ($1S^2$). Hydrogen, therefore show some properties similar to alkali metals, while some others are similar to those of the halogens. Like alkali metals, hydrogen forms halides, oxides and sulphides. We have seen in unit 5 that the alkali metals have tight tendency of losing their outer most electron to form M^+ ion. Hydrogen also forms H^+ ion, but it does not do so, under normal conditions, because the ionization energy of hydrogen (1312 $kgmol^{-1}$) is much higher than that of the alkali metals, eg Li-520; Na-495; K-418 $kgmol^{-1}$. With a high ionization energy, hydrogen resembles halogens. (Their first ionization energies are fluorine (1618 $kgmol^{-1}$) chlorine (1255 $kgmol^{-1}$) bromine (l142 $kgmol^{-1}$) and iodine (1007 $kgmol^{-1}$). Due to its high ionization energy, hydrogen forms large numbers of covalent compounds by sharing a pair of electrons. Hydrogen like halogens, forms a diatomic molecule by sharing apair of electrons between the two atoms. By picking up an electron, hydrogen forms the hydride ion (H^-), just like the halogens form the halide ion (X^-). From the previous discussion, it is clear that hydrogen resembles both the alkali metals as well as the halogens. So hydrogen can be placed with either of them in the period table. However conventionally, it is kept along with the alkali metals in group 1 in the periodic table.

3.2 Isotopes of Hydrogen

Atoms of an element which have the same atomic number but different mass number are called ISOTOPES. Hydrogen has three different Isotopes having mass numbers 1, 2, and 3 called ordinary hydrogen or Protium ^1H, deuterium (D) or ^2H and Tritium (T) or ^3H respectively. These isotopes differ from one another in respect of the presence of neutrons. Ordinary hydrogen has no neutrons, deuterium has one and tritium has two neutrons in the nucleus (fig 7)

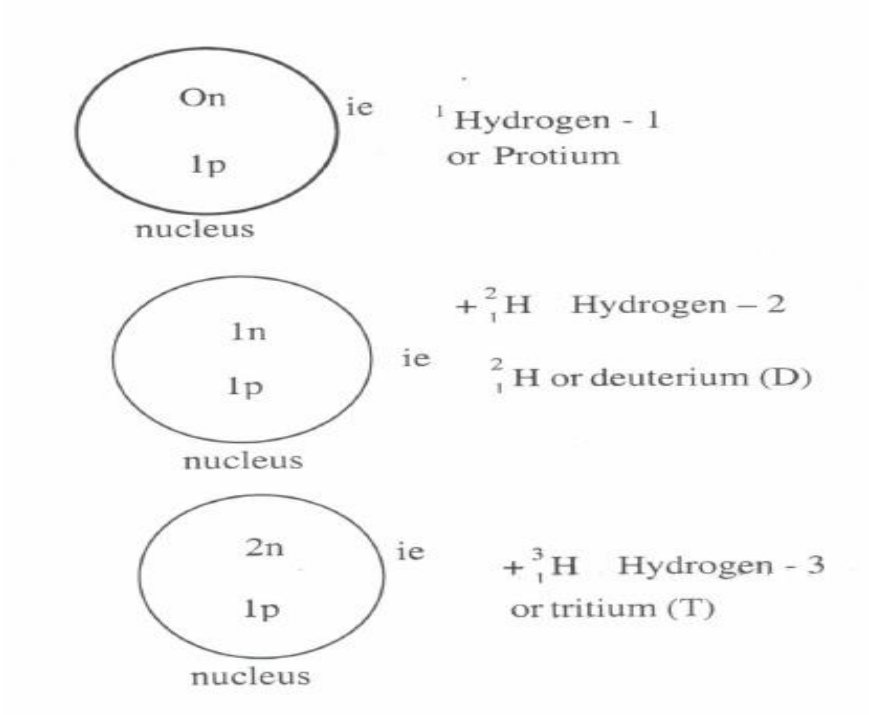

Fig 7. Isotopes of hydrogen

Deuterium is also called heavy hydrogen. These Isotopes have the same electronic configuration and therefore their chemical properties are almost the same. The only differenceis in the rate of reactions. For example, protium has a lower energy of activation than deuterium in its reaction with halogens and therefore, reacts faster.

The physical properties of hydrogen, deuterium and tritium differ considerably due to their large mass differences. Some of the important physical properties of hydrogen, deuterium and tritium have been trreated.

In-text Question

Question
Establish a relationship between hydrogen and group 1 element of the periodic table

Answer

Hydrogen is the first element of the periodic table, with an electronic configuration of $1S^1$, this electronic configuration is similar to the outer electronic configuration of the alkali metals (ns^1).

Hydrogen therefore show some properties similar to alkali metals. Like alkali metals, hydrogen forms halides, oxides and sulphides.

3.3 Deuterium Compounds

Naturally occurring hydrogen contains 0.0156% deuterium like water (H_2O) which is the oxide of hydrogen, deuterium also forms an oxide, D_2O, which is known as HEAVY WATER. It can be obtained from ordinary water which contains 0.016% of deuterium oxide. This can be done either by fractional distillation or by electrolysis. Hydrogen is liberated more quickly than deuterium at the cathode and the residual liquid continuously gets richer in deuterium content on prolonged electrolysis of water. Deuterium oxide is used as a moderator in nuclear reactions since it slows down neutrons quickly. Physical properties of H_2O and D_2O also differ from each other as in the case of H_2, D_2 these are stated

Hydrogen and deuterium are obtained by similar methods.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

$$2Na + 2D_2O \longrightarrow 2NaOD + D_2$$

Many deuterium compounds, similar to those of hydrogen, are obtained from D_2O

$$PCl_3 + 3D_2O \longrightarrow D_3PO_3 + 3DCl$$

$$Mg_3N_2 + 6D_2O \longrightarrow 3Mg(OD)_2 + 2ND_2$$

$$CaC_2 + 2D_2O \longrightarrow Ca(OD)_2 + C_2D_2$$

We can also employ exchange reactions like those given below for the preparation of deuterium compounds

$$NaOH + DO \longrightarrow NaOD + HDO$$

$$NH_4Cl + D_2O \longrightarrow HDO + NH_3DCl$$
$$\downarrow D_2O$$

NH_2D_2Cl
↓D2O
D_2O
$ND_4CI \longleftrightarrow NHD_3CI$

3.4 Tritium

Tritium differs from the other two isotopes of hydrogen in being radioactive. Naturally occurring hydrogen contains nearly 10-15% tritium. The concentration of tritium increased by over a hundred fold when thermonuclear weapon testing began in 1954 but is now subsiding again as a result of the ban on atmospheric weapon testing.
Tritium was first obtained synthetically by the bombardment of deuterium compounds such as $(ND_4)SO_4$ with fast deuterons.

$$^{2}_{1}D + {}^{2}_{1}D \longrightarrow {}^{3}_{1}T + {}^{1}_{1}H$$

It is now prepared on a large scale by irradiation of lithium-6 in the form of Li/Mg alloy of LiF with slow neutrons in a reactor.

$$^{3}_{1}Li + {}^{1}_{0}n \longrightarrow {}^{3}_{1}T + {}^{4}_{2}He$$

The following reaction occurs in nature.

$$^{14}_{7}N + {}^{1}_{0}n \longrightarrow {}^{3}_{1}T + {}^{12}_{6}C$$

Tritium is radioactive and decays by emission of a beta-particle. Its half-life period is 12.3years

$$^{3}_{1}T \longrightarrow {}^{3}_{2}He + \beta \text{ Particle}$$

Tritium can be easily in corporated in to biological molecules because it behaves chemically, just like ordinary hydrogen. The radiation that tritium gives off within an organism, as a result of its decay, can cause many diseases, including cancer.

3.5 ORTHO and PARA HYDROGEN

Ortho and Para are two different forms of hydrogen molecule. These different forms arise as a result of differences in the direction of nuclear spin. When two hydrogen atoms combine to form a molecule there are two possibilities. The two nuclei will either spin in the same direction (parallel spins) to give the form called ORTHO HYDROGEN, or they would spin in opposite directions to give PARA HYDROGEN. See fig 8. This phenomenon is known as SPIN ISOMERISM.

Parallel spin
(Ortho hydrogen)

opposite spin
(Para hydrogen)

Fig .8: Ortho and Para forms of hydrogen

Due to spin Isomerism, differences in the internal energy of the two forms of hydrogen arises, causing differences in the physical properties like boiling point, specific heat and thermal conductivity. Para hydrogen has a lower internal energy than that of ortho hydrogen. Hydrogen gas is an equilibrium mixture of ortho and para hydrogen. The ratio of ortho to Para hydrogen varies with temperature as shown in fig 9.

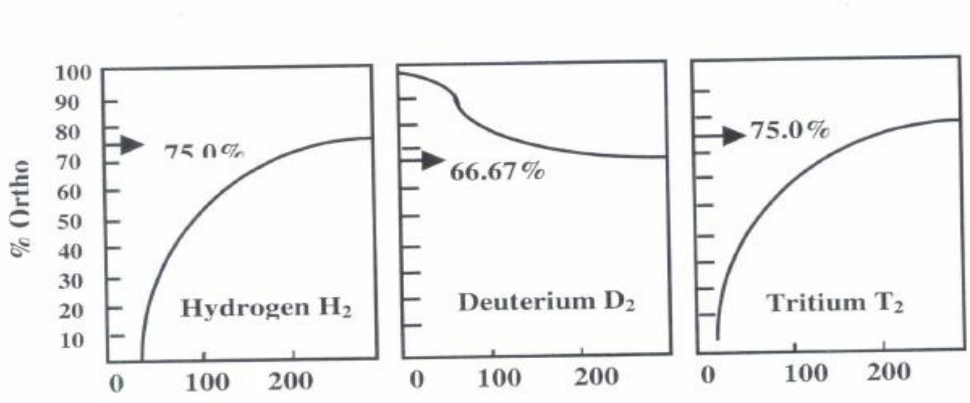

Fig 9: Ortho-Para equillibria for H2, D2 and T2,

Evidently, this ratio increases with the rise in temperature up to a temperature of about 300k (27°C) and remains constant thereafter. The percentage of hydroge at 300 K and above is 75%. This means it is not possible to get 100% ortho hydrogen at any temperature.

The equilibrium mixture of Para and Ortho hydrogen changes to almost 100% Para hydrogen when cooled to nearby absolute zero. Para hydrogen is stable for weeks in the absence of catalysts like activated charcoal, Fe, Ni Pt, O_2, NO_2 etc. these catalyze the conversion of Para to Ortho hydrogen, Deuterium and tritium also exhibit spin Isomerism and exist in Ortho and Para forms.

However, the ratio of Ortho to Paraforms in deuterium and tritium is different from that in hydrogen. The variation of Ortho /Para ratio at different temperatures is also different if you look carefully in fig 9 you will see that tritium resembles hydrogen more closely than deuterium in this respect.

In-text Question

Question
Establish the percentage ratio of Para hydrogen as temperature changes

Answer
The equilibrium mixture of Para and Ortho hydrogen changes to almost 100% Para hydrogen when cooled to nearby absolute zero.

4.0 SELF-ASSESSMENT EXERCISES

1. Write “T” for true and “F” for false in the given books for the following statements about Ortho and Para forms of hydrogen:

   (i) Ortho and Para hydrogen are different due difference in their nuclear spins.

(ii) Ortho and Para hydrogen are different due to difference in their electron spins
(iii) Physical properties Ortho and Para hydrogen are similar
(iv) Para hydrogen is more stable at lower temperatures
(v) Percentage of Ortho hydrogen in the mixture is 70%

Anwsers

1. (i) T, (ii) T, (iii) F, (iv) T and (v) F

5.0 CONCLUSION

We can conclude this unit by observing that hydrogen holds a unique position in the periodic table. It is the first element in the periodic table and also exhibits properties of the Alkali metals as well as that of the hydrogen. Hydrogen also exists in different forms thus explaining some of its properties. Ortho and Para are two different forms of hydrogen molecule. Due to spin Isomerism, differences in the internal energy of the two forms of hydrogen arises, causing differences in the physical properties like boiling point, specific heat and thermal conductivity.

6.0 SUMMARY

In this unit we studied the followings:

1. That hydrogen with an electronic configuration of $1S^1$ occupies a unique position in the periodic table
2. That hydrogen has Isotopes known as deuterium, tritium and the normal hydrogen we know.
3. That the weights of these Isotopes are H=1, Deuterium (D) and Tritium (Ti)
4. That hydrogen has in addition to H, D and T two other forms, Ortho and Para Hydrogen.
5. That these two forms arise as a result of differences in spins of the two molecules that make up the H_2 molecule.

CLASS ACTIVITY (CLASS TUTOR TO DIRECT)

1. Explain the formation of hydride ion
2. Why are the chemical properties of Isotopes similar?

7.0 FURTHER READING

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6. Isotopes of hydrogen
   https://www.youtube.com/watch?v=qtu1hm3535e
7. Ortho and para hydrogen
   https://www.youtube.com/watch?v=c3ffxmBsrtc

MODULE 2
UNIT 2: MANUFACTURE OF HYDROGEN

1.0 INTRODUCTION

In the last unit (unit 8) you studied the unique position of hydrogen in the periodic table, you also studied the various isotopes of hydrogen and also the two forms of the hydrogen molecule.

In this unit we shall be studying the ways hydrogen is manufactured, its properties and uses.

2.0 INTENDED LEARNING OUTCOMES (ILOs)

At the end of your study of this unit you should be able to:

1. List at least 3 methods used in the manufacture of hydrogen
2. Explain using appropriate equations and examples what takes place during the process of the manufacture of hydrogen.
3. List and explain a tleast five properties of hydrogen
4. List and explain with eighty percent degree of accuracy at least four uses of hydrogen.

3.0 MAIN CONTENT

3.1 Manufacture of Hydrogen

Most if not all the methods used to manufacture hydrogen make use of water. Water is a natural abundant source for the manufacture of hydrogen. Water can be reduced to hydrogen either chemically or electrically.

(a) Manufacture by chemical means
The common reducing agents are Coke (obtained from the destructive distillation of coal), carbon monoxide or hydrocarbon.

(i) The hydrogen is manufactured by allowing steam to react with red hot coke at about 1250k

$$C + H_2O \xrightarrow{1250K} CO + H_2$$

Water gas

(ii) The mixture of CO and H_2 known as water gas, is also called synthesis gas because it is used for the synthesis of methanol and other hydrocarbons.

(iii) Hydrogen is also produced by the reaction of gas (chiefly methane) with steam in the presence of nickel catalyst.

$$CH_4 + H_2O \xrightarrow[920 - 1170\ K]{\text{Ni catalysis}} CO + 3H_2$$

Similar reactioncan occur with other hydrocarbon ns. In both cases above CO is converted to CO_2.

$$CO + H_2O \xrightarrow[450 - 650\ K]{\text{Catalysis}} CO + H_2$$

Hydrogen and carbon dioxide can easily be separated from each other by bubbling the gas mixture through water in which CO_2 is fairly soluble and H_2 is virtually insoluble.

At higher temperatures, in the presence of catalysts (silica, alumina) hydrocarbon break up and rearrange in what is called cracking reactions. These reactions, which are used in refining of petroleum to produce hydrogen as a by-product. One example of simple cracking reactionis cracking of propane.

$$2CH_3 - CH_2 - CH_3 \xrightarrow[875K]{\text{Catalysis}} CH_4 + CH_2 = CH_2 + CH_3 - CH = CH_2 + H_2 \uparrow$$

Or $$2C_3H_8 \xrightarrow[875K]{\text{Catalysis}} CH_4 + C_2H_4 + C_3H_6 + H_2\uparrow$$

(b) Manufacturing by electrolysis

(i) Electrolysis of acidified water using platinum electrodes is a convenient source of hydrogen (and oxygen). On a large scale, very pure hydrogen (>99.95%) can be obtained from the electrolysis of aqueous solution of barium hydroxide between nickel electrodes.

Hydrogen obtained by electrolysis of water is relatively expensive because of the cost of electrical energy.

(ii) Hydrogen can however be obtained economically as a by-product in the electrolysis of brine during the manufacture of sodium hydroxide. During electrolysis, there is a competition at the anode between the oxidation of chloride ion and the oxidation of water.

i.e. $$2Cl^-_{(aq)} \longrightarrow Cl_2(g) + 2e^-$$

$$2H_2O \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$$

When a concentrated salt solution (brine) is used, the first reaction preferentially takes place at the cathode, the reaction is the reduction of water because it is more easily reduced than Na^+

$$2H_2O_{(1)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)}$$

The anode and the cathode reactions are combined to give the reactions thus:

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

In the laboratory hydrogen can be prepared by the reaction of water or dilute acids on electropositive metals such as alkali metals alkaline earth metals, the metals of group 12 (eg Zn) and the. Lanthanides. The reaction can be explosively violent with alkali metals (e. g 11, Rb) convenient laboratory methods employ sodium amalgam or calcium with water or zinc and tin with hydrochloric acid.

3.2 Properties of Hydrogen

(i) Hydrogen is the lightest element known. It is colourless, odourless and tasteless gas.

(ii) The hydrogen molecule is thermally stable and has little tendency to dissociate at normal temperatures, the reaction $H_{2(g)} \longrightarrow 2H_{(g)} = +436kg/Mol$ being an endothermic one. However, at high temperature in an electric or under ultraviolet light, H_2 does dissociate. The atomic hydrogen produced, exists for less than half a second after which it recombines to give molecular hydrogen and liberates a large amount of energy (436kg mol-), in form of heat. Most of the transition metals catalyze the combination reaction of hydrogen.

(iii) Atomic hydrogen is a powerful reducing agent and reduces copper, silver and mercury salts to the metallic state.
e.g. $AgNO_3 + H \longrightarrow Ag + HNO_3$

(iv) It combines with alkali metals to form hydrides e.g
$Na + H \longrightarrow NaH$

(v) It reduces sulphur to hydrogen sulphide
$S + 2H \longrightarrow H_2S$

(vi) Carbon monoxide is reduced to formaldehyde
$CO + 2H \longrightarrow HCHO$

(vii) It also reacts with oxygen at room temperature to form hydrogen peroxide.
$O2 + 2H \longrightarrow H_2O_2$

(viii) H is used for welding.
Atomic hydrogen is produced by passing ordinary hydrogen through electric arc maintained between two electrodes. The atoms set free are carried away by a stream of in coming hydrogen gas. These free atoms recombine at once on coming in contact with a metallic surface liberating a large amount of heat and thus arising temperature of the metal to say 4000-5000k. This principle is utilized in the making of the' atomic hydrogen welding torch (see fig 10). It provides an opportunity of welding at a very high temperature but in a reducing atmosphere.

(ix) Despite the fairly high bond dissociation energy of the hydrogen molecules it is moderately reactive and forms strong bonds with many other elements. It reacts with almost all elements except the noble gases.

(x) Hydrogen reacts with alkali and alkali earth metals by accepting an electron to form conic hydrides; i.e.KH, CaH_2

(xi) With non-metals it forms covalent hydrides, e.g.NH_3, H_2O and HF.

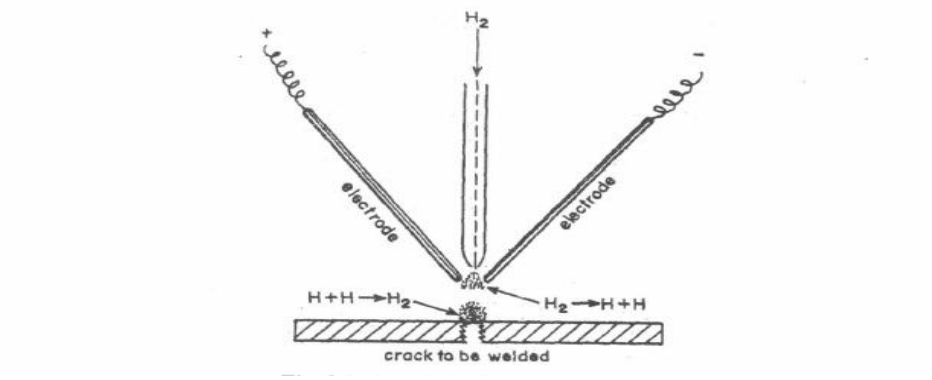

Fig.10: Atomic hydrogen welding torch

(xii) Hydrogen is easily oxidized to water and; therefore, it acts as a very good reducing agent in a variety of situations

(xiii) Hydrogen is used in metallurgy to reduce metal oxides to metals in cases where carbon cannot be used because the metal can form a carbide. Such metals include Mo and W.

$$WO + 3H_2 \longrightarrow W + 3H_2O$$

$$(NH_4)MoO_4 + 3\ H2 \longrightarrow Mo2NH_3 + 4H_2O$$

(xiv) Hydrogen adds on the multiple bonds in organic compounds. In the presence of catalysts such as finely divided nickel, palladium or mixtures of metal oxides, unsaturated organic compound are thus reduced to saturated compounds. For example,

$$\underset{\text{2-butene}}{CH_3CH = CHCH_3} + H_2 \xrightarrow[\text{Pd, 1 atm}]{\text{278 K}} \underset{\text{n-butane}}{CH_3CH_2CH_2CH_3}$$

$$\underset{\text{Methylcyanide}}{CH_3C{\equiv}N} + 2H_2 \xrightarrow[ZnO/Cr_2O_3]{\text{673 K}} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

Catalytic hydrogenation of unsaturated liquid vegetable oils to solid edible fats illustrates the industrial application of the reduction reactions; for example, the reduction of an oleate (ester of oleic acid) to ester of stearic acid.

$$\underset{\text{Oleate}}{CH_3(CH_2)_7CH = CH(CH_2)_7COOR} + H_2 \longrightarrow \underset{\text{Stearate}}{CH_3(CH_2)_{16}COOR}$$

(xv) Hydrogen reacts with carbon monoxide in the presence of catalysts to form methanol.

$CO + 2H_2 \xrightarrow{Cobalt} CH_3OH$

This reaction is known as hydroforrnylation reaction and is used in the industrial preparation of methanol.

In-text Question

Question
Complete the reaction: $C + H_2O \xrightarrow{1250\ K}$

Answer
$CO + H_2$ (Water gas)

3.3 Uses of Hydrogen

Some of the uses of hydrogen include the following:

1. The largest single use of hydrogen is in the syntheses of ammonia which is used in the manufacture of nitric acid and nitrogenous fertilizers.
2. Hydrogen is used in the hydrogenation of vegetable oils and the manufacture of methanol.
3. In space crafts, hydrogen gas is used in fuel cells for generating electrical energy and for providing clean drinking water to the astronauts. In a fuel cell, electrical energy is generated by the reaction of hydrogen leaf.
4. This is sometimes called **"cold combustion"** A hydrogen oxygen fuel cell may have an alkaline of acidic electrolyte.
   The one in fig 9.2 has porous carbon electrodes and KOH as electrolyte.

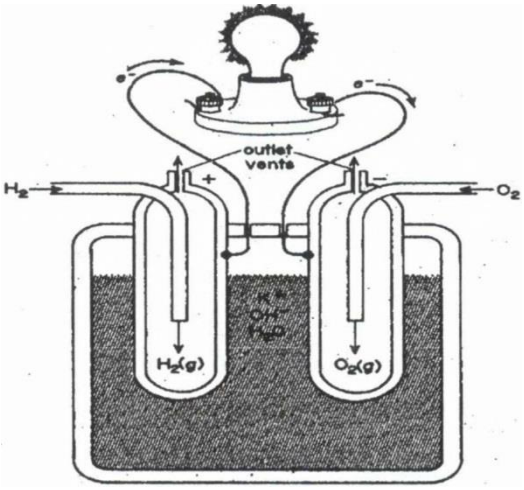

Fig 11: A hydrogen-oxygen fuel cell with KOH electrolyte and porous carbon electrodes

The half-cell reactions are given below:

$H_{2(g)} + 2OH \longrightarrow 2H_2O + 2e \qquad E^0 = -0.8280V$ anode

$1/2O_{2(g)} + H_2O_{(l)} + e \longrightarrow 2OH^-$ $E^0 = 0.401$ V, cathode

$H_{2(g)} + 1/2O_{2(g)} \longrightarrow H_2O_{(1)}$ $E^0 = 1.229$ V

With acidic electrolyte, the half-cell reacts irons are:

$H_{2(g)} \longrightarrow 2H + 2e$ $E^0 = 0$V anode

$1/2O_{2(g)} + 2H + 2e \longrightarrow H_2O_{(l)}$ $E^0 = 1.22911$ V, cathode

$H_{2(g)} + 1/2O_{2(g)} \longrightarrow H_2O_{(1)}$ $E^0 = 1.229$ V

We can see from the equations above that the electromotive force of the cell remains the same whether we use alkaline or acidic electrolyte. This is because we are using the same reactants at the electrodes in both cases.

Fuel cells have several advantages over other sources of energy. Firstly, in a fuel cell unlike in the dry cell or storage battery (which requires recharging also), the cathode and anode reactants are continuously supplied so that energy can be indefinitely withdrawn from it. Secondly, in a fuel cell energy is extracted from the reactants under almost ideal conditions. Therefore, the thermodynamic efficiency of the fuel cells is higher than of most of the ordinary combustion processed. Fuel cells have efficiencies approaching 75% whereas power plants that burn fuels have efficiencies of only about 40%.
Combustion of hydrogen is a highly exothermic reaction and produces no pollutants;
$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(1)}$ $_{\Delta}H = -572$ kJ/mol
Liquid hydrogen is therefore, used as a rocket fuel.

It is now clear that world reserves of fossil fuels like coal, oil and gas are finite, so they cannot last forever. Nuclear and hydro electric power cannot meet the world's energy needs. Moreover, these resources post a danger to the world's environment. With these facts in mind there is now an active search for alternative source of energy. In addition to solar power, hydrogen is being considered a potential fuel for the future.

Hydrogen as a fuel has many advantages over the conventional fossil fuels and electric power. It is available in unlimited quantities in sea water. It is pollution free because the major product of its combustion is water with only traces of nitrogen oxides. It releases greater energy per limit weight of fuel in comparison to gasoline and other fuels. Hydrogen can be transported as a gas in high pressure pipelines, as a liquid in tankers and even as a solid in form of metal hydrides. Unlike electricity hydrogen can b stored and used when needed.

Hydrogen however has the following disadvantages viz:

i. Hydrogen like electricity is a secondary source of energy because it is produced using energy from a primary source such as coal, nuclear fission or sun.

ii. Preparation of hydrogen through electrolysis is not economical at present in fact more energy has to be spent in electrolysis of water than what can be liberated by burning hydrogen as a fuel.

iii. Decomposition of water by solar energy in presences of catalysis is known as photochemical decomposition of water. Using catalysts scientists in France have been able to achieve the efficient decomposition of water under visible and ultra violet light. If this process can be made industrial, a convenient method of converting solar energy directly to a useful form of store chemical energy will be available.

In-text Question
Question
State the why hydrogen is regarded as a secondary source of energy

Answer
Hydrogen is a secondary source of energy because it is produced using energy from a primary source such as coal, nuclear fission or sun.

4.0 SELF ASSESSMENT EXERCISES

1. Complete the following chemical reactions which take place during the formation of hydrogen.

   $C + H_2O \longrightarrow$

   $CH_4 + H_2O \longrightarrow$

   $CO + H_2O \longrightarrow$

   $2NaCl + 2H_2O \xrightarrow{\text{Electrolysis}}$

   $Ca + 2H_2O \longrightarrow$

2. Write five important industrial uses of hydrogen

Answer to Exercises

1. (i) $C + H_2O \longrightarrow CO + H_2$

   (ii) $CH_4 + H_2O \longrightarrow 3CO + H_2$

   (iii) $CO + H_2O \longrightarrow CO_2 + H_2$

   (iv) $2NaCl + 2H_2O \xrightarrow{\text{Electrolysis}} 2NaOH + H_2 + Cl_2$

   (v) $Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$

2. Used in
   Manufacture of ammonia
   Manufacture of Methanol
   Hydrogenation of vegetable oils
   Extraction of Molybdenum and tungsten
   In fuel cells

5.0 CONCLUSION

We can conclude this unit by observing that the major material for the manufacture of hydrogen is water. Since water is abundant, the production of hydrogen should be simple. However, it is not efficient to produce hydrogen by electrolysis. This is no economical because of the cost of electricity. The single most important use of hydrogen is in the manufacture of ammonia which is used in the production of nitric acid and nitrogenous fertilizers. Hydrogen is also used in space crafts as a source of fuel cell.

6.0 SUMMARY

In summary we have studied the following in this unit. They are:

1. That the major source for the manufacture of hydrogen is water
2. That there are two primary methods for the manufacture of hydrogen
   a. manufacture by chemical means
   b. manufacture by electrolysis
3. That even though manufacturing by electrolysis would have been preferred it is too expensive, because of the cost of the energy needed for electrolysis.
4. That the largest use of hydrogen is in the manufacture of Ammonia, which is used to manufacture nitric acid and nitrogenous fertilizers.
5. That hydrogen is made use of in the production of fuel cells for spacecrafts.
6. That hydrogen is also used in extraction of metal and Hydrogenation of vegetable oils.

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. Write Chemical equation for the following reactions:
   (i) Formation of methanol from coal
   (ii) Reduction of methyl cyanide
   (iii) Conversion of Oleic acid into stearic and
   (iv) Reduction of ammonium molybdate to molybdenum

7.0 FURTHER READING

1. J. G Wilson, A. B. Newell (1971) General and Inorganic Chemistry (2nd edition) Published by Cambridge University Pres

2. F. A Cotton, G. Wilkinson and P. L. Gayus (1995) Basic Inorganic Chemistry. (3nd edition) John Wiley and Sons Published

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5. **Manufacture of Hydrogen**
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6. **Properties of Hydrogen**
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7. **Uses of Hydrogen**
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MODULE 2
UNIT 3: IONIC OR SALT-LIKEHYDRIDES

1.0 INTRODUCTION

You will recall that in unit 7, we became aware of the fact that hydrogen forms more compounds than any other element. We also saw in unit 9, that despite the fairly high bond dissociation energy of the hydrogen molecule, it is moderately reactive and forms strong bonds with many other elements. You also learned that it forms ionic and covalent hydrides with metals and non-metals respectively. In this unit you will be studying the formation of hydrides, their types and characteristics of the hydrides.

2.0 INTENDED LEARNING OUTCOMES (ILOs)

By the time you have studied this unit you should be able to:

1. List the three classes of hydrides
2. Discuss for each of the different types of hydrides and their properties.

As already pointed out at the beginning of this unit. Hydrogen combines with a number of elements to form hydrides. As electronegativity of the element increases the stability of the hydrides also increases. Three types of hydride compounds are formed depending upon the electronegativity of the element. They are classified into:

(i) Ionic or salt like or salrichydrides
(ii) Covalent or molecule hydrides
(iii) Metallic or non-stoichiometric hydrides

3.0 MAIN CONTENT

3.1 IONIC OR SALT-LIKEHYDRIDES

These are formed by metals with low electronegativity values and are more electropositive with respect to hydrogen. These hydrides are formed by transfer of an electron from the metal to the hydrogen atom. Hydride ion is a peculiar chemical species and in contrast to proton which has small size, it is unusually large. It is larger than any of the negative ions except iodide.

The reason or this apparent paradox lies in the lack of control by a single nuclear proton over two naturally repelling electrons.

Alkali and Alkaline-earth metal of groups l and 2 are sufficiently electropositive and force the hydrogen atom to accept an electron to form the hydride ion, H^- e.g. Lithium hydride LiH^- and calcium hydride $Ca^{2+}(H^-)_2$
Ionic hydrides are formed by heating metals in hydrogen at 973K. Ionic hydrides are white crystalline solids. They have high melting points and conduct electricity in liquid state, liberating hydrogen at the anode. Their density is higher than that of the metal.

They are powerful reducing agents especially at high temperatures e.g.

$2CO + NaH \longrightarrow HCOONa + C$

$SiC1_4 + 4NaH \longrightarrow SiH_4 + 4NaCl$

$PbSO_4 + 2CaH_2 \longrightarrow PbS + 2Ca(OH)_2$
Li^+H^- and Na^+H^- are used in making valuable reducing agents like lithium aluminum hydride ($LiAlH_4$) and sodium- boro-hydride ($NaBH_4$). The complex hydrides are frequently used in the reduction of aldehydes, ketones, acids and their derivatives to give alcohols.

2-COOH $\xrightarrow{LiAlH_4/NaBH_4)}$ $R\text{-}CH_2OH$
Organic acid Primary alcohol

$>C=0 \xrightarrow{LiAlH_4/NaBH_4} >CHOH$
Ketone/aldehyde Secondary alcohol

3.2 COVALENT HYDRIDE

These bonds are formed by elements of comparatively higher electronegativity such as the P- block elements and Be and Mg. The bonds formed in this class of hydrides are mostly covalent in character but in some cases, for example, in HF, the bond may be partially ionic.

The covalent hydrides can be prepared either by direct reaction of non-metals with hydrogen under suitable conditions or by the reaction of H20 or acids or nitrides, carbides, bonides, silicides, stanides of alkali and alkaline earth metals or by the reduction of halides. These are illustrated by the following reactions.

$N_2 + 3H_2 \xrightarrow{\text{Catalyst, 750 K}} 2NH_3$

$Mg_3N_2 + 6H_2O \xrightarrow{\text{600 - 1000 atm}} 3Mg(OH)_2 + 2NH_3$

$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

$AsCl_3 + 6H \xrightarrow{Zn + HCI} 4AsH_3 + 3HCl$

$4PC1_3 + 3LiAlH_4 \xrightarrow{\text{Ether}} 4PH_3 + 3LiCl + 3AlCl_3$

These hydrides have molecular lattice made up of individual saturated covalent molecules, with only weak Vander Waals forces and in some cases along with hydrogen bonds. This accounts for their softness, low melting and boiling points, their volatility and lack of conductivity. Some covalent hydrides are unstable in the presence of air, e.g. stannane, SnH_4.

Some covalent hydride hydrides of groups 2 and 13 are electron deficient. These have structures between ionic and covalent hydrides. These are either dimeric, e.g boronhydride (B_2H_6), or polymeric, eg beryllium hydride $(BeH_2)_n$, magnesium hydride $(MgH_2)_n$ and aluminium hydride $(AlH_3)_n$.

In-text Question
Question
Discuss what is expected to happen when hydrogen reacts to form hydrides

Answer
Hydrogen combines with a number of elements to form hydrides. As electronegativity of the element increases the stability of the hydrides also increases.

3.3 METALLIC HYDRIDES

When heated, hydrogen reacts with many transition metals (lantharindes and actinides) to form metallic hydrides. Most of these have metallic appearance and are less dense than the parent metal. They all conduct heat and electricity though not as well as the parentmetal. They are almost always non-stoichiometric, being deficient in Hydrogen. For example, $TiH_{5.8}$, $VH_{0.56}$, CrH_{17}, $NiH_{0.6}$, $TaH_{0.7}$, $LaH_{22.76}$, YbH_{28} etc.

Most of these hydrides are stable to water up to 375K but are quantitatively decomposed by acids and show some reducing properties.

Formerly these hydrides were formed as interstitial compounds in which hydrogen was through to be accommodated in the interstices in the metal lattice producing distortion but no change in its type. But recent studies have shown that except for hydrides of nickel palladium, cerium and actinium, other hydrides of this class have lattice of a type different from that of the parent metal. For example, the hexagonal close packed lattice of some lanthanides is transformed to a face• centred cubic lattice in their dihydrides. As pointed out earlier, these interstitial hydrides are poorer conductors of electricity, exhibit less Para magnetism and are more brittle than the parent metal. These characteristics suggest that hydrogen is present in the metal lattice as hydrogen atoms rather than as hydrogen molecules. The single electron of hydrogen is paired with an electron of the metal, thereby reducing the extent of metallic bonding. Breaking of the H-H bond is in agreement with the fact that their metals catalyze reactions of hydrogen.

In-text Question
Question
Explain why it is possible for hydrogen to react with the alkali and alkaline earth metal of group 1 and 2.

Anwser
Alkali and Alkaline-earth metal of groups 1 and 2 are sufficiently electropositive than hydrogen and force the hydrogen atom to accept an electron to form the hydride ion, H^-

4.0 SELF ASSESSMENT EXERCISES

1. Silt is an example of which of the following type of hydrides
   (a) Ionic (b) Interstitial (c) Metallic (d) Covalent.

2. List 3 properties of ionic hydrides

Answers

1. (d) Covalent hydride

2. (i) They have high melting points
   (ii) They conduct electricity in fused state liberating hydrogen at the anode
   (iii) Their density is higher than that of the metal.

5.0 CONCLUSION

We can conclude this unit by putting the fact that despite the fairly high bond dissonation energy of the hydrogen molecule, it reacts with certain elements to form three types of hydrides viz, ionic, covalent and metallic hydrides. Some covalent hydride hydrides of groups 2 and 13 are electron deficient. These have structures between ionic and covalent hydrides. When heated, hydrogen reacts with many transition metals (lantharindes and actinides) to form metallic hydrides. Most of these have metallic appearance and are less dense than the parent metal. They all conduct heat and electricity though not as well as the parentmetal.

6.0 SUMMARY

In this unit we learned the following:

1. That hydrogen leads with certain metals to form hydrides
2. That these hydrides are classified into three viz ionic or salt- like hydrides, covalent hydrides and metallic hydrides
3. That ionic hydrides are powerful reducing agents, covalent hydrides are soft have low melting points and are poor conductors of electricity.

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. What types of bonding do you expect of?
   (i) Sodium hydride
   (ii) Methane
   (iii) Ammonia

7.0 FURTHER READING

1. J. G Wilson, A. B. Newell (1971) General and Inorganic Chemistry (2nd edition) Published by Cambridge University Pres

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5. **Ionic or salt-likehydrides**
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6. **Covalent Hydride**
   https://www.youtube.com/watch?v=ZKZwt8y4a6E

7. **Metallic Hydrides**
   https://www.youtube.com/watch?v=xxiEclP1NGI

MODULE 2

UNIT 4: HYDROGEN BONDING

1.0 INTRODUCTION

A very important aspectof the chemistry of hydrogen is its formation of hydrogen bonds.

When hydrogen is covalently bonded to a highly electronegative element like F, O, or N, the electronegative element attracts the electron pair towards itself giving rise to an induced positive charge (δ^+) on the hydrogen atom and negative charge (δ^-) on the electronegative atom for example,

$H^{\delta+}X^{\delta-}$ where X is the electronegative atom. When this happens the hydrogen, due to its positive character, will attract another electronegative atom of the neighbouring molecule forming a bond. This bond is known as hydrogen bond. This is illustrated below

---------- $H^{\delta+}X^{\delta-}$---------- $H^{\delta+}X^{\delta-}$---------- $H^{\delta+}X^{\delta-}$----------

δ^- denotes covalent bond.

δ^+ denotes hydrogen bond.

In this unit you will be studying the types of bonding, the effect of hydrogen bonding on boiling and melting points and on water solubility of the compound containing hydrogen bonded elements.

2.0 INTENDED LEARNING OUTCOMES (ILOs)

By the time you have studied this unit you should be able to:

1. Define hydrogen bonding
2. List and discuss the two types of hydrogen bonding
3. List and discuss the effect of bonding on boiling and melting points
4. Discuss the effect of bonding on the solubility of a substance
5. Briefly discuss, giving examples, the polarizing power of H^+

3.0 MAIN CONTENT

3.1 HYDROGEN BOND

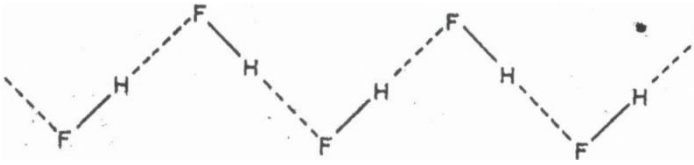
Hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with electronegative atom of another molecule, generally of the same compound.

The hydrogen bond energy is only about 7-59 $kJmol^{-1}$ compared to the normal covalent bond energy of 389-665 $kJmol^{-1}$ for H-N, H-0 and H-F bonds. This, hydrogen bond is much weaker than a covalent bond. Obviously, its length is also much more than the covalent bond. There are two types of hydrogen bonding. These are:

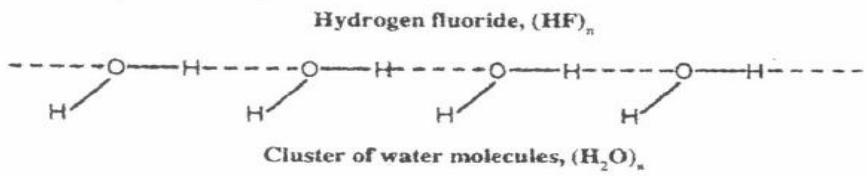
(i) Intermolecular hydrogen bonding
(ii) Intramolecular hydrogenbonding

3.2 Intermoleccular Hydrogen Bonding

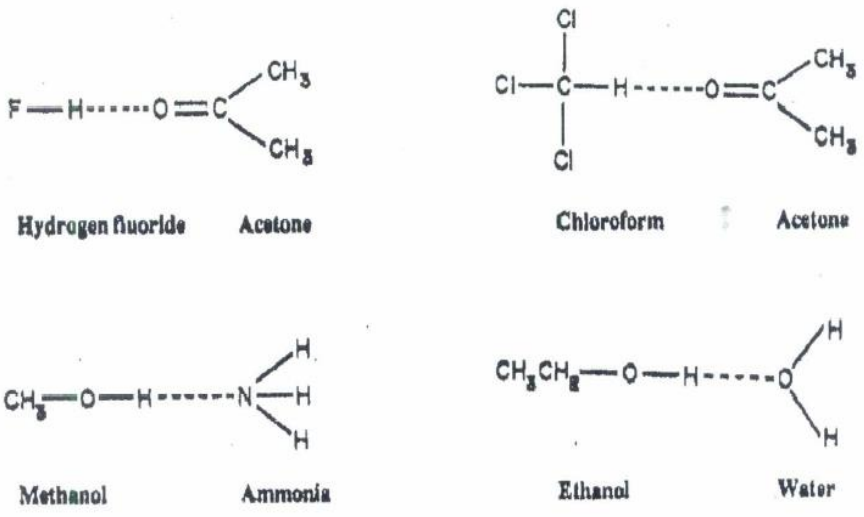
In this case, two or more molecules hydrogen bonding. Some common hydrogen bonding occurring between of the same are involved in examples of intermolecular the the molecules of the same compound are HF, H_2O, alcohols etc.



Hydrogen fluoride, (HF)n



Examples of the intermolecular hydrogen bonding between two different kinds of molecules are as following.



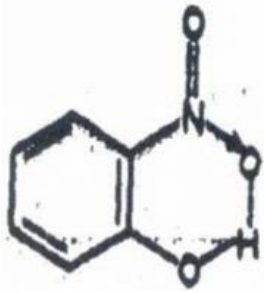
In-text Question

Question
State what you understand by hydrogen bond.

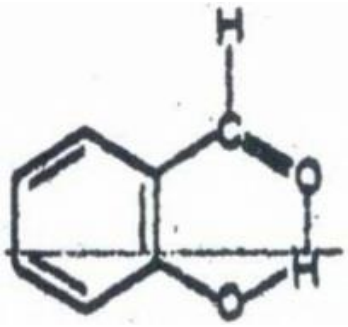
Answer
It can be defined as "the attractive force which binds hydrogen atom of one molecule with electronegative atom of another molecule, generally of the same compound".

3.3 Intramolecular Hydrogen Bonding

Intramolecular hydrogen bond is formed between two atoms of the same molecule. As a consequence of this, generally a five or six membered ring called chelatering is formed.



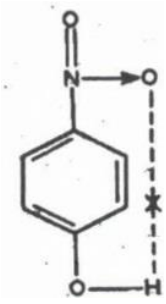
3- Nitrophenol



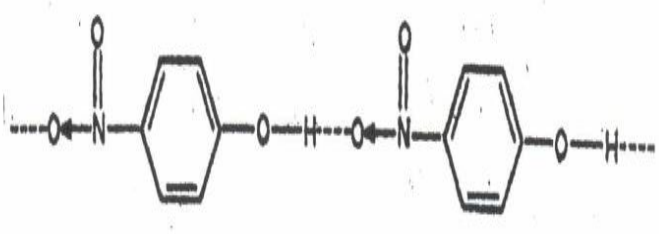
Salicyladehyde.

You have seen above, that intramolecular hydrogen bonding takes place in molecules like 3-nitrophenol and salicyladehyde.

Intramolecular hydrogen bonding does not take place in p-nitrophenol because of the large distance between the two groups (N02 and QH) in p- nitrophenol



This type of hydrogen bonding is not possible. It does however show the usual intermolecular hydrogen bonding.



It is significant to note that the vas majority of intramolecular hydrogen bonding occurs where a five or six membered ring can be formed because of the stability associated with such rings.

3.4 Effects of Hydrogen Bonding

Hydrogen bonding plays a very significant role in determining the properties of compounds. In this section we shall discuss its effect on the melting point, boiling point and solubility in water.

3.4.1 Boiling Point and Melting Point

If you examine the values for the melting and boiling points shown in fig.12, you will see that the melting and boiling points of the hydrides of group14 elements ie CH_4 SiH_4, GeH_4 and Sn H_4 show a general increase with increase in molecular weight. However, NH_3 in Group 15, HF in Group17 and **water have abnormally high melting and boiling points as compared** to other hydrides in their respective groups in the periodic table. This anomaly is explained on the basis of hydrogen bond formation. In compounds where the molecules are linked by hydrogen bonds, some extra energy is required to break the intermolecular hydrogen b o n d and this is responsible for their higher boiling and melting points. Intra molecular hydrogen bond, however h a s the opposite effects. For example, in ortho nitrophenol the groups present in ortho position are involved in intramolecular hydrogen bonding thus preventing the intermolecular hydrogen bond formation, ie association of the molecule. Due to the intramolecular chelated structure, o-nitrophenol is seen to be volatile wherea sp-nitrophenol is not.

3.4.2 Water Solubility

Solubility of a substance increases markedly when hydrogen bonding is possible between the solvent and the solute molecules. For example, lower alcohols like, methanol, ethanol etc are highly miscible with water due to the hydrogen bonding with water molecules.

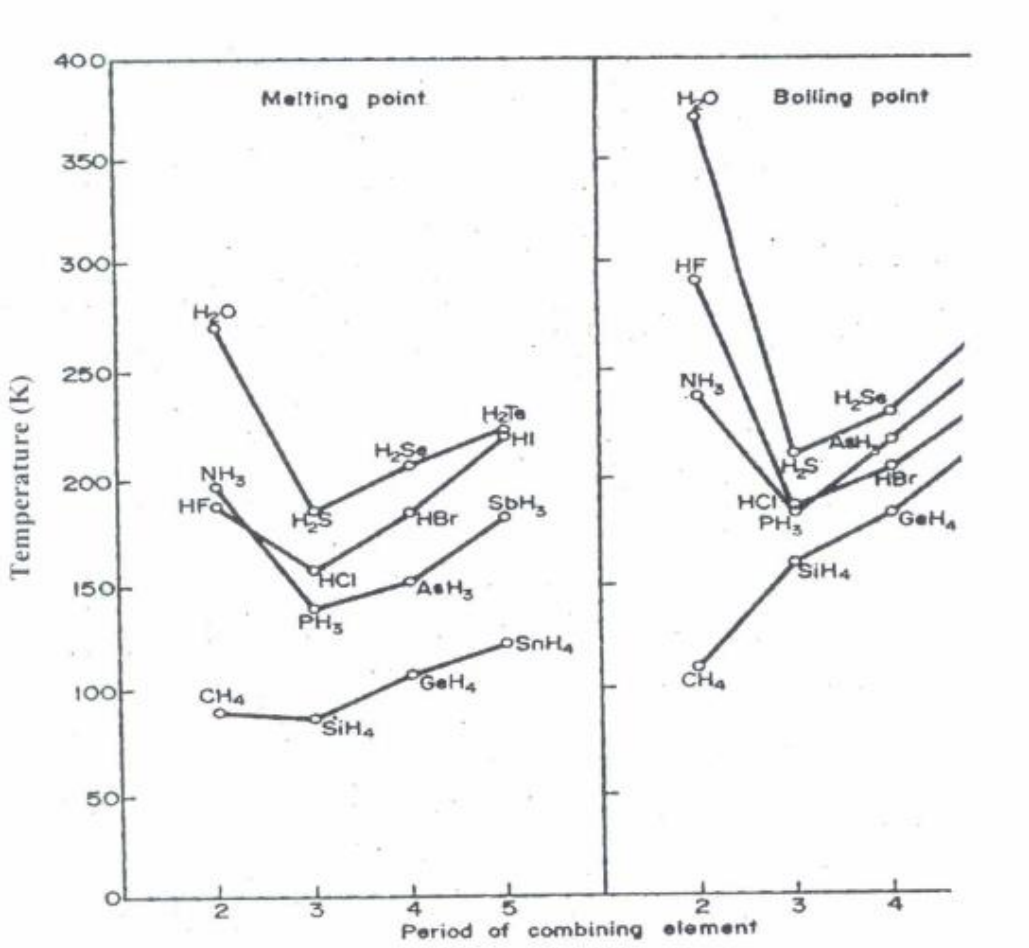


Fig.12: (a) Melting pointcurves and (b) Boiling point curves of the molecular hydride

3.5 POLARISING POWER OF H^+

We know that the polarizing power of a cation, ie its ability to distort or polarize an anion is directly proportional to its positive charge and inversely proportional to its size. We can also say that the polarizing power of a cation is proportional to the ratio of its charge to its size. This ratio is known as the ionic potential of the cation. As the hydrogen cation, ie proton is vanishgly small, it has a very high ionic potential and a vast polarizing power.

As result of this polarizing power for protons, H^+ hardly exist freely. They are generally found associated with other molecules. For example, with ammonia and water, these form species like NH_3, H_3O^+ H_5O^+, and HgO_4^+ etc. The aquated proton species are represented as H^+. Enthalpy of formation of these aquated proton species is large (-1075kg mol^{-1}). It is mainly because of this reason that many covalent hydrides (H-X) are acidic in aqueous solution, ie they release H^+ ions even though H-X bonds are often very strong in them.

In-text Question

Question
Why is H_2O a liquid and H_2S a gas at room temperature?

Anwser

Water have abnormally high melting and boiling points as compared to other hydrides. This anomaly is explained on the basis of hydrogen bond formation. In compounds where the molecules are linked by hydrogen bonds, some extra energy is required to break the intermolecular hydrogen bond and this is responsible for their higher boiling and melting points. Intra molecular hydrogen bond, however has the opposite effects resulting in intramolecular hydrogen bonding hence H_2S is gaseous.

4.0 SELF ASSESSMENT EXERCISES

1. State why group 2 metals are harder and have higher melting points compared to the Group 1 metals?

2. What is the effect of hydrogen bonding on the properties of H_2O, HF and NH_3?

   Answer

1. Since Group 2 elements have two valence electrons, they have stronger metallic bonding and show higher cohesive properties than Group 1 neighbours, thus they are harder and have higher meeting points as compared to the Group 1 elements.

2. Hydrogen has strong polarizing power, as a result of this polarizing power for protons, H^+ hardly exist freely. They are generally found associated with other molecules. For example, with ammonia and water, these form species like NH_3, H_3O^+. It is mainly because of this reason that many covalent hydrides (H-X) are acidic in aqueous solution, ie they release H^+ ions even though H- X bonds are often very strong in them.

5.0 CONCLUSION

We can conclude this unit by stating that hydrogen bond formation is a very important phenomenon and it helps in explaining the behaviour of some compounds. Variations in boiling and melting points and solubility of substances are explainable by the existence of hydrogen bonds. However, NH_3 in Group 15, HF in Group17 and water have abnormally high melting and boiling points as compared to other hydrides in their respective groups in the periodic table. This anomaly is explained on the basis of hydrogen bond formation. The polarizing power of a cation, ie its ability to distort or polarize an anion is directly proportional to its positive charge and inversely proportional to its size.

6.0 SUMMARY

In summary you have studied the following in this unit:

1. That hydrogen bond is defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom of another molecule, generally of the same compound.
2. That there are two types of hydrogen bonds viz:
   (i) Intermolecular hydrogen bond
   (ii) Intramolecular hydrogen bond
3. That the hydrogen bonding in substances affect their melting points, boiling points and their solubility in water.

CLASS ACTIVITY (THETUTOR TO DIRECT)

1. Which hydrogen bond do you expect to be stronger and why? (a) S-H-------O or (b) O-N---- S
2. Explain why the boiling points of hydrogen halides follow the trend
3. When a hydrogen bond is symbolized by X- H-------- Y, what do the solid and dotted lines represent? Which distance is shorter?

7.0 REFERENCES AND FURTHER READING

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2. F. A Cotton, G. Wilkinson and P. L. Gayus (1995) Basic Inorganic Chemistry. (3nd edition) John Wiley and Sons Published

3. Gary L. Miessler, Paul J. Fischer and Donald A. Tour (2014) Inorganic Chemistry. 5th edition. Pearson Publishers. ISBN 10:0-321-81105-4

4. J. D Lee (2016) Concise Inorganic Chemistry. (5th edition)Wiley Publishers

5. HYDROGEN BOND
https://www.youtube.com/watch?v=RSRiywp9v9w

6. Intermolecular Hydrogen Bonding
https://www.youtube.com/watch?v=dBBEpPFNCEs

7. Intramolecular Hydrogen Bonding
https://www.youtube.com/watch?v=V_zBrMq2GZg

8 Effects of Hydrogen Bonding
https://www.youtube.com/watch?v=JP6u5Gwa6q0

MODULE 3

UNIT 1: GENERAL PHYSICAL & CHEMICAL CHARACTERISTICS OF THE ALKALI METALS

1.0 INTRODUCTION

You will no doubt recall that at the beginning of our studies we learned how the efforts of leading scientists resulted in the formation of the periodic table as we know it today. You recall that the end product of that effort is the arrangement of the elements according to their atomic numbers. You also recall how in the last few units we saw that the properties of the elements in a periodic table are indeed a periodic function of their atomic numbers as stated by the periodic law. We also saw that elements belonging to the same groups have the same properties.

In earlier units, you studied hydrogen and learned about its unique position. Hydrogen, you recall gas properties which resemble the group1 elements in some respects and the group 17 elements in others.

In this unit you will be studying the elements of group 1, their occurrence extraction and uses. You will also be studying their physical properties.

The elements of group1and 2 are called the S-block elements because the outer most electron(s) in these elements occupy the S-orbital. Group1 elements consists of Li, Na, K, Rb, C and Fr, they are called ALKALI METALS because they form hydroxides which are strong alkalis

2.0 INTENDED LEARNING OUTCOMES (ILOs)

By the time you have finished studying this unit you should be able to:

1. List for each member of the alkali group where they can be found.
2. Give for each member at least one use
3. Discuss, the atomic size, density, melting and boiling points, ionization energy and electronegativity of members of the group.

3.0 MAIN CONTENT

3.1 Alkali Metals

Alkali metals are useful as metals as well as in the form of their compounds.

3.2 Occurrence

The alkali metals are highly reactive so they do not occur in the Free State in nature. They occur in the combined form in the earth's crust in the following relative abundance: Sodium 2.27%, potassium 1.84% lithium, rubidium and calcium in trace amounts 1.8x10-3 %, 7.8x10-3 % and 0.26x10-3 % respectively.

Sodium as sodium chloride is the most abundant metal in sea water (Ml.08%). Lithium occurs in alumina silicate rocks, e.g spodumene, LiAI $(SiO_3)_2$ and Lepidolite (Li, Na, $K)_2(F, OH)_2$ Sodium in rock salt, NaCl, in Chile Saltpetre $NaNO_3$, and in Cryolite, Na3AIF6, Potassium in camallite, KCl, in $MgCI_2.6H_2O$, in Saltpetre KNO_3 and in Kainite, KCl, $MgSO_4.3H_20$.

Rubidium and calcium are rare elements and generally occur in small quantities along with other alkali metals. For example, carmallite contains up to 0.94% rubidium chloride, Lepidolite, and containing about 0.2 to 0.7 percent of calcium expressed as calcium oxide. Francium being a radioactive element with a very short half-life period (21.8 minutes) occurs in very minute traces in nature.

In-text Question

Question
Discuss a character of alkali metals which defines their reactivity.

Anwser
Alkali metals are highly reactive and so they do not occur in the freestate in nature. Therefore, they occur in the combined form in the earth's crust. Examples of the relative abundance as they occur include: Sodium 2.27%, Potassium 1.84%, lithium, rubidium and calcium in trace amounts 1.8×10^{-3} %, 7.8×10^{-3} % and 0.26×10^{-3} %.

3.3 Extraction of Alkali Metals

Lithium and sodium are extracted by electrolysis of their fused (Molten) chlorides.

Potassiumis obtained by the reduction of its chloride with sodium vapor. This reduction by Na appears to be contrary to the normal order of reactivity, K>Na. However, at about 1150k the following equilibrium is set up

$$Na_{(g)} + K^+_{(l)} \rightleftharpoons Na^+_{(1)} + K_{(g)}$$

Since potassium is more volatile, it distils off more readily displacing the equilibrium to the right and allowing the forward reaction to proceed. Rubidium and Cesium, can be prepared by the reduction of their chlorides with calcium metal at 1000 K under calcium pressure. Rubidium and caesium salts are obtained during the recrystallization of other naturally occurring alkali metal salts. Francium is produced as a result of α- emission (1%) during the radioactive decay of actinium (see fig 13)

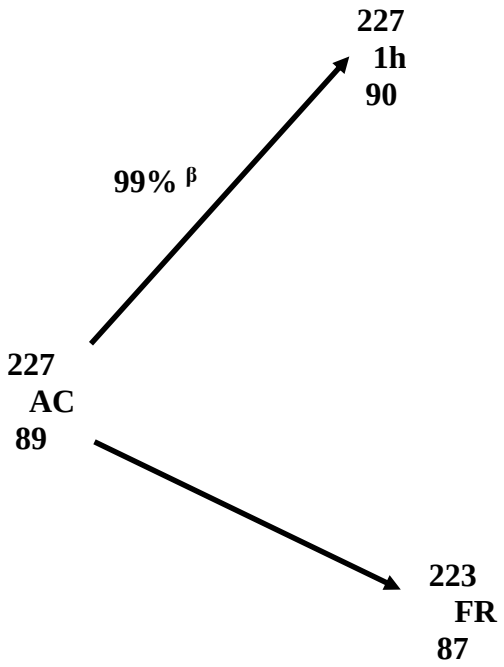


Fig.13: Production of francium as a result of a decay.

3.4 Uses of Alkali Metals

The alkali metals are very good conductors of heat and electricity. How ever due to their highly reactive nature they cannot be used for this purpose.

Sodium in polyethylene enclosed cables is used in some underground high voltage transmission applications.

Because of the high specific heat and thermal conductivity, liquid sodium is used as a coolant in nuclear reactors. You must have seen bright yellow lights on the streets and particularly on the highways. These are sodium vapour lamps and the light from them can penetrate fog well.

Caesium has the distinction of being the metal from which electrons are ejected most easily on exposure to light. This phenomenon is called photoelectric effect. Photocells, which are a device for converting light into electricity are based on this phenomenon.

Other every day uses of alkali metal compounds include the following:

Lithium in the form of lithium stearate is used for the production of lubricating greases.

The hydrides of lithium and sodium viz $LiAlH_4$ and $NaBH_4$ are used as reducing agents in synthetic organic chemistry. Lithium and potassium compounds are used in picture tubes of colour televisions

Can you imagine food without common salt? Apart from being an essential constituent of food, sodium chloride has many other important industrial uses like in the manufacture of NaOH, Na_2CO_3, Cl_2, and H_2 gases. Apart from sodium chloride, other compounds of sodium also have many uses. Caustic soda or sodium hydroxide is used in making soaps, sodium carbonate also known as washing soda, in laundering and the manufacture of glass, sodium bicarbonate as baking soda in baking powder in medicine and in fire extinguishers.

Potassium compounds also have many uses. Potassium hydroxide is used in liquid detergents. Potassium superoxide in breathing apparatus, potassium chlorate in matches and explosives and potassium bromide (KBr) in photography. Potassium nitrate is used along with charcoal and sulphur in gun powder. Potassium is a major component of plant fertilizers, where it is used in form of chloride and nitrate salts.

3.5 Physical Properties

Most of the physical properties of the alkali metals are directly relocated to atomic properties of elements. Variation of physical properties from one element to the other in a group is governed by the trends of the various atomic properties earlier discussed in units 4-8. We shall now apply them to understand the group trends in the various physical properties of the group1 elements given in table 15.

Table 15: Properties of the Group 1 metals

Properties	**Lithium Li**	**Sodium Na**	**Potassiu m K**	**Rubidium Rb**	**Caesium Cs**
Atomic number	3	11	19	37	55
Electronic configuration	$[He]2s^1$	$[Ne]3s^l$	$[Ar]4s^l$	$[Kr]5s^1$	$[Xe]6s^l$
Atomic weight	6.939	22.898	39.102	85.47	132.905
Covalent radius(pm)	123	156	203	216	235
Ionic radius(pm)	60	95	133	148	169
Boiling point(K)	1620	1154	1038	961	978
Melting point(K)	453	371	337	312	301.5
Density(10^3 x kgm^{-3})	0.53	0.97	0.86	1.53	1.87
Electronegativity(Pauling)	1.0	0.9	0.8	0.8	0.7
Electronegativity(AIR)	1.155	1.0	0.9	0.9	0.85
Ionisation energy($kJmol^{-1}$	520	495	1.0	403	374

Atomic size

From your studies in unit 4, you will recall that the alkali metals are the largest in their corresponding periods in the periodic table. The size of the atom or its ion increases on descending the group (see Table 15). This is due to the addition of an extra shell of electrons as we move down the group from one element to the next. The addition of the extra shell of electrons out-weighs the effects of increased nuclear charge and thus there is an increase in size from Li to Cs. This trend is shown in fig.14.

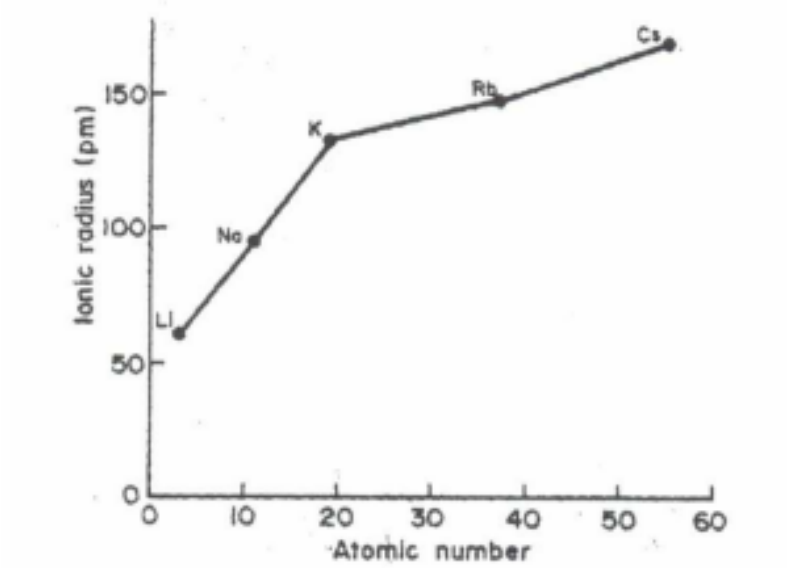


Fig14: Trend in ionic radii of Group1 elements

Density

Related to atomic size is the density of the elements. Density can be defined as mass per unit volume. For solids the density is a function of atomic weight, size of the atom and the structure of the solid (ie the closeness of the packing of the atoms).

There are two general trends observed in the densities of the elements in the periodic table. Along a period there is a general increase in density because of the increase in the size of the atom. Thus in a particular period the alkali metals have the lowest density, considering the solid elements only. In a group also density increases on going down the group. Since the elemental structuring are often the same within any group, the factors which determine the density are atomic mass and volume. As you can see from table 15 density increases as wemove from Li to Cs. This means that the increase in atomic weight from one element to the next in passing down the group over weighs the effect of increase in the size of the atom. There are however some exceptions to this general trend and in this particular group of alkali metals you can see from table 15 that the density of potassium is less than that of sodium. Thus potassium is an exception in this trend.

Melting Points and Boiling Points

These metals are soft and can be cut with a knife. It's a result of increase in size and repulsion of the non-bonded electrons, their cohesive energy and tendency for metallic bonding decreases down the group and thus softness increases as we go down from Li to Cs. These metals have low melting and boiling points which also reflect the low values of cohesive energy between the atoms.Their melting and boiling points decreases as we go down the group (see fig 15).

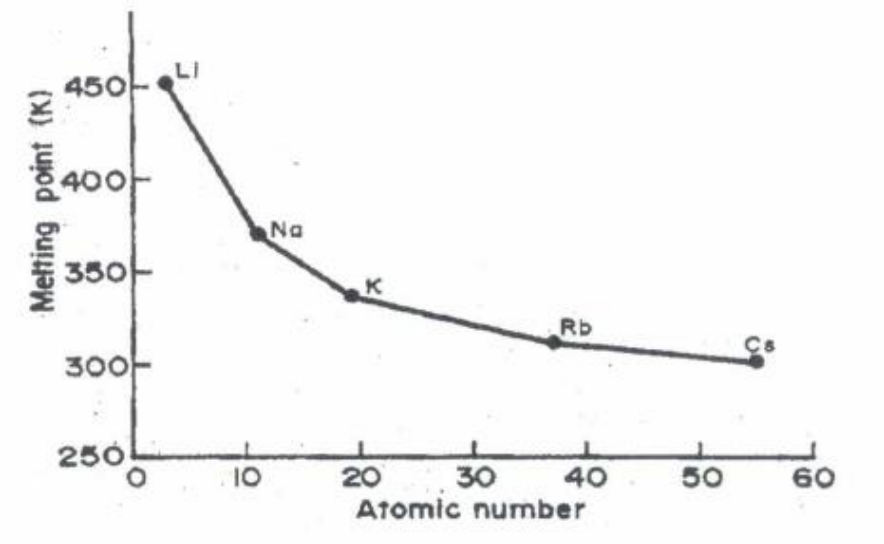


Fig 15: Trend in the melting point of Group 1 element

Thermal and Electrical Conductivity

In alkali metals, electrons of the noble gas core efficiently shield the lone valence shell electron from the nuclear charge. Therefore, the effective nuclear charge felt by the electron in the valence shell of an atom of an alkali metal is the least and their atoms are the largest in respective periods. As a consequence, the sole valence electron is very loosely held by the nucleus. It can move freely from one metal ion to the other in the lattice. This makes the alkali metals good conductors of heat and electricity. This loosely bond electron is also responsive for the silvery luster of the alkali metals when freshly cut.

Ionisation energy

By losing the loosely bond solitary outer most electron, these elements can acquire the electronic configuration of the preceding noble gas elements. They have, therefore, a high tendency of giving up this electron to form univalent cations. Their first ionization energies are the lowest in the respective periods and so they are the most reactive of all metals. As we go down the group, their atomic size increases, their ionization energies decrease, resulting in an increase in their reactivity. The effective nuclear charge felt by the electrons increases after the removal of one electron from the atom of any element and hence, their second ionization energies are always higher than the first. It is even more so in the case of the alkali metals, because their charged ions (Li^+, Na^+, K^+ etc) have the stable noble gas configuration of the stable noble gas configuration of the proceeding group. Removal of an electron from a stable noble gas configuration is extremely difficult. These metals, therefore, form univalent cations only. Fig.16 shows the trend in the first ionisation energies of the alkali metals down the group.

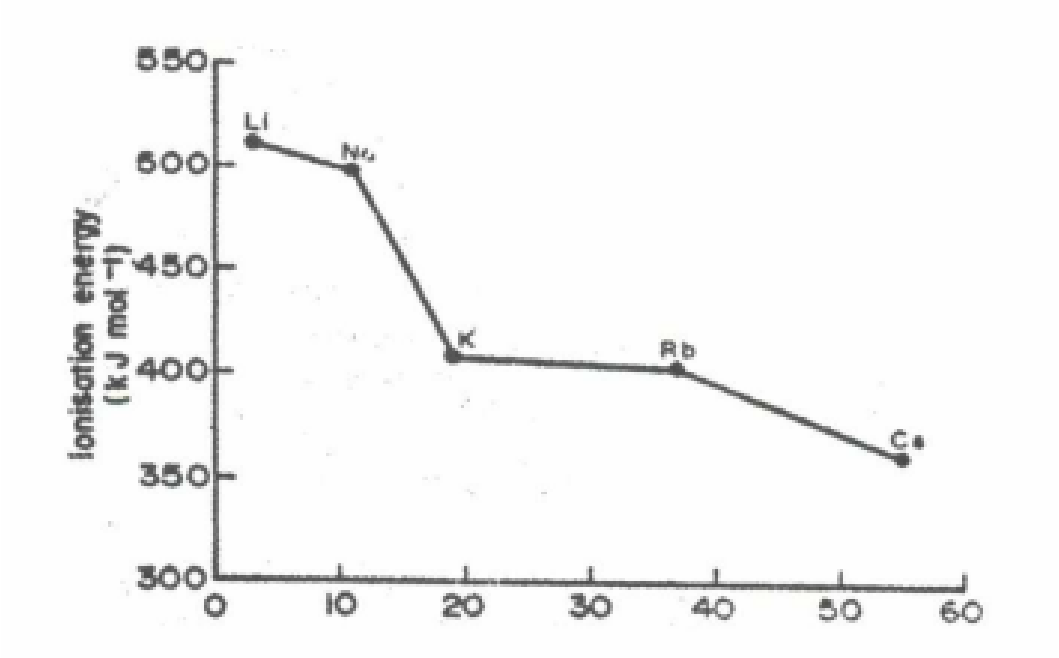


Fig 16: Trend in first ionization energies of alkali metals

On account of their low ionization energies these elements have a high tendency to form cations. In other words, they have a high electropositive or metallic character which increases as we move down in the group from Li to Cs. In fact Rb and Cs are so highly electropositive that they emit electrons even when exposed to light. That is they exhibit photo electric effect.

Electronegativity

Because alkali metals have a tendency to loose electron easily rather than to gain, values of electronegativity of these elements are very small. In fact, alkali metals are the least electronegative elements in the periodic table. As expected the electronegativity decreases on moving down the group.

Ionic character of compounds

Compounds formed by alkali metals with highly electronegative elements like halogens and oxygen, are largely ionic in nature because of the large electronegativity difference.

You can see that the trends in ionic character (in fig.17) show that the ionic character increases with increase in cation size and decreases with increase in anion size. Because of the small size of Li^+, it has more polarizing power and therefore favours covalent bonding.

Solubility, Lattice Energy and Hydration Energy

Alkali metal salts like halides, oxides, hydroxides, carbonates, sulphates etc exhibit some interesting trends in their solubility in water. First let us remind ourselves that lattice energy is the driving force for the formation of anionic compound and its stability. Lattice energy is directly proportional to the charge on the ions and inversely proportional to the distance between the cation. This distance is taken as the sum of radii of cation and anion ($r_c + r_a$).

Let us again remind ourselves that lattice energy is the enthalpy change when one mole of crystal lattice is formed from the isolated gaseous ions and hydration energy is the enthalpy change when one mole of solute is dissolved inwater. In a group. The charge on cations remains constant. Thus, lattice energy depends mainly on the size of the cation.

Similarly, hydration energy varies with the charge and size of the cation. The higher the charge and the smaller the size of the ion, the more is the hydration energy. In a group, lattice energy and hydration energy decrease as we move down. While the decrease in lattice energy favours the solubility, the decrease in hydration energy makes the compound insoluble.

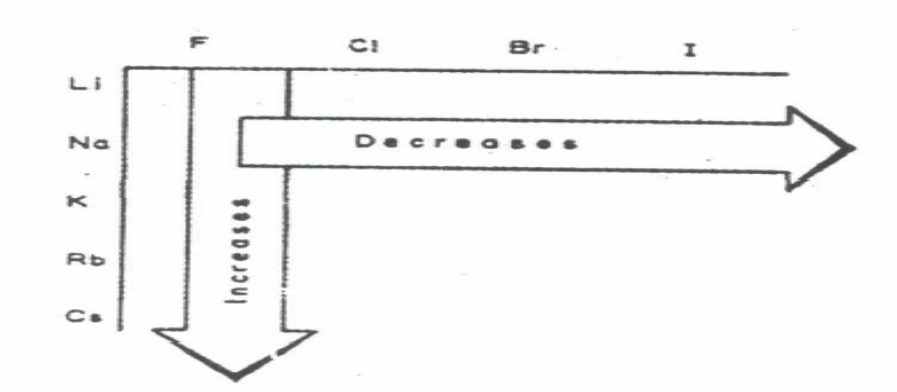


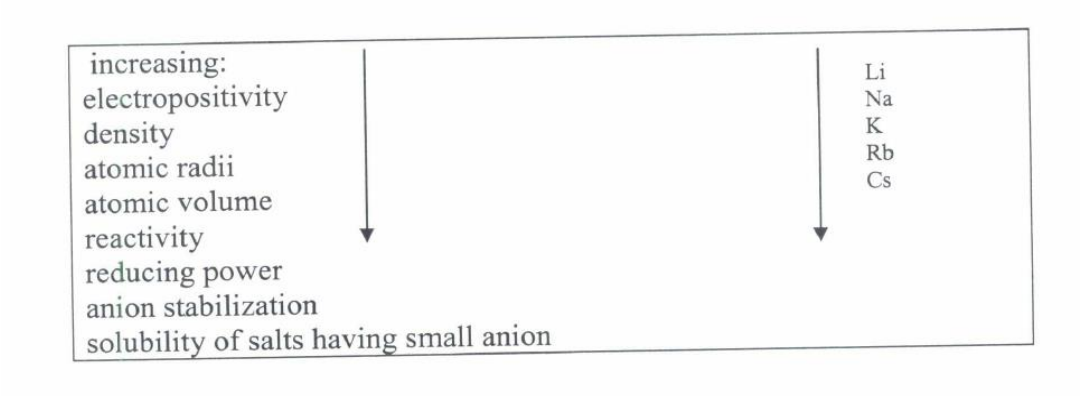
Figure 17: Trend in ionic character of alkali halides metals

For the salts of small anions (like F, O^{2-}, OH^- etc) the lattice energy which is inversely proportional to $r_c + r_a$, is very sensitive to the change in the size of the cation, anion being very small in size has little contribution in the total ($r_c + r_a$) and decreases sharply as we move down the group. Thus, in these salts, the decrease in lattice energy is greater than the decrease in hydration energy and therefore, the solubility of these salts increases as we go down the group. For example, in the case of alkali metal fluorides, the solubility increases in the order LiF<NaF<KF<RbF<CsF.

For the salts having large anions ((SO_4^{2-}, I^-, NO_3^-, HCO_3^-, CO_3^{2-}, etc) as $r_a >> r_c$, the radii of the cation has little contribution in the total ($r_c + r_a$) and decreases sharply as we move down the group. Thus, in these salts, the decrease in lattice energy is greater than the decrease in hydration energy and therefore, the solubility of these salts increases as we go down the group. For example, in the case of alkali metal carbonates, lithium carbonate is highly soluble while the solubility of calcium carbonate is very little.

Another important factor contributing to the solubility of the compound is the match in the size of the cation and anion. Whenever there is a mis match, eg cationis small, anion is large or vice-versa, this will result in the increased solubility of the compound. Let us keep the cation constant, say calcium. If we, then change the anion from fluoride to iodide, then the solubility of the compound will vary as CsF>CsCl>CsBr>Csl. Thus, calcium fluoride will be most soluble and calcium iodide will be the least. Similarly, from lithium fluoride to lithium iodide: the solubility will increase in the order: LiF<LiCl<LiBr<Lil.

Table 16: The main treads in the properties of alkali metals



The density of K is less than that of Na:
There can be many more examples which can be explained on the basis of above reasoning. Table 16 shows a summary of the trends discussed in this section.

In-text Question

Question
Explain why the elements of group1 are called alkali metals?

Answer
The elements of group1and even group 2 are called the S-block elements because the outer most electron(s) in these elements occupy the S-orbital. Group1 elements consists of Li, Na, K, Rb, C and Fr, they are called ALKALI METALS because they foam hydroxides which are strong alkalis

4.0 SELF ASSESSMENT EXERCISE

1. Explain in brief why the hydride bridge in $(BeH_2)_n$ considered to be electron deficient, but not the halide bridge in $(BeC1_2)_n$

2. Given below are some of the statement about the alkali metals. Write "T" if True and "F" if you think it is false.
   1. Sodium is the most abundant alkali metal in the earth
   2. Sodium is the most abundant metallic element in sea water
   3. Alkali metals occur in the Free State in nature
   4. Lepidolite is an ore of lithium
   5. Atomic radii of the alkali metals decrease down the group
   6. Ionization energy increases from lithium to francium
   7. Melting and boiling points of alkali metals decrease down the slope.
   8 Lithium is the highest of all the metallic elements
   9 Solubility of alkali metal fluorides in water increases down the group
   10 Ionic character of alkali metal halides decreases down the group.

   Answers

1. The Hydrogen bridge in $(BeH_2)_n$ is held together by one electron only and is electron deficient in the sense that there is less than one electron pair for each pair of bonded atoms. But in $(BeCl_2)_n$, each pair of bonded pair of atoms has the normal electron pair and so, its bridge is not election deficient.

2. 1. T, 2. F, 3. F, 4. T, 5. F, 6. F, 7. T, 8. F, 9. T and 10. F

5.0 CONCLUSION

We can conclude this unit by observing that the alkali metals as a group are very reactive, in fact so reactive that they can hardly be found in a free state. They occur in a combined form.
Alkali metal compounds are very useful for every day life. They are good conductors of heart as well as electricity. These metals have low melting and boiling points which also reflect the low values of cohesive energy between the atoms. Their melting and boiling points decreases as we go down the group, their solubility increases in the order LiF<NaF<KF<RbF<CsF, for the salts having large anions ($(SO^{2-}_4$, I^-, $NO3^-$, $HCO3^-$, CO^{2-}_3, etc) as ra>>rc, the radii of the cation has little contribution in the total ($r_c + r_a$) and decreases sharply as we move down the group. Alkali metal salts like halides, oxides, hydroxides, carbonates, sulphates etc exhibit some interesting trends in their solubility in water.

6.0 SUMMARY

In summary we have studied the following:

1. That the alkali metals can only be found in a combined state.
2. That the alkali metals are very reactive
3. That the alkali metals are very useful, some of their uses include being used as electrical conductors.
4. They are also used at homes for example sodium chloride is used as table salt.

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. Why do alkali metals not occur as free elements in nature?
2. Explain why
   (i) Alkali metals are good conductors of electricity
   (ii) Lithium has the highest ionization energy in the group
   (iii) Sodium forms +I ion and not +2 ion
   (iv). Group 1 elements form ionic compounds
3. Explain why hydroxides become stronger alkalis on descending the group.

7.0 FOR FURTHER READING

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5. **Alkali Metals**
   https://www.youtube.com/watch?v=dZGDUKQa_6g
6. **Occurrence**
   https://www.youtube.com/watch?v=7C-deQqhQjs
7. **Extraction of Alkali Metals**
   https://www.youtube.com/watch?v=xN5Z3uAUU-o
8. **Uses of Alkali Metals**
   https://www.youtube.com/watch?v=E8aja-j9S4o
9. **Physical Properties**
   https://www.youtube.com/watch?v=Cq_5gt2Uslw

MODULE 3

UNIT 2: COMPOUNDS OF ALKALI METALS

1.0 INTRODUCTION

In the last unit (unit 12) you studied the elements of group1 otherwise known as, Alkali metals. You studied the occurrences, extraction, uses and physical properties of the alkali metals.

In this unit you will be studying the chemical properties of the alkali metals. You will also study the oxides, hydroxides sulphides, hydrides carbides and thermal stability of salts of the alkali metals.

2.0 INTENDED LEARNING OUTCOMES (ILOs)

By the time you have completed the study of this unit you should be able to do the following:

1. List the types of oxides formed by alkali metals
2. Explain using equations, ther eactions involved in the formation of the oxides
3. Explain using equations the formation of sulphides, carbides and hydrides by alkali metals
4. Explain using examples the stability of salts formed by alkali metals

3.0 MAIN CONTENT

3.1 COMPOUNDS OF ALKALI METAL

In the previous (unit 12) you studied the important physical properties of the alkali metals. In accordance with their highly electropositive character these metals are very reactive and are powerful reducing agents reacting with water and most non-metals. They form crystalline ionic salts with high melting and boiling points. These salts are usually Soluble in water giving conducting solution. Now we shall discuss oxides some of the important classe soft these salts.

3.2 Oxides and Hydroxides

As alkali metals are very reactive their lustre is lost in air due to the formation of oxide with atmospheric oxygen. Three types of oxides are formed by the alkali metals viz, normal oxides having O^{2-} ion and the peroxides having O_2^{2-} [O- O] ion, both of which are diamagnetic and colourless. The

third one which is coloured and paramagnetic is super oxide containing O^{2-} ion. Controlled oxidations of these metals are shown below

$2Li \xrightarrow{1/2O_2} Li_2O \xrightarrow{1/2O_2} Li_2O_2$

$2Na \xrightarrow{1/2O_2} Na_2O \xrightarrow{1/2O_2} Na_2O_2$

$2K \xrightarrow{1/2O_2} K_2O \xrightarrow{1/2O_2} K_2O_2 \xrightarrow{O_2} K_2O_2$

$2Rb \xrightarrow{1/2O_2} Rb_2O \xrightarrow{1/2O_2} Rb_2O_2 \xrightarrow{O_2} 2RbO_2$

$2CS \xrightarrow{1/2O_2} CS_2O \xrightarrow{1/2O_2} CS_2O_2 \xrightarrow{O_2} 2CSO_2$

In the scheme shown above the products underlined are the main products when the metals are burnt in a free supply of air. You may notice in the above scheme that Lithium forms normal oxide, sodium forms peroxide while potassium, rubidium and caesium form superoxide as the main product. All the group 1 metal oxides are strongly basic and react vigorously giving hydroxide.

$LiO + H_2O \longrightarrow 2LiOH$ (less violent)

$Na_2O_2 + 2H_2O_2 \longrightarrow NaOH + H_2O_2$

$2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$

As we see, the peroxides and the super oxides on reaction with water give H_2O_2 which in tum is a powerful oxidizing agent. Thus the peroxides and the super oxides are also oxidizing in nature. The basic strength of the hydroxides increases down the group. As the charge density (charge/size ratio) of the cation decreases between M^+ and OH^- also decreases. So, OH^- can be liberated readily into the solution as we go down the group.

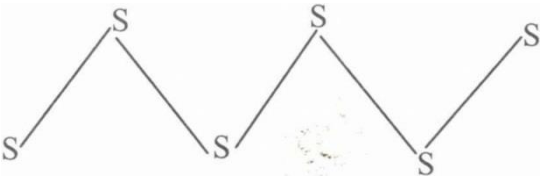
In-text Question

Question
Give a reason for the loss of the lustre of alkali metal.

Answer
The alkali metals are very reactive their lustre is lost in air due to the formation of oxide with atmospheric oxygen.

3.3 Sulphides

Alkali metals reacts with sulphur to form two types of sulphides; simple sulphides of Na_2S and poly sulphides like Na_2S_n where n = 2, 3, 4, or 6. These poly sulphides have a zig-zag chain structure as shown below.



3.4 Hydrides

Alkali metals react with hydrogen and form ionic hydrides, M^+H^-. These hydrides on reaction with water liberate hydrogen. Thus they are useful source of hydrogen:

$$MH + H_2O \longrightarrow MOH + H_2.$$

Lithium hydride on reaction with A1Cl3 in other solution forms lithium aluminium hydride which is a useful reducing agent in organic chemistry.

$$4LiH + A1C1_3 \longrightarrow LiA1H_4 + 3LiC1$$

Similarly, sodium hydride forms sodium borohydride which is also used as a reducing agent.

3.5 Carbides

Lithium reacts with carbon to form ionic carbides, where as similar carbides of other metals are not formed on reacting with carbon. They can, however, be formed on heating the metal with acetylene or when acetylene is passed through a solution of the metal in liquid ammonia:

$$Na + C_2H_2 \xrightarrow{LiQ.NH3} NaHC_2 \longrightarrow Na_2C_2^-$$

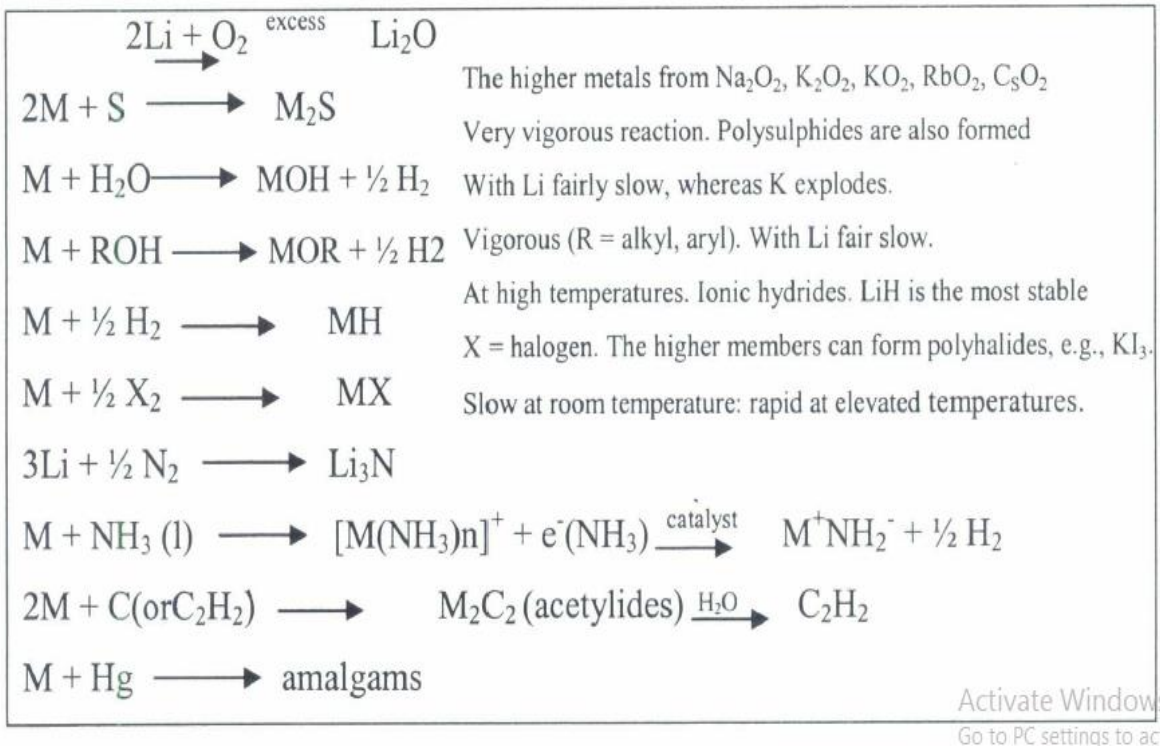
These carbides contain the carbide ion $(C{=}C)^{2-}$ on hydrolysis they give acetylene. Hence, are termed as acetylides;

$Na_2C_2 + 2H_2O \longrightarrow 2NaOH + C_2H_2$.

Alkali metals also form covalent compounds such as methyl lithium, $LiCH_3$ and ethyl sodium NaC_2H_5. These come under the separate class of organometallic compounds.

The main reactions of group 1 elements are sumarized in Table 13.1

Table 17: showing the main reactions of group 1 elements



3.6 Thermal Stability of Salts

The case with which a salt decomposes is related to the enthalpy of formation of the salt. (The standard enthalpy of formation of a compound is the enthalpy change when one mole of the compound in the standard state is formed from the elements in the standard state). The enthalpy of formation H_f of a salt MA (M is the metal, A the anion) is given by

$H_f = (H + I) + (H - E_A) - H_{1att}$

Where H is the enthalpy of atomisation, I is the ionisation energy and E_A is the electron affinity. Since for any salt in a particular group the terms involving the anion a lone remain constant the value of HF for such compounds is dependent upon the sum of the enthalpy terms of the particular metal ($H_{atom} + I_{metal}$) and the lattice energy H_{latt}· The larger the lattice energy, the more negative the enthalpy of formation and so, the more stable is the compound. All these terms become smaller on descending the series from lithium to caesium. The relative stabilities of the salts are therefore decide by the parameter which decreases more rapidly the lattice energy or the sum of the metal enthalpies.

In the salts having small anions of high charge density, eg F^-, N^{3-}, OH^-, O^{2-} etc the change in lattice energy is much dependent on the size of the cation and decreases rapidly on descending the group. Thus, as the size of the cation increases, lattice energy decreases more than the change in the sun of the metal enthalpies. Therefore, as we go down the group the stability of these salts having small anions decreases. Thus in alkali metal fluorides, the stability decreases in the order LiF>NaF>KF> RbF>CsF.

The opposite trend is observed in the stability of the salts containing large anions of low charge density, eg Br^-, I^-, NO^- etc. In such cases, the lattice energy is relatively in sensitive to the change in cation size and there is more rapid decrease in ionization energy and atonisation enthalpy on descending the group. The lower 'values of these favour the stability of the compounds. Thus, the stability of the compounds having large anions increases as we move down the group from lithium to caesium.

The stability of the compounds can also be explained by using the concept of polarizing power. The simple idea is that, as the charge density of the metal ion increases, the thermal stability ofthe salts of large polarizing anions, relative to some decomposition product decreases. In general, the least polarizing metal ion are those of the most electropositive metal ions and these form the most stable salts with large anions. In other words, small cations form stable salts with small anions and large cations form stable with large anions.

Let us take for example carbonate of Group 1 metals. The carbonates of sodium potassium and caesium are resistant to the heat of a burner flame. However, lithium carbonate decomposes to its oxide and carbon dioxide under the same conditions.

$Li_2CO_3 \longrightarrow Li_2O + CO_2$

The tendency of Li_2CO_3 to undergo thermal decomposition may be explained in terms of the gain in electrostatic attraction that occurs when extremely small Li^+ ion combines with the smaller oxide ion rather than the much larger carbonate ion. The other carbonates of group (Na^- Cs) are more stable because the cations have a lower charge density and are considerably larger in size and so their decomposition is less favourable energetically.

All the metals except lithium form stable bicarbonates (Lithium bicarbonate is formed only in aqueous solution and has not been isolated). When we heat the alkali metal bicarbonates, they are decomposed to carbonates and simultaneously, carbon dioxide and water are liberated.

$2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$

The thermal stability of group1hydroxides also follows a similar trend as that of carbonates. Thus with the exception of LiOH which on heating decomposes to Li_2O, all other group1 hydroxides are stable.

Similarly, lithium nitrate also decomposes on heating to give Li_2O, NO_2 and O_2 but all other alkali metal nitrates decompose on strong heating to nitrates liberating oxygen.

$4LiNO_3 \longrightarrow 2Li_2O + O_2 + 4NO_2$

$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$

In-text Question

Question
Establish a relationship between anion and cation size, charge density and lattice energy.

Answer
Salts having small anions of high charge density such as F^-, N^{3-} , OH^-, O^{2-} etc, the change in lattice energy is much dependent on the size of the cation and decreases rapidly on descending the group. So as the size of the cation increases, lattice energy decreases more than the change in the sum of the metal enthalpies. Therefore, as we go down the group the stability of these salts having small anions decreases.

4.0 SELF ASSESSMET EXERCISES

1. Explain briefly why alkali metals act as strong reducing agents.

2. The thermally least stable alkali metal fluorideis;

(i) LiF (ii) NaF (iii) KF (iv) RbF (v) CSF

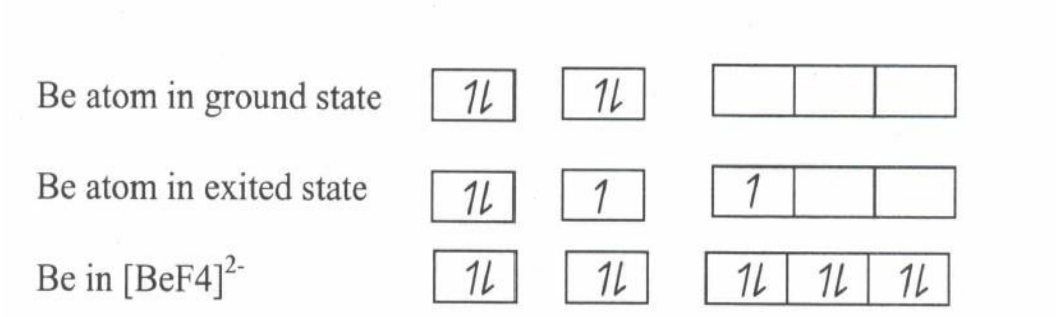
3. Why is it that Be forms mostly complexes with tetrahedral structure.

Answers

1. The outermost election in alkali metals is very loosely held so it can be removed easily. This makes alkali metals strong reducing agents.

2. (v) (CSF)

3. Be tends to form complexes with the tetrahedral arrangement because of the available orbitals as shown below



5.0 CONCLUSION

We can conclude this unit by observing that alkali metals being very reactive form oxides, hydroxides and peroxides. Also that the stability of alkali salts depends on the enthalpy of formation of the salt and sizes of cation and anion. Alkali metals also form covalent compounds such as methyl lithium, $LiCH_3$ and ethyl sodium NaC_2H_5. These come under the separate class of organometallic compounds. The larger the lattice energy, the more negative the enthalpy of formation and so, the more stable is the compound. The thermal stability of group1hydroxides also follows a similar trend as that of carbonates. The stability of the compounds can also be explained by using the concept of polarizing power. When we heat the alkali metal bicarbonates, they are decomposed to carbonates and simultaneously, carbon dioxide and water are liberated.
The thermal stability of group1hydroxides also follows a similar trend as that of carbonates.

6.0 SUMMARY

In summary we can say that in this unit you have studied the following:
1. That alkali metals form oxides, hydroxides and peroxides.
2. That three types of oxides are formed viz normal oxides, peroxides and superoxides
3. That three normal oxides, peroxides and superoxides
4. The alkali salt's stability is dependent upon the enthalpy of formation

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. Why do peroxides and superoxides oxidise in aqueous solution?
2. Explain why lithium forms more complexes

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   https://www.youtube.com/watch?v=VbAeB5BTJV8
7. **Hydrides**
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8. **Thermal Stability of Salts**
   https://www.youtube.com/watch?v=njnecrmZpbY

MODULE 3

UNIT 3: SOLVATION OF ALKALI METAL IONS

1.0 INTRODUCTION

In unit 12 you studied the formation of oxides, hydroxides, carbides and sulphides by the alkali metals. In this unit you will be studying the behaviour of the alkali metals in solutions. You will also study the complexation behaviour of the alkali metals. In your study of the chemical properties of the alkali metals, you must have noticed that lithium behaved differently from the rest of the alkali metals. In this unit you will be studying the anomalous behaviour of lithium.

2.0 INTENDED LEARNING OUTCOMES (ILOs)

By the time you have completed your study of this unit, you should be in a position to:

1. Discuss the salvation of alkali metals describing the behavior of each member of the alkali metals when in solution of water.
2. Describe using equations the behavior of the alkali metals when dissolved in liquid ammonia
3. Explain what is meant by complexation (complex formation) by describing the role of the alkali metal in relation to the surrounding molecules
4. List at least four anomalous behaviour of lithium

3.0 MAIN CONTENT

3.1 SOLVATION OF THE ALKALI METAL

When a metal is surrounded by solvent molecules, the phenomenon is called SOLVATION of the metal ion. When the solvent is water the phenomenon is now called HYDRATION.

Hydration is therefore salvation with water as the solvent. The alkali metal ions are highly hydrated. The smaller the size of the ion, the greater its degree of hydration. This is because the smaller the size, the more will be its charge density and the more will be its attraction for the polar solvent molecules. (See unit 11). Thus Li^+ ion, which is the smallest gets more hydrated than Na^+ and so on. The degree of hydration decreases on moving down the group. As a result of differences in their degree of hydration, the hydrated ionic radii of the alkali metal ions decrease as we go down the group from lithium to caesium. Lithium has the largest hydrated radius while Cs^+ has the smallest hydrated radius in the first group. You will agree that the smaller the size of the ion and the lighter it is, the more will be its mobility and thus conductance. In this regard we should expect the highest conductance of the alkali metals, but it is not so. Because the hydrated Li is the largest of all the alkali metal ions. In solution its mobility is less and so Li^+ ion is the least conducting in solution. The ionic conductance in solution actually decreases in the order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$.

3.2 Solutions of Alkali Metals in Liquid Ammonia

All the alkali metals are highly soluble in liquid ammonia giving a deep blue colour. The solubilities of the metals for 100g of ammonia are Li, 10g; Na, 25g and K, 49g. The dissolution of the alkali metal is accompanied by its dissociation into the metal ions and the electrons. The metal ion and the electrons then get associated with ammonia solvent molecules. Electrons associated with the solvent are known as SOLVATED ELECTRONS.

$Na_{(s)} + NH_{3(l)} \longrightarrow Na^{+}(NH_3)x\ ^{+}e\ (NH_3)_y$

The alkali metal solutions in liquid ammonia are highly conducting and behave almost as metals. Their specific conductivities are almost the same, because the anion i.e solvated electron, in all the cases is the same.The small difference in the conductivity is due to the value of the metal itself. The solution of alkali metals in liquid ammonia is blue in colour due to the presence of solvated electrons, and therefore the solutions are also paramagnetic. With increasing concentration there is a decrease in paramagnetizing suggesting that the electron can get associated to form diamagnetic electron pairs. Although there may be other equilibria also.

$Na_{(s)}$ (dispersed) $\rightleftharpoons$ Na (in solution) $\rightleftharpoons$ $Na^{+}\ e^{-}$

$2e \rightleftharpoons e_2$

On increasing the concentration above 3M, the colour of the solution changes to copper bronze having metallic luster, because the metal ions form clusters. Apart from lithium other alkali metals can be recovered unchanged from solution. Lithium, in ammonia solution form a complex of the type $[Li(NH_3)_4]^{+}$

The blue solution of alkali metals are moderately stable at temperatures where ammonia is still a liquid. The reaction that results in the formation of an amide.

$Na + NH_{3(l)} \rightleftharpoons NaNH_2 + 1/2H_2$

Can occur photochemically and is catalyzed by transition metal salts. The alkali metal solutions in liquid ammonia are powerful reducing agents and are used for this purpose in inorganic and organic reactions.

In-text Question

Question
Explain why the ionic conductance of lithium in solution is the smallest.

Anwser
Due to the fact that the hydrated Li is the largest of all the alkali metal ions. In solution its mobility is less and so Li^{+} ion is the least conducting in solution. The ionic conductance in solution actually decreases in the order $Cs^{+} > Rb^{+} > K^{+} > Na^{+} > Li^{+}$.

3.3 Complexation Behaviour of Alkali Metals

A complex compound can be defined as a compound with a central atom or ion surrounded by a group of ions of molecules called “ligands”. These ligands are usually bond to the metal by a “coordinate bond” i.e a bond formed by the donation of a lone pair of electrons from one atom (of the liquid) to the other (metal /ion). Although both metal and the ligand are usually capable of independent

existence as stable chemical species, yet when the complex is formed, it generally retains its identity in solution. For example, in solution, Fe^{+} and CN^{-} can exist independently but once the complex $[Fe(CN)]_6^{+4}$ is formed it exists in solution as such. It does not dissociate into Fe^{+} and CN^{-}, as a result it will not give any positive result when tested in Fe^{+} and CN^{-}. It is thus a complex specie. The most stable complexes would be formed by the lightly polarizing cations. This is because they have a strong tendency of interacting with electron clouds of other anionic or neutral electron rich species (ligands).

According to the model above, a very weak coordinating ability is expected in the group 1 metals because of their large size and low charge of the cations M^{+}. According to this view, stability of the complexes of the alkali metals should decrease in the order Li>Na> K>Rb>Cs and this is the observed trend.

Alkali metals form few complexes mostly **chelates** with the ligands like B^{-} ducetones, nitrophenils, nitroso, naphthols etc as shown in fig 18. They have low stability.

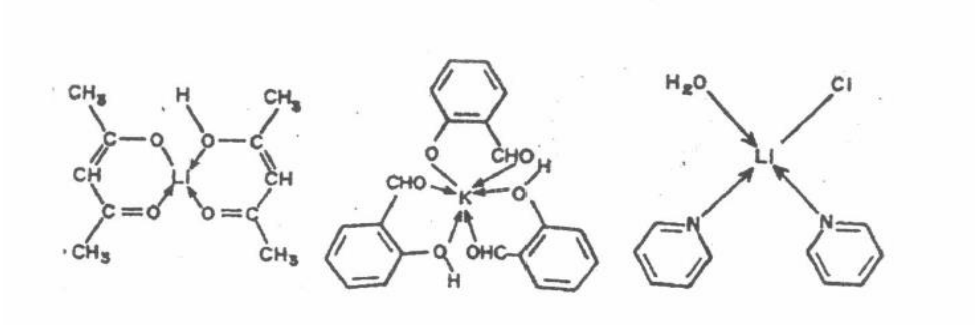

Fig18: Source complex of alkali metal ions

Lithium, being the most polarizing cation of all the alkali metals forms tetrahedral complexes with ligands like NH_3, L_5H_5N etc. With ammonia it forms the complex of the type $[Li(NH_5)_4]I$, whereas with pyridine a complex of the type $[LiCl(C_5H_5N)_2(H_2O)]$ is formed

3.4 Anomalous Natures of Lithium

On descending any group of S or P block elements of the periodic table, one notices that, there is a general decrease in electronegativity or increase in electronegativity. The difference in electronegativety between the first and second elements of each group is much greater than that between any two successive elements. This is reflected in the properties of the elements. Thus not only is the element more electronegative than the other elements of the group, but it is much more electronegative than expected by simple extrapolations.

This trend of bigger than expected differences in properties between the first member of a group and the rest of the elements is shown in group1where Li elements markedly different from the rest of the members of the group.

Let us take a look at these summaries again as they apply in group 1. Due to the very small size of lithium, the metallic bonding between the atoms in the metallic lattice is very strong giving rise to strong cohesive forces. This is shown in its relatively higher melting point, and boiling point, hardness and homonuclear bond energy.

The relatively higher attraction of lithium for its outer electron results in its relatively higher centre electronegativity ionization energy, hydration energy, electron affinity and of course smaller atomic radii relative to the other homologues.

Similar anomalies are also found in the chemical properties, but the different appear greater as we shall see in the following accounts.

(i) Lithium salts of large polarisable anions are thermally less stable than those of other alkali metals e.g Lithium carbonate decomposes at 950 K, whereas no decomposition of sodium carbonate takes place below I050 K.

(ii) Lithium does not form solid bicarbonate trioxide or superoxides, because these are unstable at room temperature. On the other hand, those of other alkali metals require a higher temperature to affect their decomposition.

(iii)Lithium salts of anions of high charge density are less soluble than those of other alkali metals. The halides of lithium are more soluble in organic solvents.

(iv) Lithium forms stable salts with anions of high charge density owing to their high lattice energy. For examples, in air lithium forms the normal oxide, whereas the others form higher oxides, lithium reacts with nitrogen to form nitride, Li_3N the others do not react. Lithium hydride is more stable than the other hydrides and lithium carbide is formed more easily with acetylene.

(v) Lithium reacts slowly with water.

(vi) Lithium forms more stable covalent bonds than other alkali metals and, therefore, forms more stable complex compounds as earlier seen in section 3.3 of this unit. For example, lithium cannot be recovered unchanged from its liquid ammonia solution. Owing to the formation of $[Li(NH_3)_4]^+$.

In-text Question

Question
Explain why lithium forms more complexes than the other elements of group 1.

Anwser
Lithium forms more stable covalent bonds than other alkali metals, and therefore, forms more stable complex compounds. The stability of the complexes of the alkali metals should decrease in the order Li>Na> K>Rb>Cs and this is the observed trend.

4.0 SELF-ASSESSMENT EXERCISES

1. Why does ammonia act as a lewis base?
2. Why is hydrazine unstable?
3. Why are alkali metals poor complexing agents?

Anwsers

1. Ammonia has a lone pair of electronson the nitrogen atom, therefore, it acts as a Lewis base.
2. In hydrazine, there is N-N single bond with small size of nitrogen, there is considerable repulsion between these non-bonding electrons thus weakening the N-N single bond. This makes hydrazine unstable

3. It is due to a very weak coordinating ability in group 1 metals because of their large size and low charge of the cations M^+. According to this view, stability of the complexes of the alkali metals should decrease in the order Li>Na> K>Rb>Cs and this is the observed trend.

5.0 CONCLUSION

We can conclude this unit by stating that the alkali metal ions are very soluble in both water and liquid behaviour. Also that lithium shows the anomalous ammonia observed for first members of any group of the elements in the periodic table. Ligands are usually bond to the metal by a "coordinate bond" i.e a bond formed by the donation of alone pair of electrons from one atom (of the liquid) to the other (metal ion). The relatively higher attraction of lithium for its outer electron results in its relatively higher centre electronegativity ionization energy, hydration energy electron affinity and of course smaller atomic radii relative to the other homologues. Lithium salts of large polarisable anions are thermally less stable than those of other alkali metals. Lithium forms more stable covalent bonds than other alkali metals and, therefore, forms more stable complex compounds

6.0 SUMMARY

In summary we have learned the following from the foregoing unit.

1. That the alkali metals are highly soluble in water and in liquid ammoma.
2. That Li^+ ion is the least conducting in solution, when compared to the ions of the other members of the alkali metal ions in solution.
3. That the stability of alkali metal complexes is low.
4. That the stability of the complexes decreases as you go down the group. i.e Li > Na > K > Rb > Cs.
5. That lithium shows anomalous behaviour in relation to the other members of group 1. That is that in each of the properties shared by members of the group, Li shows wide differences between it and the next member of the group immediately below it.

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. Give the trend in the solubility of alkali metal iodides
2. Briefly explain the variation of conductivity in alkali metal salts giving reasons for the trend.

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7. Anomalous Natures of Lithium https://www.youtube.com/watch?v=4R9YRrph0kc

MODULE 3
UNIT 4: ALKALINE EARTH METALS

1.0 INTRODUCTION

In units 12-14, you studied the general characteristics of group1 elements, i. e the Alkali metals, and their compounds. Groups1and 2 elements belong to the S-block of the periodic table. Their electronic configurations show an outer shell of ns^1 and ns^2 for alkali and alkaline earth metals respectively. S-block elements are known to be very reactive metals and generally form ionic compounds. In this unit you will be studying the elements of group 2 consisting of beryllium, magnesium, calcium, strontium, barium and radium. Elements Ca, Sr, Ba and Ra are called **alkaline earth metals**, because their earths (earth is the old name for a mineral oxide) are alkaline in nature. (Remember that the alkali metals are so called because they form hydroxides which are strong alkalies).

Beryllium is not counted as an alkaline earth metal since its oxides is not alkaline. We shall start our study of the alkaline earth metals by studying their occurrence, extraction uses and physical properties.

2.0 INTENDED LEARNING OUTCOMES (ILOs)

At the end of your study of this unit you should be able to:

1. List at least four places where the alkaline earth metals can be found.
2. Describe at least two methods used in the extraction of the alkaline earth metals
3. List at least three uses of members of the group
4. Compare the physical properties of members of the group with each other.

3.0 MAIN CONTENT

3.1 ALKALINE EARTH METALS

The alkaline earth metals, like alkali metal are very reactive, therefore, do not occur free in nature. All of them are found in form of their salts. Let us now study their occurrences, extraction and uses. We shall also go ont o study their physical properties

3.2 Occurrence

Beryllium, the first member of the group is found in small quantities in the silicate mineral, phenacite, Be_2SiO_4, and beryll, $3BeO.Al_2O_3.6SiO_2$. Magnesium (2.76%) and calcium (4.66%) are among the eight most abundant elements in the earth's crust.
Magnesium (0.13%) is thes econd most abundant metallic element next only to sodium (chloride) in sea water. It occurs as magnesite, $MgCO_3$; dolomite $MgCa(CO_3)_2$, kieserite, $MgSO_4.H_2O$ and carmallite, $KMgCl_3.6H_2O$ in the earth's crust.
Calcium occurs extensively as calcite and limestone ($CaCO_3$) in many mountain ranges. Calcium and magnesium are very important biologically too. Calcium is found in the bones of animals and human beings.
Magnesium is found in the green (chlorophyII) plants. Strontium (0.038%) and barium (0.039%) are much less abundant and occur as carbonates and sulphates. These metals are well known because they occur as concentrated ores and are easy to extract. Radium is extremeIy scarce (10^{-10} %) and it is a radioactive element.

In-text Question

Question
Calcium and magnessium are said to be biologically useful: Discuss.

Answer
Calcium and magnesium are very important biologically because while Calcium is found in the bones of animals and human beings where they support the skeletal system. Magnesium is found in the green (chlorophyII) plants and plays part in photosynthesis.

3.3 Extraction of Alkaline Earth Metals

These metals are extracted by electrolysis of their fused chlorides, though magnesium has been manufactured by the carbon reduction of its oxide.

Beryllium is obtained by the electrolysis of molten beryllium chloride. Sodium chloride must be added to the melt as an electrolyte because $BeC1_2$ is covalent and, therefore is a very poor electrical conductor. During the electrolysis, the less active metal Be is produced at the cathode and Cl_2 is evolved at the anode. Calcium is extracted from fused calcium chloride using a graphite anode and iron cathode. Strontium chloride and Barium chloride are fused for the extraction of strontium and barium respectively.

3.4 Uses of Alkaline Earth Metals

Beryllium is used for making atomic fuel containers because it absorbs very few neutrons and does not become radioactive. Being transparent to X-rays it is used as a window material in X- ray apparatus.

It has a number of uses as alloys, eg when mixed with Cu, Berylium increases the strength of Cu. Six fold. Beryllium alloys are non-sparking, therefore, they are used in making hand tools for use in the petroleum industry. Magnesium, because of its lightness, is used as a construction alloy material, eg in air crafts. For this purpose, it is alloyed with aluminium.

Magnesium is also used as a reducing agent in the extraction of some Metals like titanium and uranium. It forms Grignard reagents RMgX, which are important organic reagents.

Calcium, strontium and barium as free metals do not find extensive uses because they are very reactive. Calcium oxide (quicklime) is a constituent of glass, mortar and Portland cement.

3.5 Physical Properties

The alkaline earth metals are quick soft metals, but are harder than the corresponding Group I elements. This is because of their two valence electrons which participate in metallic bonding. They are good conductors of electricity. In pure form they are silver coloured, but on exposure to the atmosphere, the silvery luster is lost, because of the formation of an oxide layer on the surface of the metal. Their physical properties are given in Table 18.

Table 18: Properties of the group 2 metals

Properties	**Beryllium Be**	**Magnesium Mg**	**Calcium Ca**	**Strontium Sr**	**Barium Ba**	**Radium Ra**
Atomic number	4	12	20	38	5688	
Electronic configuration	$[He]2S^2$	$[He]3S^2$	$[Ar]4S^2$	$[Kr]5S^2$	$[Xe]6S^2$	$[Rn]7S^2$
Atomic weight	9.012	24.312	40.08	87.62	137.34	226.02
Covalent radius(pm)	31	65	99	113	135	
Ionic radius(pm)	89	136	174	191	198	
Boiling point(K)	3243	1380	1760	1607	1413	1700
Melting point(K)	1553	934	1118	1062	998	700
Enthalpy of Hydration ($kJmol^{-1}$)	-2455	-1900	-1565	-1415	-1275	
Density(10^3 x kgm^{-3})	1.85	1.74	1.54	2.6	3.62	5.5
Electronegativity(Pauling)	1.5	1.2	1.0	1.0	0.9	0.9
Electronegativity(AIR)	900	738	590	549	502	509
Ionisation energy($kJmol^{-1}$	1757	1450	1146	1064	965	975

The atoms of the alkaline earth metals are smaller than those of the corresponding Group 1 elements. This is because of the increase atomic number. Because of the resulting increase in effective nuclear charge, valence shell electrons are pulled in more firmly by the nucleus, thereby reducing the size of the atom.

Similarly, their ionic radii are also smaller than those of Group 1 elements, because the removal of two orbital electrons increases the effective nuclear charge even further.
The elements are denser than Group 1 metals because they have two valence electrons per atom for bonding the atoms into a metallic lattice and as a result more mass can be packed into a smaller volume.

The density decreases slightly on moving down the group from Be to Ca but increases considerably there after up to Ra.

The atomic/ ionic radii increase from Be to Ra due to the effect of extra shells of electrons added. This out weighs the effect of increased nuclear charge. Group 2 metals have higher melting points when compared to group1 metals. The reason being the +2 charge on the cations in the metallic lattice causing them to be more strongly attracted to the 'Sea of electrons and making it difficult to pull them apart.

The first ionization energy (Table 18) of alkaline earth metals is more than that of corresponding alkali metals. This is because the alkaline earth metals have higher nuclear charge and are smaller in size. The electrons are therefore more tightly held to the nucleus. The second ionization energy of these

elements is almost twice their first ionization energy. This is because once one electron has been removed, the effective nuclear charge felt by the orbital electrons is increased, so that the remaining electrons are more lightly held and hence much more energy is needed to remove the second electron.

However, their second inonization energy is less than that of the corresponding alkali metals because of stability of a closed shell configuration of the univalent cations that are formed in the cases of the alkali earth metals.
The ionization energy of alkaline earth metals decreases on moving down the group. The metals of this group (beryllium is an exception) form ionic compounds. This is because the assembly of positive and negative ions into asymmetrical crystal lattice results in the liberation of a large amounts of energy. Electropositive character and the reducing property (tendency to loose elections) increase on moving down the group.

Since alkaline earth metals loose electrons easily, they form divalent ions which have noble gas structure with no unpaired electrons. Their compounds are diamagnetic and colourless, unless the anion is coloured. Ca, Sr and Ba compounds give characteristics flame colourations which are used to identify them. Ca (brick red flame), Sr (crims on red flame) and Ba (apple green flame).

3.6 Solubility, Lattice Energy and Hydration Energy

The solubility of alkaline earth metal compounds shows some interesting trends. The metal ions are easily hydrated, eg $MgC1_2.6H_2O$, $CaCl_2.6H_2O$, and $BaC1_2.2H_2O$). The hydrogen energies of these metals ions are much greater than those of alkali metal ions (see table 19) because of their smaller size and increased cationic charge. The lattice energies of alkaline earth metal salts (see table 19) are also much higher than those of alkali metal salts.

Hydration and lattice energies decreases with increase in size of metal ions. Decreasing lattice energy favours increased solubility, whilst decreasing hydration energy favours decreased solubility. If on moving down the group the hydration energy decreases more rapidly than the lattice energy, the compound becomes less soluble. This occurs with most of the compounds except for fluorides and hydroxides for example, solubility of sulphates decreases from $BeSO_4$ to $BaSO_4$. Due to their small ionic radii, Be^{2+} and Mg^{2+} have high hydration energies. Because of that $BeSO_4$ and $MgSO_4$ are only slightly soluble in water, whereas $SrSO_4$ and $BaSO_4$ are almost insoluble in water. In the case of fluorides and hydroxides the lattice energy decreases more rapidly than the hydration energy. This causes a reverse trend ie the flourides and hydroxides increases in solubility on moving down the group.

Table 19. The main treads in the properties of alkali metals

Period	ΔH_{hyd}			ΔH_{latt}	
	M^{2+}	MO	MCO_3	MF_2	MI_2
Be	-2494	-	-	-	-
Mg	-1921	-3923	-3378	-2906	-2292
Ca	-1577	-3517	-2986	-2610	-2058
Sr	-1443	-3312	-2318	-2459	-
Ba	-1305	-3120	-2614	2.60	-

Enthalpies of hydration, ΔH_{hyd} alkaline of alkali earth metal ions M^{2+} and lattice energies ΔH_{latt} of their oxides, carbonates fluorides and iodides in $kJmol^{-l}$

In-text Question

Question
State the difference in the hydrogen energies of group 1 and that of group 2 of the periodic table.

Answer
The hydrogen energies of alkaline earth metals ions are much greater than those of alkali metal ions because of their smaller size and increased cationic charge.

4.0 SELF ASSESSMENT EXERCISES

1. Explain briefly why of all nitrogen halides, only NF_3 is stable

2. The mechanism of the hydrolysis of phosphorous trichloride, involves the formation of an intermediate four coordinate species. Why is it impossible for NCl_3 to hydrolyse using the same mechanism?

3. Why are Group 2 elements smaller in size than their counter parts in group1?

Answers

1. This is due to strong N-F bonds

2. The formation of the kind of intermediate done for hydrolysis of PCl3, is impossible for Nitrogen because of the non-availability of d-orbitals

3. The atoms of the alkaline earth metals are smaller than those of the corresponding Group 1 elements. This is because of the increased atomic number. Because of the resulting increase in effective nuclear charge, valence shell electrons are pulled in more firmly by the charge force of the nucleus, thereby reducing the size of the atom.

5.0 CONCLUSION

In conclusion we can say alkaline earth metals, like metals are only found combined in form of their salts, because of their reactiveness. Alkaline earth metals are usually extracted by electrolysis. They are good conductors of electricity. In pure form they are silver coloured, but on exposure to the atmosphere, the silvery luster is lost, because of the formation of an oxide layer on the surface of the metal. They are used as alloys and some e.g Beryllium are used as fuel containers. The atoms of the alkaline earth metals are smaller than those of the corresponding Group 1 elements. This is because of the increase atomic number. Because of the resulting increase in effective nuclear charge, valence shell electrons are pulled in more firmly by the nucleus, thereby reducing the size of the atom. Hydration and lattice energies decreases with increase in size of metal ions.

6.0 SUMMARY

In this unit we have learned the following:

1. That alkali earth metals are very reactive
2. That because of this reactiveness alkaline earth metals exist mainly in combined forms, as salts
3. That alkaline earth metals are extracted by electrolysis
4. That beryllium is used as an alloys with other metals

5. That the atoms of the alkaline earth metals are smaller than those of the corresponding Group 1 elements.

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. Explain why the first ionization energy of beryllium m is greater than that of lithium, but the position is reversed in the case of the second ionization energy.

2. Explain why beryllium forms covalent compounds

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6. Uses of Alkaline Earth Metals
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7. Physical Properties
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UNIT 5: REACTIVITY OF ALKALINE EARTH METALS

1.0 INTRODUCTION

In unit 15, you studied some of the physical properties of the alkaline earth metals. In this unit you will be studying their chemical properties. You will also study the stability of oxysalts of alkaline earth metals.

2.0 INTENDED LEARNING OUTCOMES (ILOs)

By the time you have studied this unit, you should be able to:

1. Write the equations showing the reactions of all the alkaline earth metals with oxygen
2. Describe the action of each member of the alkaline earth metals with acid.
3. Describe the action of each member of the alkaline earth metals with water
4. Describe the structure of BeO.
5. Describe using equations the formation of the metal halides
6. Describe the formation of hydrides by alkaline earth metals
7. Describe the thermal stability of oxy salts.

3.0 MAIN CONTENT

3.1 REACTIVITY OF ALKALINE EARTH METALS

Alkaline earth metals are less reactive than alkali metals as they are less electropositive than they are. Table 20 shows some chemical reactions shown by alkaline earth metals.

Table 20: Reactions of the Group 2 metals

$2M(s) + O_2(R) \longrightarrow 2MO(s)$ $M(s) + S(s) \longrightarrow MS(s)$	All burn if heated. Some MO_2 formed. The suphides are insoluble, but hydrolyse if heated in water.
$M(s) + 2H_2O(l) \longrightarrow M(OH_2(s) + H_2(g)$	Be does not react even at red heat; Mg reacts with steam only; others react with water at room temperature
$M(s) + 2H^+(aq) \longrightarrow M2^+(aq) + H_2(g)$ $M(s) + H_2(g) \longrightarrow M^{2+}2H^-(s)$	Be only slowly; others more quickly. Not with Be. With others at high temperatures only. With Mg under pressure.
$M(s) + X_2(g) \longrightarrow MX_2(s)$	X = halogen No polyhaliders are formed
$3M(s) + N_2(g) \longrightarrow M_3N_2(s)$ $3M(s) + 2NH_3(g) \longrightarrow M_3N_2(s) + 3H_2(g)$	At red heat. Stability: Be > Mg >a (hydrolyse to NH_3) In liquid ammonia, Ca, Sr and Ba blue solution because of solvated electrons (Unit 4, section 4.4)
$Be + 2H_2O + 2OH \longrightarrow [Be(OH)_4]^{2-} + H_2(g)$ $M(s) + 2C(s) \longrightarrow MC_2(s)$	Not with other alkali earth metals At high temperatures Be forms Be_2c. Ionic compounds

Reactivity of alkaline earth metals increases with atomic number down the group. Let us consider these reactivities at atime.

1. All the metals liberate hydrogen from acids, although beryllium reacts slowly. Beryllium liberates hydrogen when treated with sodium hydroxide solution. The reaction can be represented thus:

   $Be + 2H_2O + 2OH^- \longrightarrow [Be(OH)_4]^{2-} + H_{2(g)}$.

   This shows the anomaly in the behaviours of beryllium, in having amphoteric properties

2. All the alkaline earth metals bum in oxygen to form oxides, MO.
   Oxides can also be formed by thermal decomposition of MCO_3, $M(OH)_2$, $M(NO_3)_2$ and MSO_4. With the exception of Beryllium oxide which is covalent, all other oxides are ionic in nature.

   BeO has a wurtzite (hezagonal ZnS) structure (see fig 19). In this structure each ion has four nearest neighbours distributed tetrahedrally around it. Others have sodium chloride type of structure, ie each metal ion, M2+, is surrounded by six $O2^-$ ions and each O^{2-} is surrounded by six metal ions (see fig 20). CaO is prepared on a large scale by heating calcium carbonate in lime kilns and is used in the manufacture of sodium carbonate, calcium carbide, bleaching powder, glass and cement.

3. Barium peroxide, BaO_2 is formed by passing air over heated BaO, at 500 K. Strontium peroxide SrO_2, is obtained in a similar way at high temperature and pressure. Calcium peroxide, CaO_2 is obtained as a hydrate by treating $Ca(OH)_2$ with hydrogen peroxide H_2O_2 and then dehydrating the product.

   Magnesium peroxide, MgO_2 is obtained only in the crude form by using hydrogen peroxide but no peroxide of beryllium is known. These peroxides are ionic solids having $(O\text{-}O)^{2-}$ ion and can be considered as salts of very weak acids, H_2O_2. The peroxides on treatment with dilute acids form H_2O_2.

4. Alkaline earth metals react less readily with water than alkali metals to give hydrogen and metal hydroxides. Beryllium does not react with water or steam even at red heat. Magnesium reacts with hot water and Ca, Sr and Ba reacts with cold water to form the corresponding hydroxides. Beryllium hydroxide, $Be(OH)_2$ is amphoteric; the basic strength increases in the order Mg to Ba. Aqueous solutions of calcium and barium hydroxides are known as lime water and baryta water respectively.

   $Ca(OH)_2$ reacts with CO2 to form first an insoluble $CaCO_3$ which further reacts with CO2 to give soluble bicarbonate.

   $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$

   Insoluble water precipitate

   $CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$
   Soluble

   Calcium and barium bicarbonates are stable only in solution and decompose on removal of water to give carbonates. This property of bicarbonates is the reason for STALACTITE formation (The down ward growth of $CaCO_3$ formed on the roof of a cause by the tricking of

water containing calcium compounds) and STALAGMITE (The upward growth from the floor of a cave; by the tricking of water containing calcium compounds) formation.

5. Metal halides, are obtained by direct combination with halogens as well as by the action of halogenon metals. Beryllium halides are covalent and other metal halides are ionic. Beryllium halides are hygroscopic and fume in air due to hydrolysis. They sublime and do not conduct electricity. Anhydrous beryllium halides are polymeric. Beryllium chloride vapours contain $BeCl_2$ and $(BeCl_2)_2$ but the solid is polymerized and can be represented as $(BeCl_2)_2$ (see fig 21).

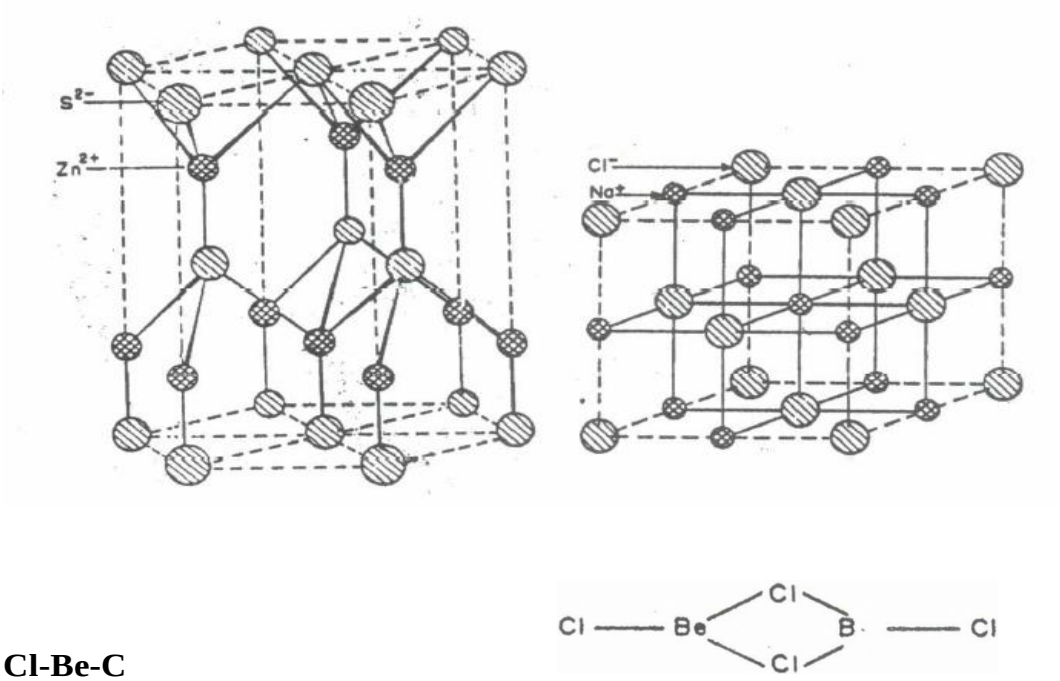

Fig 21: Beryllium chloride (a) monomer (b) dimmer and (c) polymer

The halides are hygroscopic and form hydrates. $CaCl_2$ is a well-known drying agent and anhydrous $MgCl_2$ is important in the electrolytic extraction of Mg.

6. All the Group 2 elements except beryllium form hydrides, MH_2, by direct combination with hydrogen.

   Beryllium hydride can be formed by reducing beryllium chloride with lithium aluminium hydride LiAlH4. All these hydrides are reducing agents which react with water to liberate hydrogen. Calcium strontium and barium hydrides are ionic and contain the hydride ion H^-.

Beryllium and magnesium hydrides are covalent and polymeric $(BeH_2)_n$ has an interesting structure.The polymeric solid contains hydrogen bridges between beryllium atoms (see fig 22)

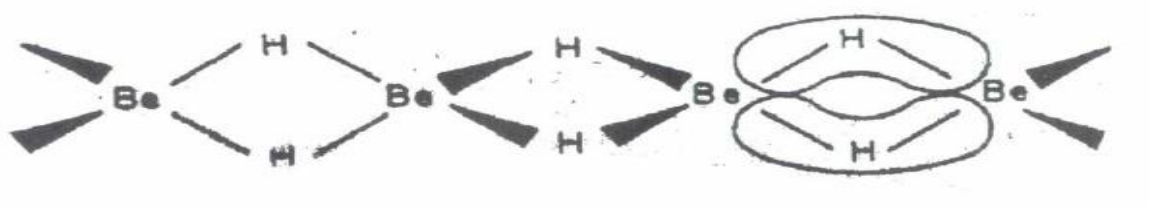

Fig 22: Beryllium hydride polymer

Each beryllium atom is bonded to four hydrogen atoms and each hydrogen atom forms two bonds as it bridges two Be atoms. Since Be has two valence electrons and H only one, it means that there are no enough electrons to form the usual type of bonds in which two electrons are shared between two atoms. Instead of this, center bonds are formed in which a "banana-shaped" molecular orbital covers three atoms Be…….H……. Be containing the two electrons. The monomeric molecule BeH_2 if formed with normal bonds, would have only four electrons in the outer shell of the beryllium atom and would be electron deficient. This would make the molecule very unstable. That is why BeH_2 exists as a cluster compound in which each atom shares its electrons with several neighbouring atoms and receives a share in their electrons in order to acquire a stable configuration.

7. All the metals in the Mg-Ba series or their oxides react directly with carbon to give the carbides (acetylides), MC_2. These carbides are ionic in nature and have a NaCl type of structure (Fig. 20) with M^{2+} replacing Na^+ and $C\equiv C^{2-}$ replacing Cl-.
Beryllium forms methanide, Be2C, with carbon, and acetylide BeC2 with acetylene

Magnesium on heating with carbon forms Mg_2C_3, which is an allylide since with water it liberates allylene (methyl/acetylene). The naming of carbides depends on the hydrocarbon they liberate on reaction with water. If acetylene is liberated it is called acetylide. If methane is liberated it is methanide etc:

$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$ (acetylene)

$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$ (methane)

$Mg2C3+4H_2O \longrightarrow 2Mg(OH)_2 + CH\text{-}C\equiv C$ (allene)

Alkaline earth metals burn in nitrogen to form nitrides; M_3N_2 it requires a lot of energy to convert. The stable N_2 molecule into nitride ion, N_{3-}, and this is recovered from the very high lattice energies of the alkaline earth metal nitrides. Beryllium compound is rather volatile while others are not. They are all colourless crystalline solids which decompose on heating and react with water to liberate ammonia and form either the metal oxide or hydroxide, e.g

$2Mg_{(s)} + N_{2(g)} \longrightarrow Mg_3^{2+}N_2^{3-}{}_{(g)}$

$Mg_3^{2+}N_2^{3-}{}_{(g)} + 6H_2O_{(l)} \longrightarrow 3Mg^{2+}(OH^-)_{2(s)} + 2NH_{3(g)}$

3.2 THERMAL STABILITY OF OXY SALTS

All Group 2 elements form oxysalts. The thermal stability of the oxy salts increases with the increase in electropositivity of the metal, it increases down the group. The salts of group 2 are thermally less stable than those of group 1. The carbonates of alkaline earth metals are stable at room temperature. On heating, they decompose into the corresponding oxides and carbon dioxide.

$MCO_3 \longrightarrow MO + CO_2$

The temperatures at which the carbonates decompose are: $BeCO_3$, <400K; $MgCO_3$, 800K; $CaCO_3$, 1200K; $SrCO_3$,1550K; $BaCO_3$, 1650K.

The sulphates are more stable than the carbonates. On heating they decompose into oxides and sulphur trioxide

$MSO_4 \longrightarrow MO + SO_3$

The order of decomposition temperature of the sulphate is: $BeSO_4$, 850K; $MgSO_4$, 1150K; $CaSO_4$, 1400K; $SrSO_4$, 1650K. Alkali metal nitrate decompose into nitrites on heating whereas alkaline earth metal nitrates decompose on heating to metal oxide, nitrogen dioxide and oxygen.

e.g $2Ca(NO_3)_2 \longrightarrow 2CaO + 4NO_2 + O_2$

In-text Question

Question
Beryllium halides undergoes the same reaction like camphor because?

Answer
They sublime and do not conduct electricity.

4.0 SELF-ASSESSMENT EXERCISES

1. Explain why noble metals like Au, Pt, Rh and Ir are not attached by nitric acid, but Au and Pt are dissolved by AQUA REGIA.

2. What are the usual coordination number e.g Be^{2+} and Mg^{2+}?
   What is the reason for the difference?

   Answers

1. Aqua Regia is a mixture of conc HNO_3 and conc HCl this mixture contains free chlorine which dissolves Au or Pt.

   Viz $HNO_3 + 3HC1 \longrightarrow 2H_2O + 2Cl + NOCl$

   $Au + 3Cl + HCl \longrightarrow HAuC1_4$

   $Pt + 4Cl + 2HC1 \longrightarrow H_2PtC1_6$

2. The usual coordinate numbers for Be^{2+} and Mg^{2+} are 4 and 6 respectively. The difference is due to the very small size of Be^{2+} and non-availability of d- orbitals in it.

5.0 CONCLUSION

We can conclude this unit by stating that the alkaline earth metals are generally less reactive than thealkali metals. Some of the reactions of the alkali earth metals include their action on acid to liberate hydrogen and their reaction with oxygen to form oxide which with the exception of that of beryllium are ionic in nature. Reactivity of alkaline earth metals increases with atomic number down the group. Alkaline earth metals react less readily with water than alkali metals to give hydrogen and metal hydroxides. Beryllium does not react with water or steam even at red heat. Magnesium reacts with hot water and Ca, Sr and Ba reacts with cold water to form the corresponding hydroxides. Each beryllium atom is bonded to four hydrogen atoms and each hydrogen atom forms two bonds as it bridges two Be atoms. All Group 2 elements form oxysalts. The thermal stability of the oxy salts increases with the increase in electropositivity of the metal, it increases down the group.

6.0 SUMMARY

In summary we have learned the following in this unit:

1. That alkaline earth metals are less reactive two than alkali metals.
2. That the alkaline earth metals react with acids to liberate hydrogen
3. That all alkaline earth metals burn in oxygen to form oxides
4. That the structure of BeO is the wurtzite (hexagonal ZnS) type, and that of other oxides is the NaCl of structure
5. That the alkaline earth metals react less readily with water
6. That the result of the reaction between alkaline earth metals and water is the formation of hydrogen and metal hydride oxides
7. That alkaline earth metals combine directly with halogens to form metal halides which are hygroscopic in nature and some eg $CaCl_2$ are used as drying agents.
8. That all Group 2 elements with the exception of beryllium form hydrides (MH_2) by direct combination with hydrogen.
9. That all the metals in the Mg - Ba series or their oxides react directly with carbon to give the carbides (acetylides) MC_2.

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. Explain in brief why the hydride bridge is $(BeH_2)_n$ is considered to be electron deficient but not the halide bridge in$(BeCl_2)_n$
2. Which is more stable to heat, beryllium carbonate or barium carbonate and why?

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MODULE 3

UNIT 6: COMPLEXING BEHAVIOUR OF ALKALINE EARTH METALS

1.0 INTRODUCTION

In units16 you studied the chemical properties of alkaline earth metals. You learned about the reactions of the alkaline earth metals with oxygen, water and acids. You also studied the thermal stability of their oxysalts. In the course form studies, you must have noticed that the first member of the alkaline earth metal always behaves differently from the rest. In this unit, you will be studying the anomalous behavior of beryllium. You will also be studying the complexation behavior of the alkaline earth metals in this unit.

2.0 INTENDED LEARNING OUTCOMES (ILOs)

At the end of your study of this unit, you should be able to:

1. List at least one complex that is formed by each member of the alkaline earth metals.
2. Describe the structure of the complexes formed by members of the group.
3. List the properties in which beryllium differs from other members of the alkaline earth metals

3.0 MAIN CONTENT

3.1 COMPLEX-FORMING BEHAVIOUR OF ALKALINE EARTH METALS

An interesting property of the alkaline earth metals is their complex behaviour. As we have seen earlier, complex formation is favoured by small, highly charged cations with suitable empty orbitals of approximately the right energy with which the Ligand orbitals can combine. Alkaline earth metal form more complexes as compared to alkaline metals. The tendency to form complex (mostly with O&N donors) decreases with increasing atomic number. Thus, of the heavier ions, only Ca^{2+} forms a complex with ethanol.

Beryllium having the smallest ion in the group tends to form complex most readily. It mostly forms complexes with tetrahedral arrangement because of the available orbitals as shown below.

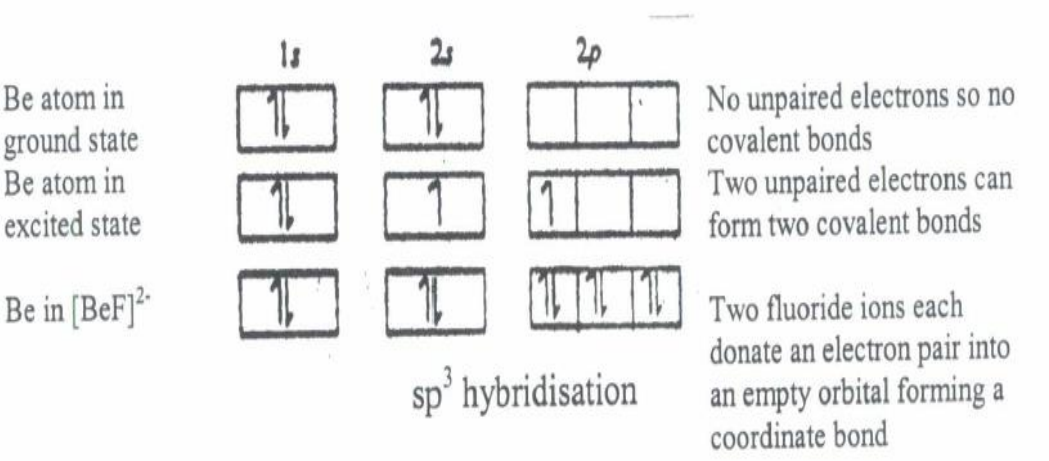


Figure 23: Below shows the tetrahedral structure of the trafluoroberyllates.

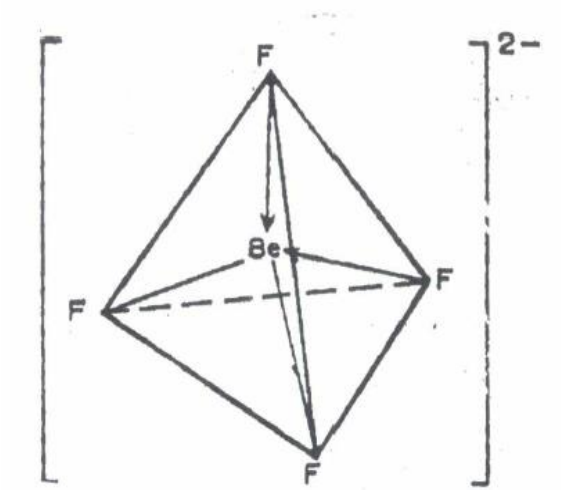


Figure 23: Tetrafluoroberylate complex ion (BeF4)2-

The arrows in figure 23 above indicate that two F ions from coordinate bonds with BeF_2. However, once these are formed, all the Be-F bonds tend to become similar.

Beryllium forms white crystalline molecular oxide - carboxylates of which BASIC BERYLLIUM ACETATE Viz $[OBe_4(CH_3COO)_6]$ is typical. It is used for the purification of Be because of its volatility and solubility in organic solvents. Beryllium forms a number of chelates with ligands like oxalates, $[Be(C_2O_4)_2]^{2-}$ (see figure 23) and B-diketonate anions.

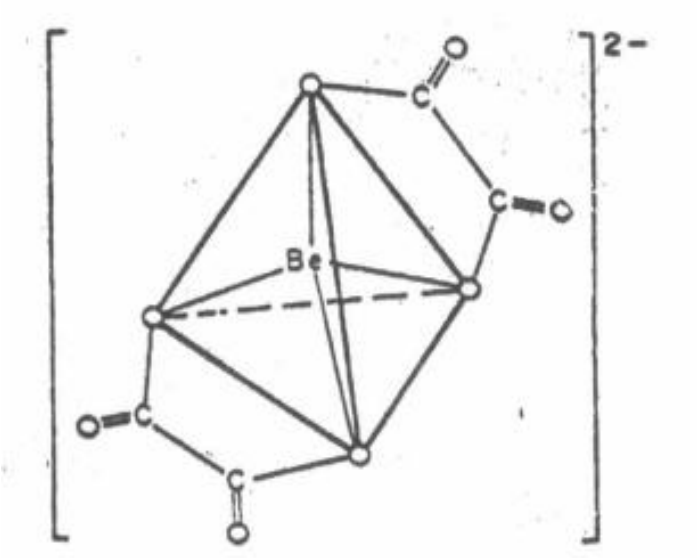


Fig 24: Beryllium Oxalate Complex, ion, $[Be(C_2O_4)_2]^{2-}$

In the hydrated salt, example $BeCO_3.4H_2O$ and $BeSO_4.4H_2O$ beryllium ions exist in the form $[Be(H_2O_4)]^{2+}$ where they show a coordination number of four. Magnesium is known to form a very important complex occurring in nature asin chlorophyll; a green pigment of plants which produces sugar in the presence of sunlight, carbon dioxide and water in a process known as photosynthesis.

$$6CO_2 + 6H_2O \xrightarrow[\text{Sunlight}]{\text{ChlorophyII}} \underset{\text{Glucose}}{C_6H_{12}O_6} + 6O_2$$

Magnesium in chlorophyII is coordinated by four nitrogen atoms in the heterocyclic porphyrinring system (see figure 25)

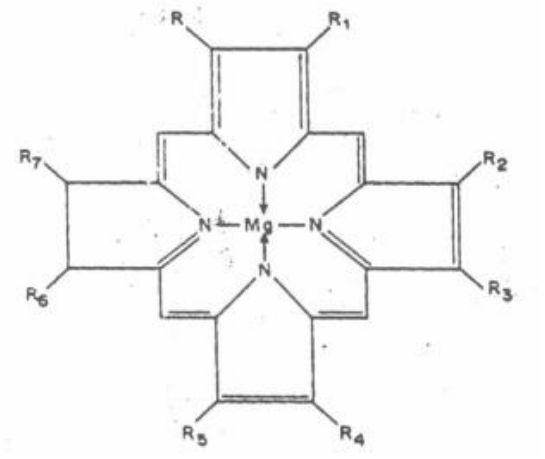


Fig 25: Skeleton of chlorophyII molecule

The rest of the alkaline earth elements from calcium to barium form complexes only with strong complexation agent such as acetyl acetone, ethylene diamine tetraacetic acid [EDTA] etc. In fact,

titrations are performed using EDTA in buffer solution to estimate the amount of Ca^{2+} and Mg^{2+} present in water to determine the hardness of water.

In-text Question

Question
Explain why Beryllium readily forms complexes

Anwser
Beryllium having the smallest ion in the group tends to form complex most readily. It mostly forms complexes with tetrahedral arrangement because of the available orbitals. The tendency to form complex decreases with increasing atomic number.

3.2 ANOMALOUS NATURE OF BERYLLIUM

Beryllium, the first member of the alkaline earth metal group, differs from the members of the group just as lithium differs from three members of its group. In facts beryllium differs more from magnesium than lithium does from sodium. As we shall see in the later units, the anomalous nature of the first member of s-and p-block groups becomes more pronounced toward the middle of the table.

Beryllium also shows a diagonal resemblance to aluminium in the same way as lithium does to magnesium. The properties in which beryllium differ from magnesium it shares with aluminium in general. Let us now look at these properties one at a time.

A. The cohesive properties of beryllium are much greater than those of magnesium and other elements in the group. As a result, it is much harder and has higher melting points.

B. It has smaller atomic radii higher electron affinity and higher ionization energy.

C. Its higher polarizing power leads to all its compounds being largely covalent with lower melting and boiling points, and enthalpies of formation (example BeF_2, m.p 1073 K while for the rest of the group is about 1573 K). All the compound of Be are more soluble in organic solvents than the corresponding magnesium compounds. They hydrolyse in water and in this respect they rather resemble aluminium.

In-text Question

Question
State the function and formula of BASIC BERYLLIUM ACETATE

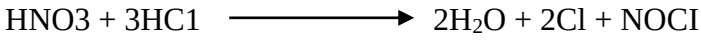
Anwser
It is used for the purification of Be because of its volatility and solubility in organic solvents.
$[OBe_4(CH_3COO)_6]$

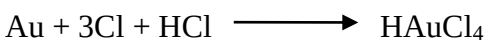
4.0 SELF-ASSESSMENT EXERCISE

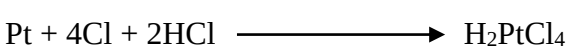
1. Explain why noble metals like Au, Pt, Rh and Ir are not attacked by nitric acid, but Au and pt are dissolved by Aqua regia

Answer

1. Aqua regia is a mixture of concentrated HN03 and concentrated HCl. This mixture contains free chlorine which dissolves Au or Pt viz







5.0 CONCLUSION

In conclusion, we have seen in this unit that alkaline earth metals form more complex than the alkali metals of group1. We have also seen that complex formation favour smaller cations. The ability to form complexes decreases with increasing atomic number. Thus Be forms more complexes than Mg, Ca and Ba. Beryllium shows behaviours which differ from that expected from a member of group 2. Magnesium is known to form a very important complex occurring in nature asin chlorophyll; a green pigment of plants which produces sugar in the presence of sunlight, carbon dioxide and water in a process known as photosynthesis. Beryllium also shows a diagonal resemblance to aluminium in the same way as lithium does to magnesium. The properties in which beryllium differ from magnesium it shares with aluminium in general.

6.0 SUMMARY

In this unit we have studied the following:

1. Alkaline earth metals form complexes
2. Beryllium being smaller in size than the other member of the group forms more complexes.
3. Magnesium forms important complexes that occur in nature. An example of such a complex is the one found in chlorophyll, the green pigment found in plant.
4. Beryllium the first member of the alkaline earth metal shows anomalous behaviour that is, it behaves differently than it is expected to do as a member of the group.
5. This anomalous behaviour is manifested in it having much higher melting and boiling points. It also has smaller atomic radii, higher electron affinity and higher ionization energy.

CLASS ACTIVITY (THE TUTOR TO DIRECT)

1. Why do alkaline earth metals form more complexes as compound than the alkaline metals? Give only two reasons

7.0 REFERENCE AND FURTHER READING

1. F. A Cotton, G. Wilkinson and P. L. Gayus (1995) Basic Inorganic Chemistry. (3nd edition) John Wiley and Sons Published

2. Gary L. Miessler, Paul J. Fischer and Donald A. Tour (2014) Inorganic Chemistry. 5th edition. Pearson Publishers. ISBN 10:0-321-81105-4

3. J. D Lee (2016) Concise Inorganic Chemistry. (5th edition)Wiley Publishers

4. Anomalous nature of beryllium

https://www.youtube.com/watch?v=5DCbD4sTWOQ