COURSE GUIDE

CHM 204
STRUCTURE AND BONDING

Course Team   Prof. Abimbola Ogunsipe (Course Developer/ Writer) -FUPR Effurun, Delta State
Prof. Olusegun Abiola (Course Editor) - FUPR Effurun, Delta State
Prof. Nnabuk Okon Eddy (Course Reviewer/Writer) University of Nigeria, Nsukka

NATIONAL OPEN UNIVERSITY OF NIGERIA

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INTRODUCTIONS

The physical properties of an atom is related to the number of proton while the number of electron influences the chemical properties. However, both physical and chemical properties are ultimately explained in terms of the structure and bonding.

Several models on structure and bonding have been proposed and it seems there is no unique model that can completely predict structure and bonding on its own. The development of atomic structure progressively received light from earliest work to the present state of quantum theory. Generally atom is still known as a component that has electron, neutron and proton (i.e elemental particles), which are involves in defining atomic structure. Knowledge of the structure is essential because their behaviour, usefulness and other applications is based on their structures. Bonding is defined when two or more atoms combine together. The combination requires a force that holds them together, without which there will be no compound or molecules. The structure of a compound depends on the type of bonding. For example, most ionic compounds are assumes NaCl or CsCl crystalline structure and therefore have high melting and boiling points among other properties. Covalent compounds with low boiling and melting point have weak bonds. Some weaker forces also present them weaker.

Generally, there are two major types of bonding, depending on how electron is arranged or engaged to give a compound. Bonding that involve the transfer of electron (from an atom with low ionization energy) to an electronegative atom is called ionic or electrostatic or electrovalent bond. However, where electron can not be transferred or accepted, the preferred bonding route is called covalent bond and is a consequence of sharing of electron. Once a bond is formed, several analysis can be assigned. For example, covalent character in ionic bond, asymmetry centre for positive and negative charges, charge distribution, etc. All these concepts are discussed under structure and bonding.

COURSE COMPETENCIES

Structure and bonding (CHM 204) is a course which addresses the behaviour of behaviour of compounds due to the nature of bonding which involves (ionic: transfer and acceptance of electrons), covalent (sharing of electrons). Factors that influence structure and bonding of compounds and their implication are also treated under this course. Influence of bonding on the shape of molecules are discussed through hybridization, valence shell electron paired repulsion, molecular orbital and quantum theories. The

course traces originated models on the structure of compounds and considered nature of bonding.
This course is aimed to bring the student to the knowledge of fundamental aspect, theory and laws in structure and bonding

COURSE OBJECTIVES

When you have studied this course, you should be able to:

- To introduce the students to different models on atomic structure
- To introduce the student to quantum model, orbitals and atomic orbitals
- To introduce the student to how chemical bonds are formed and their effect on structure and bonding
- To introduce the concept of covalent character in ionic bond
- To explain the chemistry of the main group elements including their structures and bonding

WORKING THROUGH THIS COURSE

The course is structured into five models. Modules 1 to 3 consist of two units each while modules 4 and 5 consist of one unit each. It is necessary that for the student to study and understand the content of all the units in the respective modules.

You will be provided with the following materials:
1.   Course Guide
2.   Study Units

STUDY UNITS

The outline for this course include, Idea of quantum states. Orbitals, shape and energy, simple valence theory. Electron repulsion theory; atomic spectra.

The structure and chemistry of some representative main group element compounds.

This course materials is organised into three Modules. Module 1 consist of two units, module 2, two units and module 3, three units. Descriptions of each unit are as follows,

Module 1

Unit 1   Chemical bonding
Unit 2   Theory of bonding

Module 2

Unit 1 Valence shell electron paired repulsion
Unit 2 Quantum Mechanics

Module 3

Unit 1   Chemistry of the main group element
Unit 2   Second and higher main group elements

Module 1, Study Unit 1 introduces the students to different types of chemical bonds (including ionic and covalent), how they are formed, their properties and consequences on the structures of such compounds

In Study Unit 2 of module1, Lewis structure of molecules is linked to valence bond theory. Molecular orbital theory is discussed in detail while hybridization theory is discussed and applied in predicting the geometric of molecules.

Study Unit 1 (Module 2) In this study unit, the concept of valence shell electron paired repulsion is deeply visualized in developing geometric of molecules. Steric number and other associated concept are also discussed.

Study 2 (Module 2) In this study unit, quantum mechanic is used to derived the Schrodinger equation and the derived equation is applied to structure and bonding variables including atomic orbitals, molecular orbitals, quantum number and other parameters

In Study Unit 1 of Module 3, considers the periodic table, position of hydrogen in the periodic table, the alkali metals and periodicity of ionization potential, atomic radius, electronegativity, electron affinity and other properties.

Study Unit 2 (Module 2) consider the chemistry, structure and bonding in groups 13 to 18 main group elements. Their usefulness are also discussed in detail.

TEXTBOOKS AND REFERENCES

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PRESENTATION SCHEDULE

This course is presented in three different modules. Each module consists of two study units. Each module begins with introduction, study outcomes and main content. Within the main content, fundamental facts are presented along with inline Worked examples and answers. Each unit ends with summary, conclusion, bibliography, Worked examples/answers and activity for student to test their comprehension.

ASSESSMENT

There are two aspects of assessment for this course: the tutor-marked assignment (TMA) and end of course examination. The TMAs shall constitute the continuous assessment component of the course. They will be marked by the tutor and equally account for 30 % of the total course score. Each learner shall be examined in four TMAs before the end of course examination. The end of course examination shall constitute 70% of the total course score.

HOW TO GET THE MOST FROM THE COURSE

Student are expected to comprehends best information out of this course through careful study of each units. It is recommended that student should test their ability to answer questions that follow each unit as well as questions in reference materials related to this course

MAIN

COURSE

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MODULE 1

Unit 1   Chemical bonding
Unit 2   Theory of bonding

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UNIT 1   CHEMICAL BONDING

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          3.2   Covalent Bond
          3.3   Covalent Character in Ionic Bond
          3.4   Bond Enthalpy
          3.5   Bond Haber Cycle
4.0   Conclusion
5.0   Summary
6.0   Tutor Mark Assignments
7.0   References/Further Readings

1.0   INTRODUCTION

Every chemical system seeks to be stabilized with the minimum attainable energy or energy level. The electronic configurations of the noble gases indicate stability due to completely filled energy/electronic level. Therefore, the tendency for all atoms to attain stability is measured by considering the configuration of the nearest noble gas. A completely filled valence energy level represent octet configuration (when p-orbital is involved) or duplet configuration (for s-orbital alone). Achievement of stability or minimum energy level is possible when atoms combine with each other. Since chemical reactions involves only the valence electrons, the combination can lead to stability through two major process, namely,

(i)   Electron donation/acceptance
(ii)   Sharing of electron

The most important types of chemical bonds are characterized as either ionic or covalent. In ionic bonding, atoms transfer electrons to each other. Ionic bonds require at least one electron donor and one electron acceptor. In contrast, atoms with the comparative electronegativity tend to share electrons

in covalent bonds, because neither atom preferentially attracts or repels the shared electrons.

When atom attain stability through sharing electrons or by transfer and acceptance of electron, the process is called bonding and the new force that holds the atom together is called chemical bonding. When bonding occurs, the resulting molecule or compound has a lower energy than its constituent atoms. Bonding is achieved by redistributing the valence (or bonding) electrons. In ionic bonding, this redistribution occurs by the atoms transferring one or moreelectrons. The term *ionic bond* describes the electrostatic attraction of two oppositely charged ions in a crystalline lattice. Molecules that consist of charged ions with opposite charges are called *ionic molecules*. These ionic compounds are generally solids with high melting points and conduct electrical current. Ionic compounds are generally formed from metal and non-metal elements.

Ions are completely different in physical and chemical properties from the neutral atoms of the element. The notation of the + and - charges on ions is very important as it conveys a definite meaning. Whereas elements are neutral in charge, IONS have either a positive or negative charge depending upon whether there is an excess of protons (positive ion) or excess of electrons (negative ion).

2.0   OBJECTIVES

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

*   Know how atoms achieved stability through chemical bonding
*   Understand the attainment of octet or duplet configuration as a condition for stability
*   Know the two major types of bonding in compounds
*   Know the conditions needed for the various bonding
*   Understand the properties of the various bonds

3.0   MAIN CONTENT

3.1   Ionic Bonds

Elements in the first few columns of the periodic table have few more electrons than predicted by the octet rule: they therefore lose the electrons in the outermost shells fairly easily. For example, the alkali metals (group I), such as sodium (Na) or potassium (K), which have 11 and 19

electrons respectively, e a s i l y lose one electron to form mono- positive ions, Na^+ and K^+. Elements in the *last* few columns of the periodic table have one, two or three *fewer* electrons than predicted by the octet rule: they therefore gain electrons fairly easily. For example, the halogens (group VII), such as fluorine (F) or chlorine (Cl), which have 9 and 17 electrons, respectively, easily gain one electron to form mono-negative ions, F^- or Cl^- . These ions have 10 and 18 electrons, respectively. Also, elements in group II form doubly positive ions such as Mg^{++} or Ca^{++}, and elements in group VI form doubly negative ions such as O^{--} or S^{--}. All these ions obey the octet rule and so are fairly stable.

The resulting ions, which have opposite charges, will be attracted to one another, and will draw closer, until they "touch". This happens when the inner shell of electrons on the sodium ion (the smaller sphere) starts to overlap with the outer shell of electrons on the chloride anion (the bigger sphere). This pair of ions looks like this:

Ionic bonding involves the transfer of valence electron(s) between atoms. It is a type of chemical bond that generates two oppositely charged ions. In ionic bonds, the metal loses electrons to become a positively charged cation, whereas the nonmetal accepts those electrons to become a negatively charged anion. Ionic bonds require an electron donor, often a metal, and an electron acceptor, a nonmetal. This implies that the electron donating specie (metals in most cases) must have low ionization energy while the electron accepting specie should have comparable values of electronegativity.

Ionic bonding is observed in metals that have few electrons in their outer-most orbitals. By losing those electrons, these metals can achieve noble gas configuration and satisfy the octet rule. Similarly, nonmetals that have close to 8 electrons in their valence shells tend to readily accept electrons to achieve noble gas configuration. In ionic bonding, more than 1 electron can be donated or received to satisfy the octet rule. The charges on the anion and cation correspond to the number of electrons donated or received. In ionic bonds, the net charge of the compound must be zero since the positive charges in the metal is equally balance by equivalent negative charges in the nonmetals.

Consider sodium, which has 11 electrons and eleven protons. Its electronic configuration is $1s^2 2s^2 2p^6 3s^1$. Also the electronic configuration of neon is $1s^2 2s^2 2p^6$ indicating that sodium has excess of one electron over neon and

its configuration can be written as, $[Ne]3s^1$. When sodium ionize, it configuration changes to

$$Na^+ = 1s^2 2s^2 2p^6 = [Ne]$$
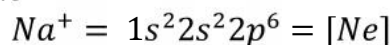
Therefore, sodium ion is isoelectronic with neon and through ionization, its attain the octet configuration and becomes stable.

Chlorine has seventeen electrons in its outermost level and its electronic configuration given below and is one electron less the octet configuration defines by argon

$$Cl = 1s^2 2s^2 2p^6 3s^2 3p^5$$
$$Ar = 1s^2 2s^2 2p^6 3s^2 3p^6$$
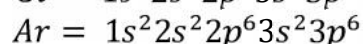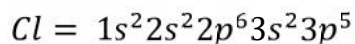
It is easier for chlorine to ionize by gaining electron than to lose electron and when it ionizes, its configuration becomes isoelectronic with argon, the nearest noble gas

$$Cl^- = 1s^2 2s^2 2p^6 3s^2 3p^6 = [Ar]$$
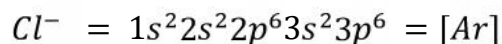
From the above, the one electron from sodium can be accepted by chlorine thus establishing an electrostatic interaction through chemical bond formation. The higher the ionization energy, the less is the tendency to lose electron and the more difficult is the tendency for that metal to go into ionic (also called electrovalent or electrostatic bond). On the other hand, the lower the electron affinity, the less is the tendency to accept electron and form ions that can combine to form ionic bond. Hence since the number of electrons lost is equal to the number of electrons accepted by the electronegative specie, the compound formed is electrically neutral and not charged specie. The process involves in ionic bond formation is also indicated in the diagram below
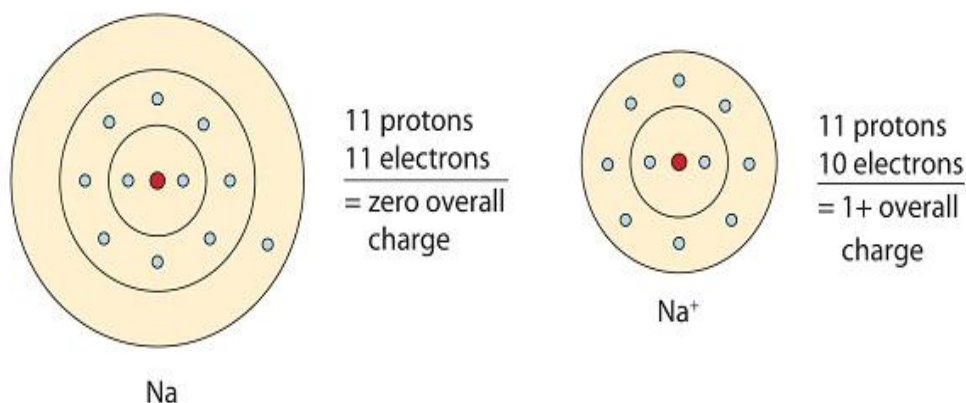

This sodium molecule donates the lone electron in its valence orbital in order to achieve octet configuration. This creates a positively charged cation due to the loss of electron.
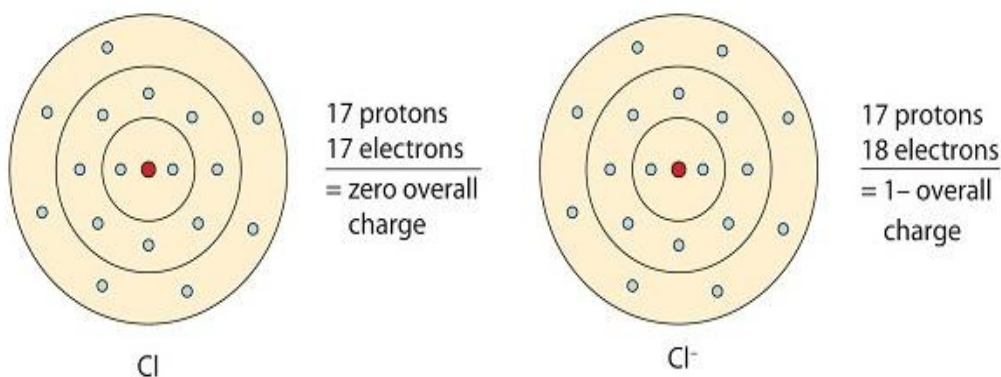
This chlorine atom receives one electron to achieve its octet configuration, which creates a negatively charged anion.
The predicted overall energy of the ionic bonding process, which includes the ionization energy of the metal and electron affinity of the nonmetal, is usually positive, indicating that the reaction is endothermic and unfavorable. However, this reaction is highly favorable because of the electrostatic attraction between the particles. At the ideal interatomic distance, attraction between these particles releases enough energy to facilitate the reaction. Most ionic compounds tend to dissociate in polar solvents because they are often polar. This phenomenon is due to the opposite charges on each ion.
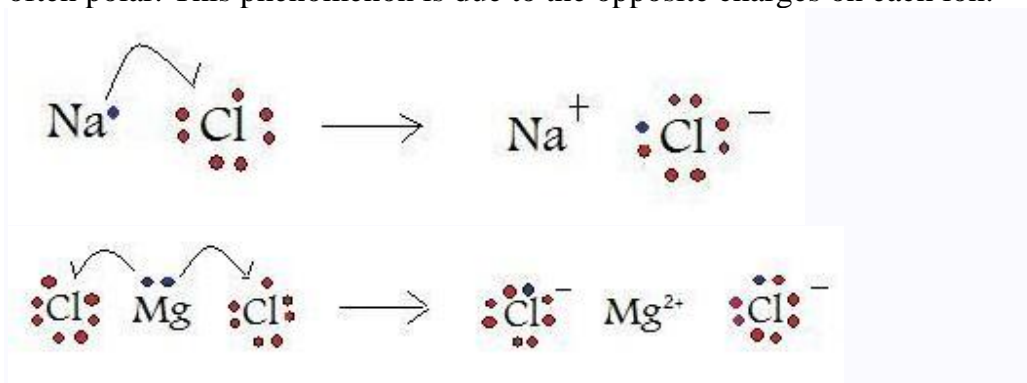
In the above example, the magnesium atom is donating both of its valence electrons to chlorine atoms. Each chlorine atom can only accept 1 electron before it can achieve its noble gas configuration; therefore, 2 atoms of chlorine are required to accept the 2 electrons donated by the magnesium. Notice that the net charge of the compound is 0.

3.1.1 Properties of ionic compounds

(i)   They form crystals. ...
(ii)   They have higher enthalpies of fusion and vaporization than molecular compounds.
(iii)   They are hard.and bristle because of strong bonding force

(iv)   They have high melting points and also high boiling points.
(v)   They dissolve in water and other solvents) with high dielectric
   constant) to form electrolyte, which conduct electricity

3.1.2 Structure of ionic compound

n ionic crystal consists of ions bound together by electrostatic attraction. The arrangement of ions in a regular, geometric structure is called a crystal lattice. There are two common crystal form for most ionic compounds. These are **sodium chloride** and **caesium chloride** structures.   The arrangement is a function of unit cell representation. Unit cell is defined as the smallest portion of structure which when repeatedly stacked together at all directions, can reproduce the entire lattice
.

In sodium structure, each ion in sodium chloride is surrounded by six neighboring ions of opposite charge. The arrangement is made up of two interpenetrating face-centered cubic lattices (f.c.c.) of each type of ion (Na^+, Cl^-) to form a *simple cubic lattice* with each type o**f ion occupying alternate corners**
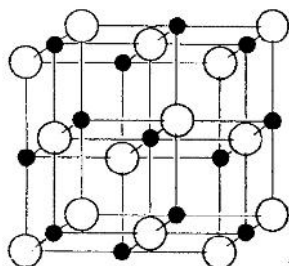
NaCl structure
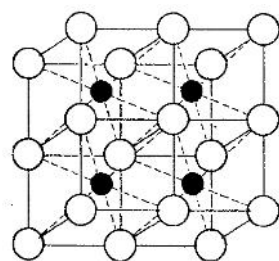
CsCl structure

The CsCl structure arises because in some compounds, the positive and negative ions usually differ so much in size that packing is often much less efficient forcing the solid to assume lattice geometries that differ from the face centre cubic pagking. For example, The radius of the Cs^+ ion is 168 pm (compared to 98 pm for Na^+), and cannot possibly fit into the octahedral hole of a simple cubic lattice of chloride ions (181 pm ionic radius). The CsCl

lattice therefore assumes a different arrangement. The CsCl structure shown above is made up of two inter-penetrating simple lattices of each type of ion (Cs^+, Cl^-) to form a *body-centered   cubic lattice (b.c.c.)*

3.2   Covalent bond

Covalent bonding involves the sharing of electrons between atoms. This type of bonding occurs between two atoms of the same element or of elements close to each other in the periodic table. This bonding occurs primarily between non-metals; however, it can also be observed to some extent between non-metals and metals.

If atoms have similar electronegativities (the same affinity for electrons), covalent bonds are most likely to occur. Because both atoms have the same affinity for electrons and neither has a tendency to donate them, they share electrons in order to achieve octet configuration and become more stable. In addition, the ionization energy of the atom is too large and the electron affinity of the atom is too small for ionic bonding to occur. For example: carbon does not form ionic bonds because it has 4 valence electrons, half of an octet. To form ionic bonds, Carbon molecules must either gain or lose 4 electrons. This is highly unfavourable; therefore, carbon molecules share their 4 valence electrons through single, double, and triple bonds so that each atom can achieve noble gas configurations. Covalent bonds include interactions of the sigma and pi orbitals; therefore, covalent bonds lead to formation of single, double, triple, and quadruple bonds. Example of covalent bond is in PCl_3. The valence electron in phosphorus is five while chlorine has seven. Therefore, three chlorine molecules can use three electrons from the phosphorus and form PCl_3 having one pair of non bonding electron. This combination satisfies the octet rule for both P and Cl
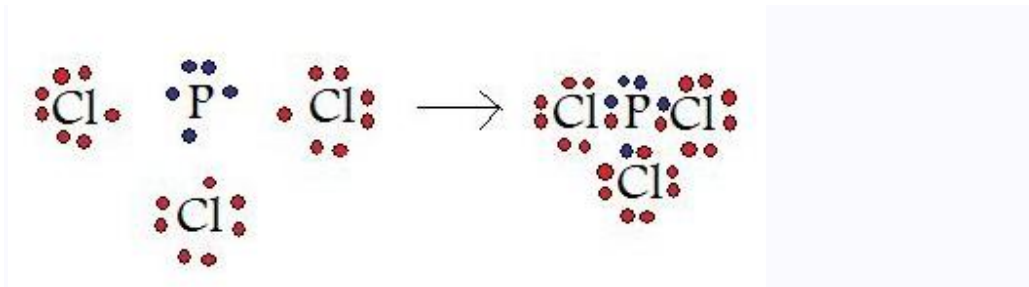

We can also use the Bohr notation to represent the formation of hydrogen, fluorine and carbon dioxide molecules (as shown below) with valence electrons designated by colored dots. In the formation of H_2, both hydrogen atoms achieve a helium-like pair of 1s-electrons by sharing, In the other examples carbon, oxygen and fluorine achieve neon-like valence octets by

sharing of electron pairs. Carbon dioxide formation involves two pairs of electrons (four in all) been shared by the same two atoms. This is an example of a double covalent bond.
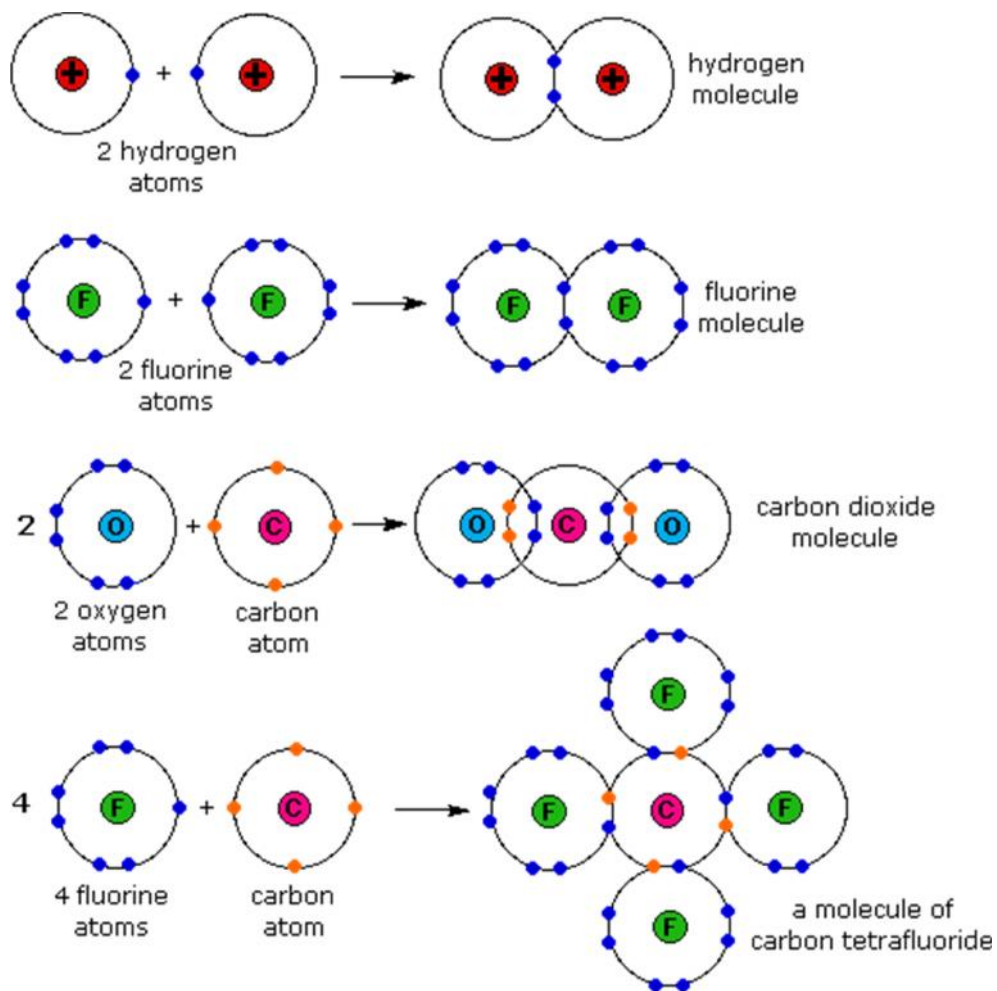
We can also draw Couper-Kekulé formulas in which each shared electron pair is represented by a line between the atom symbols. Non-bonding valence electrons are shown as dots. These was developed by A. Couper and A. Kekulé, are applied for the compounds given below
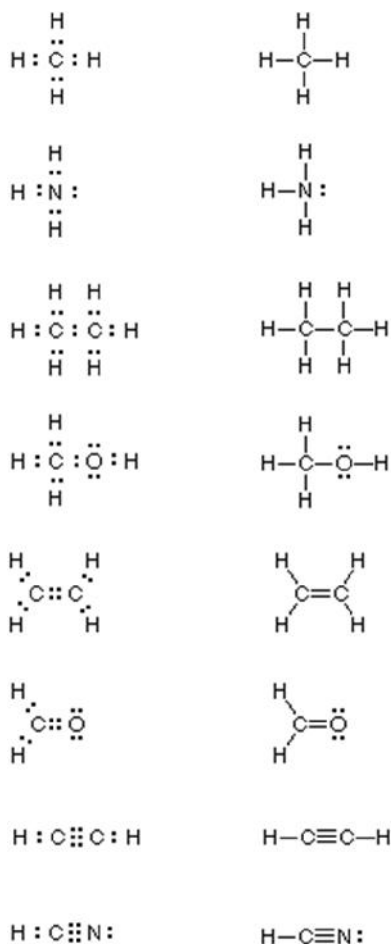
3.2.1 Charge Distribution

In the diatomic molecules, electron pair are donated and shared evenly and there is no fixed local charges within a molecule.However, in most covalent compounds some degree of local charge separation, resulting in bond and / or molecular dipoles are observed. A dipole exists when the centers of positive and negative charge distribution do not coincide.

3.2.2 Formal Charges

A large local charge separation usually results when a shared electron pair is donated unilaterally. The three Kekulé formulas shown here illustrate this condition for ozone, nitromethane and azide anion.
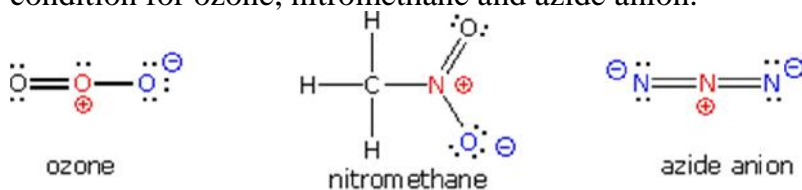
In ozone the central oxygen atom has three bonds and a full positive charge while the right hand oxygen has a single bond and is negatively charged. The overall charge of the ozone molecule is zero. Similarly, nitromethane has a positive-charged nitrogen and a negative-charged oxygen, the total molecular charge again being zero. Finally, azide anion has two negative-charged nitrogens and one positive-charged nitrogen, the total charge is minus one.

Generally, when the valence shell electron of covalently bonded compound and the number of covalent bonds to an atom is greater than its normal valencyy, then it will carry a positive charge. If the number of covalent bonds to an atom is less than its normal valence it will carry a negative charge. The formal charge on an atom may also be calculated by the following formula:

$$\text{Formal Charge} = \text{Valence Electrons in Neutral Atom} - \left(\text{Unshared Valence Electrons} + \text{Half of the Shared Electrons} \right)$$

Different in nuclear charges, and shielding by inner electron shells, the different atoms of the periodic table have different affinities for nearby electrons. The ability of an element to attract or hold onto electrons is called **electronegativity**. Eelectronegativity values was established by Linus Pauling, as shown in the table below

Table 1 : Electronegativity of some elements

H (2.20)						
Li(0.98)	Be(1.57)	B (2.04)	C (2.55)	N (3.04)	O (3.44)	F (3.98)
Na(0.90)	Mg (1.31)	Al (1.61)	Si (1.90)	P(2.19)	S (2.58)	Cl (3.16)
K(0.62)	Ca (1.00)	Ga (1.81)	Ge (2.01)	As (2.18)	Se (2.55)	Br (2.96)

Fluorine has the greatest electronegativity of all the elements, and the heavier alkali metals such as potassium, rubidium and caesium have the lowest electronegativities. Carbon has electronegativity that is within the middle of the range, which explains its behaviour in chemical reactions.

When two different atoms are bonded covalently, the shared electrons are attracted to the more electronegative atom of the bond, resulting in a shift of electron density toward the more electronegative atom. Such a covalent bond is **polar**, and will have a **dipole** (one end is positive and the other end negative). The degree of polarity and the magnitude of the bond dipole will be proportional to the difference in electronegativity of the bonded atoms. For example, a O–H bond is more polar than a C–H bond, with the hydrogen atom in -OH being more positive than the hydrogen bonded to carbon (in

CH). Also, C–Cl and C–Li bonds are both polar, but the carbon end is positive in the former and negative in the latter. The dipolar nature of these bonds is often indicated by a partial charge notation (+/–) or by an arrow pointing to the negative end of the bond.

Although there is a small electronegativity difference between carbon and hydrogen, the C–H bond is regarded as weakly polar at best, and hydrocarbons in general are considered to be non-polar compounds.

The shift of electron density in a covalent bond toward the more electronegative atom or group can be assessed through the bonds to hydrogen, which is an index of acidity. If the bonding electron pair moves away from the hydrogen nucleus the proton will be more easily transferred to a base (it will be more acidic). For example methane is non-acidic because the C–H bond is nearly non-polar. However, O–H bond of water is polar, and is more acidic than methane. H–F is more acidic than water due to greater electronegativity difference in its atoms.

Electronegativity differences may also be transmitted through connecting covalent bonds by an **inductive effect**. Replacing one of the hydrogens of water by a more electronegative atom increases the acidity of the remaining O–H bond. Tis explain why hydrogen peroxide, HO–O–H, is ten thousand times more acidic than water, and hypochlorous acid, Cl–O–H is one hundred million times more acidic. This inductive transfer of polarity decreases as the number of transmitting bonds increases, and the presence of more than one highly electronegative atom has a cumulative effect. For example, trifluoro ethanol, CF_3CH_2–O–H is about ten thousand times more acidic than ethanol, CH_3CH_2–O–H.

## 3.3   Covalent character in ionic compound

Ionic and covalent bonds are the two extremes of bonding. Polar covalent is the intermediate type of bonding between the two extremes. Some ionic bonds contain covalent characteristics and some covalent bonds are partially ionic. For example, most carbon-based compounds are covalently bonded but can also be partially ionic. Polarity is a measure of the separation of charge in a compound. A compound's polarity is dependent on the symmetry of the compound and on differences in electronegativity between atoms. Polarity occurs when the electron pushing elements, found on the left side of

the periodic table, exchanges electrons with the electron pulling elements, on the right side of the table. This creates a spectrum of polarity, with ionic (polar) at one extreme, covalent (nonpolar) at another, and polar covalent in the middle.

Ionic bonds differ from covalent bonds. Both types result in the stable electronic states associated with the noble gases. However, in covalent bonds, the electrons are shared between the two atoms. All ionic bonds have some covalent character, but the larger the difference in electronegativity between the two atoms, the greater the ionic character of the interaction.

3.4   Lattice energy

Lattice energy is a measure of the bond strength in an ionic compound. It estimates the bond strength in ionic compounds. It is defined as the heat of formation for ions of opposite charge in the gas phase to combine into an ionic solid. As an example, the lattice energy of sodium chloride, NaCl, is the energy released when gaseous Na^+ and Cl^- ions come together to form a lattice of alternating ions in the NaCl crystal.

$$Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)} \quad \Delta H = -787.3 \, kJ/mol$$
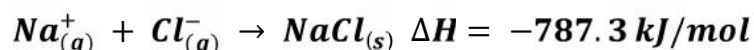
The negative sign of the energy is indicative of an exothermic reaction. Lattice energy can also be considered as the energy required to separate a mole of an ionic solid into the gaseous form of its ions (that is, the reverse of the reaction shown above and is consistent with Laplace law).
Born and Lande (1918) model for lattice energy can be written as

$$E = \frac{N_A M z^+ z^- e^2}{4\pi\varepsilon_0 r^0}\left(1 - \frac{1}{n}\right)$$

where N_A is Avogadro's constant; M is the Madelung constant, which depends on the crystal geometry; z^+ is the charge number of the cation; z^- is the charge number of the anion; e is the elementary charge of the electron; n is the Born exponent, a characteristic of the compressibility of the solid; ε_0 is the permittivity of free space; and r_0 is the distance to the closest ion.
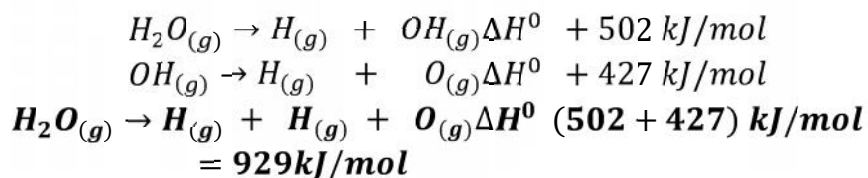This model identifies two main factors that contribute to the lattice energy of an ionic solid: the charge on the ions, and the radius, or size, of the ions. Consequently, as the charge of the ions increases, the lattice energy increases. But as the size of the ions increases, the lattice energy decreases. Lattice energies are also important in predicting the solubility of ionic solids

in H_2O. Ionic compounds with smaller lattice energies tend to be more soluble in H_2O.

3.5 Bond Enthalpy

Chemical bonds hold compounds together. This maybe electrovalent or covalent. Most often, the reactants have their individual bonds associated with it. Therefore, before they can react, bonds have to be broken and before products formation, new bonds must be formed Bonds are broken in the reactants while new bonds are formed in the products. Bond enthalpy is the energy needed to break bond in gaseous molecules under standard condition. Due to some complications that may arise in using actual values of bond enthalpy, average bond enthalpies are often used. For example, water consist of two O-H bond and it has been found that the energy needed to break the first)-H bond is significantly higher than the energy needed to break the second O-H bond. Also, the energy needed to break O-H bond in molecule such as +ethanol is quite different from the energy needed to break the O-H bond in water and other molecules. Hence the use of average bond enthalpy is justified.

Let us consider the bond enthalpy associated with the breaking of H and O bonds in water and hydroxyl.

$$H_2O_{(g)} \rightarrow H_{(g)} \; + \; OH_{(g)} \Delta H^0 \; + 502 \, kJ/mol$$
$$OH_{(g)} \rightarrow H_{(g)} \; + \; O_{(g)} \Delta H^0 \; + 427 \, kJ/mol$$
$$\boldsymbol{H_2O_{(g)} \rightarrow H_{(g)} \; + \; H_{(g)} \; + \; O_{(g)} \Delta H^0 \; (502 + 427) \, kJ/mol}$$
$$= \boldsymbol{929 kJ/mol}$$

Therefore, the average bond enthalpy for O-H is $929/2 = 464.50$ kJ/mol. The average bond enthalpies and the corresponding bond lengths for some bonds are presented in the Table 2. All bond energies are obtained in the gaseous state so that the enthalpy change associated with the breaking and formation of intermolecular force can be eliminated.

Bond breaking is an exothermic process while the formation of new bond is an endothermic process. The amount of energy absorbed during the formation of bond is the same as the amount of energy liberated during the breaking of bond. This is the consequence of the second law of thermochemistry (i.e Laplace law), which states that the enthalpy change needed for the formation of a compound is the same as the enthalpy change (but with reverse sign) needed for the decomposition of the compound.

In the course of breaking bonds in the reactants and the formation of new bonds in the products the difference between the bond energies of the reactants and that of the products represents the enthalpy change of the reaction. That is,

$$H = \sum (bond\ broking\ energies) - \sum f(bond\ forming\ energies)$$

Therefore, when $\sum(bond broking energies)$ $\sum(bond dorming energies)$, the reaction is endothermic and when $\sum(bond broking energies) < \sum(bond dorming energies)$, the reaction is exothermic. Bond breaking involves separation of atoms that were bonded in a molecule indicating that energy is required (i.e endothermic reaction). However bond forming involves bringing the atoms that are bonded by electrostatic attraction, hence energy is released.

Table 2: Average bond enthalpy and bond length for some bonds

| Bond	Average bond enthalpy (kJ/mol)	Bond length (10^{-9} m)
H-H	436	0.074
C-C	347	0.154
C=C	612	0.134
C-H	413	0.108
O=O	498	0.121
O-H	464	0.096
C=O	746	0.120
Cl-Cl	243	0.199

3.6   Born-Haber cycle

Lattice energy cannot be determined experimentally due to the difficulty in isolating gaseous ions. The energy value can be estimated using the Born-Haber cycle, or it can be calculated theoretically with an electrostatic examination of the crystal structure. The Born-Haber cycle was developed by Max Born and Fritz Haber (German Chemists). The cycle analyses details enthalpies and lattice energy associated with the formation of ionic compounds from its constituent elements. Born-Haber cycle has found wider application in calculating enthalpy and lattice energy of compounds that can not be easily determined experimentally. Lattice energy is the enthalpy change involves in the formation of an ionic compounds from gaseous ions hence the process is exothermic. On the other hand, the endothermic process associated with the breaking of ionic compound into gaseous ions is also

equivalent to the lattice energy. Born-Haber cycle applies Hess law of thermochemistry to solve problems involving enthalpy change.

In order to analyse the Born-Haber cycle, let us consider the formation of $NaCl_{(s)}$. The steps involves are as follows:

i.   Sodium atom in the solid state is changed into sodium atom in the gaseous state. The enthalpy change is called atomization energy, ΔH_{Atom}. i.e,
$$\rightarrow Na_{(g)} \Delta H^0_{Atom} = 107 \, kJ/mol$$
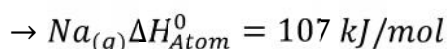
ii.   Sodium ion in the gaseous state ionizes to lose one electron, The enthalpy change associated with the ionization is called ionization energy, ΔH_{IE},
$$Na_{(g)} \rightarrow Na^+_{(g)} + e^- \Delta H^0_{IE} = +496 \, kJ/mol$$
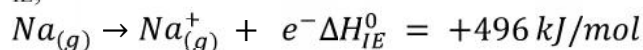
iii.   Chlorine molecule dissociates into chlorine atoms in the gaseous state. The enthalpy change associated with this process is called dissociation energy, ΔH^0_D,
$$\frac{1}{2} Cl_{2(g)} \rightarrow \Delta H^0_D = +243 \, kJ/mol$$
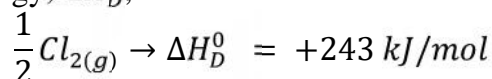
iv.   The gaseous chlorine atom $gaCl_{(g)}$ in one electron from that was lost by sodium and become ionizes into chloride ion. The enthalpy change associated with the ionization is called electron affinity, ΔH^0_{EA}
$$Cl_{(g)} + e^- \rightarrow Cl^-_{(g)} \Delta H^0_{EA} = -349 \, kJ/mol$$

v.   Sodium ion (formed in step ii) and chloride ion (formed in step iv) combine together to form one mole of NaCl. The enthalpy change associated with this combination is called lattice energy,
$$Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)} \Delta H^0_{Latt} =$$
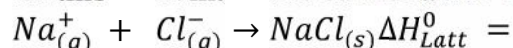
The entire steps involves in the formation of NaCl from its constituent element can be represented in a cycle called Born-Haber cycle as shown in the figure below
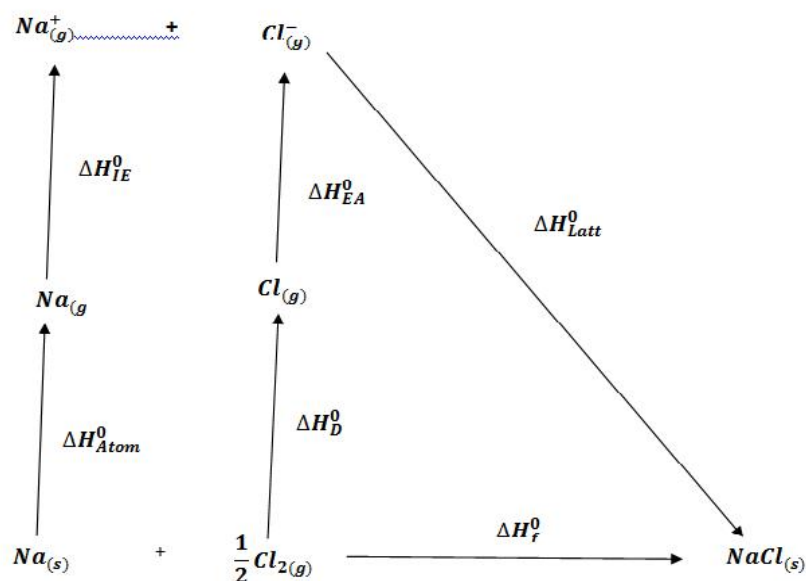
From the above diagram , it is evident that the underlisted equation represent conservation principle, according to Hess law

$$\Delta H_f^0 = \Delta H_{Atom}^0 + \Delta H_{IE}^0 + \Delta H_D^0 + \Delta H_{EA}^0 + \Delta H_{Latt}^0$$

Therefore, if the value of ΔH_f^0 is known, the ΔH_{Latt}^0 can easily be computed using the following equation,

$$\Delta H_{Latt}^0 = \Delta H_{Atom}^0 + \Delta H_{IE}^0 + \Delta H_D^0 + \Delta H_{EA}^0 - \Delta H_f^0$$

Substituting for the respective values of the enthalpy, the lattice energy becomes,

$$\Delta H_{Latt}^0 = 107 + \frac{1}{2}(243) + 496 - 349 + 411 = 786.5 \; kJ/mol$$

Another method that can be used to calculate the lattice energy is the ionic model method. This method is based on the assumption that the crystal is formed from perfect spherical ions and that the only interaction is due to electrostatic force between the ions. For an ion pair, the energy needed to separate the ions depends on the sum of the ionic radii on the product of the ionic charges. Consequently, an increase in ionic charge will increase ionic attraction between them. In crystal, ions are surrounded by oppositely charge ions, hence the overall force of attraction between oppositely charged ion will overwhelm the force repulsion between ions with same charge. The ionic model for calculating lattice energy can be expressed as follows,

$$\Delta H_{Latt}^0 = \frac{K_{mn}}{(R_{M^{n+}} + R_{X^{n-}})}$$

where K_{mn} is a constant, which depends on the geometry of the lattice, $R_{M^{n+}}$ and $R_{X^{m-}}$ are ionic radius of the cation and anion respectively. In most cases, the ionic model has been found to yield theoretical values of lattice energy that are in good agreement with those calculated from Born-Haber cycle. Table 3 presents values of lattice energy calculated from Born-Haber cycle and ionic models for sodium and silver halides. The results generally shows that the lattice energy obtained from experiment (i.e Born-Haber cycle) are relatively higher than those calculated from ionic model. The difference can be attributed to polarization effect. For example, the small positively charged sodium ion can distort the electron cloud of the large and
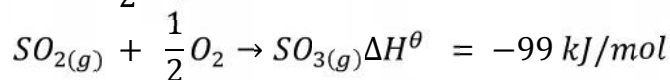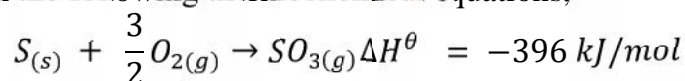
Table 3: Lattice energy for some sodium and silver halides calculated from Born-Haber cycle and ionic model methods

Compound	Born-Haber	Ionic model	% Difference
NaCl	790	769	2.7
NaBr	754	732	2.9
NaI	705	682	3.3
AgCl	918	864	5.9
AgBr	905	830	8.3
AgI	892	808	9.4

squashy iodide ion leading to the introduction of some covalent character in the compound. Since the ionic model does not take the effect of polarization into consideration, values of lattice energy obtained from this model is expected to be relatively lower than those obtained from Born-Haber cycle, which is an experimental method. The differences between the two set of results is seems to increase from Cl to I due to increasing strength of polarization. Generally, electronegativity of halides decreases from Cl to I which correspond to increase in covalent character, increase in ionic radii and expected increase in polarization.
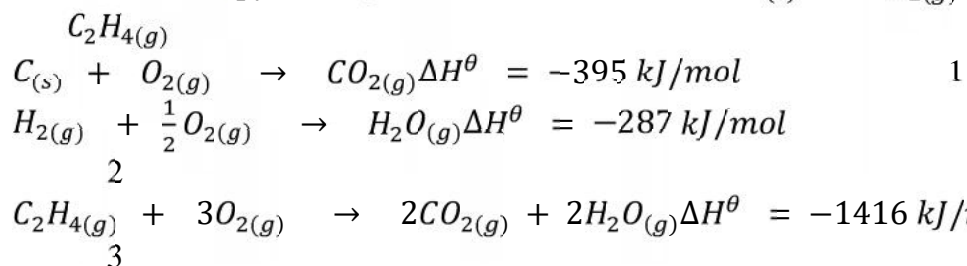
SELF ASSESSMENT EXERCISE

i.   Given the following thermochemical equations,

$$S_{(s)} + \frac{3}{2}O_{2(g)} \rightarrow SO_{3(g)} \Delta H^{\theta} = -396\ kJ/mol$$

$$SO_{2(g)} + \frac{1}{2}O_2 \rightarrow SO_{3(g)} \Delta H^{\theta} = -99\ kJ/mol$$

Calculate the standard enthalpy change for the reaction, $S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$

ii　　Given the under listed thermochemical equations, calculate the standard enthalpy change for the reaction, $2C_{(s)} + 2H_{2(g)} \rightarrow C_2H_{4(g)}$

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H^{\theta} = -395 \ kJ/mol \qquad\qquad 1$$

$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)} \quad \Delta H^{\theta} = -287 \ kJ/mol$$
$$2$$

$$C_2H_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(g)} \quad \Delta H^{\theta} = -1416 \ kJ/mol$$
$$3$$

iii　　Calculate the entropy change associated with the follow/ing reaction. Given that the entropy data for C_2H_4, H_2 and C_2H_6 are 219.56, 130.92 and 229.87 J/K/mol respectively. Based on the equation for the reaction, reconcile the expected direction of the entropy change with the calculated

$$C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}$$
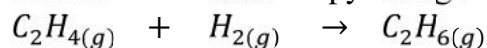
4.0　CONCLUSION

Ionic bonds are form between elements which readily lose electrons and others which readily gain electrons. Because the interaction between charges as given by Coulomb's law is the same in all directions, ionic compounds do not form molecules. Instead, they form periodic lattices with billions of ions, in which each ion is surrounded by many ions of opposite charge. Therefore, ionic compounds are almost always solids at room temperature. By careful consideration of the properties of each ion, it is possible to design ionic solids with certain well-defined and desirable properties, like superconductors.

5.0　SUMMARY

Oppositely charged ions have a strong mutual electrostatic attraction when brought together, but, if brought too close, the electron clouds repel each other. Thus, a pair of mutually attracted ions will maintain a certain distance from each other. This distance is called the bond length, and the electrostatic attraction of the ions constitutes an ionic (or electrovalent) bond. However, in situation where electron transfer and acceptance is not feasible, due to high ionization energy or low electron affinity, the prefer and feasible bond is covalent bond, which involves sharing of electrons. However, no bond is entirely ionic or covalent indicating that covalent character can be found in ionic compound and vice versa.
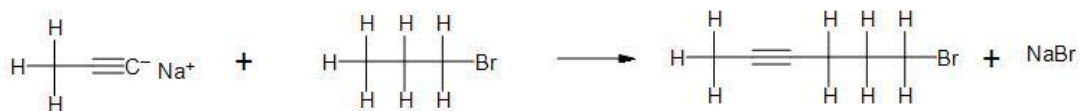
6.0   TUTOR MARK ASSIGNMENT
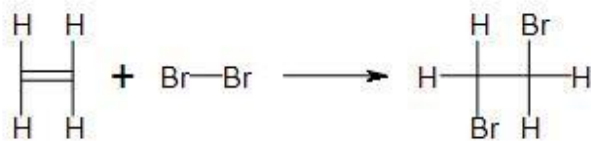
1. Are these compounds ionic or covalent?

CH_4 Fe_2O_3 KNO_3 I_2 C_4 H_2O $BeCl_2$
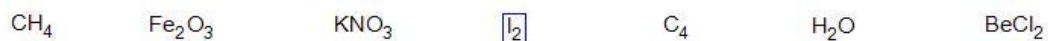
2. In the following reactions, indicate whether the reactants and products are ionic or covalently bonded.

$$Na_2CO_3 + CaCl_2 \longrightarrow CaCO_3 + 2\,NaCl$$

b) Clarification: What is the nature of the bond between sodium and amide? What kind of bond forms between the anion carbon chain and sodium?

c)

7.0   REFERENCES/FURTHER READINGS

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UNIT 2   THEORY OF BONDING

1.0   Introduction
2.0   Objective
3.0   Main content
      3.1   The valence bond theory
      3.2   Hybridization theory
          3.3.1 Types of hybridization
               3.3.1.1 Sp hybridization:
               3.3.1.2 SP^2 hybridization
               2.3.1.3 Sp^3 hybridization
      3.4   Theory of resonance
      3.5   Walsh's rule
      3.6   Molecular orbital theory (MOT)
          3.6.1   Linear combination of atomic orbital (LCAO)
      3.7   Bond order
          3.7.1   Bond order for heteronuclear diatomic molecule
4.2   Conclusion
5.0   Summary
6.0   Tutor Mark Assignments
7.0   References/Further Readings

1.0   INTRODUCTION

There are two major approaches that can be used to calculate molecular structure. These are the valence bond theory (VBT) and the molecular orbital theory (MOT). VBT assumes that all bonds are localized bonds formed between two atoms by the donation of an electron from each atom and that electrons occupy atomic orbitals of individual atoms within a molecule, and that the electrons of one atom are attracted to the nucleus of another atom. The basis of VB theory is the Lewis concept of the electron pair bond. On the other hand, the MOT relies on the combination of atomic orbitals to form bonding and antibonding molecular orbitals. The former stabilizes the molecule while the latter destabilizes the molecule. However, these theories lack the capacity to explain the nature of bonding in some molecules, hence where the VBT fails, hybridization theory explain bonding in terms of promotion of electrons, the formation of hybrid orbitals before overlapping. Beyond the VBT, the MOT and hybridization, is the quantum mechanics, which has the potential of explaining chemical bonding in most compounds by considering the behaviour of electrons during bonding. Combination of all these theories are discussed in this study section

2.0 OBJECTIVE

When you have studied this session, you should be able to:

- Understand the valence bond theory of bonding in molecules and the conditions for overlap
- How atomic orbitals are mixed through hybridization in order to form bonding
- Know different types of hybridization and provide examples for each
- Know why resonance hybrid is needed to describe the chemical structure of some compounds and how to calculate resonance energy
- Understand the theory and application of Walsh's rule
- Understand the molecular orbital theory and their applications in explaining bonding in some compounds
- Differentiate between bonding molecular orbital and antibonding molecular orbitals
- Understand how pi and sigma bonds are formed
- Use the molecular orbital theory to calculate bond order and interpret magnetic property, stability and other properties of some compounds using bond order
- Understand theories of bonding in hydrogen molecular ion, helium and hydrogen atoms
- Be able to solve mathematical problems associated with theories of bonding

3.0 Main Content

3.1 The Valence bond theory

The VBT considered that a bond is formed when an electron in an atomic orbital of one atom pairs its spin with that of an electron in atomic orbital of another atom. For example, in molecular hydrogen, the spatial wave functions for electron in each of the atom can be written as,

$$\psi = \psi_{(r_1)}\psi_{(r_2)} = \psi(A)(1)\psi(B)(2) \tag{1}$$

where A and B denotes the two atomic nuclei. In the case of hydrogen atom, the outcome of $\psi(A)(1)$ and $\psi(B)(2)$ are equally likely because the atoms are indistinguishable. The application of quantum mechanics requires that the total probability should be derived from superposition of the wave function for each. Hence the valence bond wave function for hydrogen molecule can be written as, $\psi = \psi(A)(1)\psi(B)(2) + \psi(B)(1)\psi(A)(2)$.

The linear combination given by equation 1will have an energy lower than that of any of the combining wave function because of constructive interference between $Œ(A)(1)Œ(B)(2)$ and $Œ(B)(1)Œ(A)(2)$. This implies that there will be an enhancement of the probability density of electron in the intermolecular region.

The valence bond theory relies on the overlap of orbitals of the combining atoms. Orbital overlap requires that the following conditions are met,
i.   Completely filled orbital cannot overlap. Consequently, only half
ii.   filled orbital from one atom can combine with half-filled orbital from the other atom to form a new orbital, having opposite spin of electron
iii.   The atoms with bonding orbitals should be closely and properly align with the axis of their orbital
The strength of bond formed depends on the magnitude of the overlap, the greater the overlap, the greater the bond strength. Overlap orbital has energy lower than that of the isolated atoms, hence overlapping stabilises the compound. The stabilization energy (or bond energy) is the amount of energy given off or released per mole at the time of overlapping of atomic orbitals to form a bond. Since overlapping stabilizes the b orbital, it implies that it is a function of the distance of separation between the combining atoms. There are three major types of interaction that can be encounter when atoms come close to each other. These include,
i.   Repulsion between nuclei
ii.   Repulsion between electrons
iii.   Attraction between electron and nuclei.
The strength of overlap increases as the atoms approaches each other more closely. However, there exist a distance of closest approach such that forces of repulsion and attraction are in equilibrium. This distance is called bond length. The closer the atoms are to each other, the greater the overlap and hence the better is the strength of the bond. Consequently, molecules with shorter bond length are stronger than those with longer bond length.
The formation of hydrogen molecule can be explained using the valence bond theory. In this case, electron from the 1s orbitals of the two hydrogen atoms overlap and form a relatively larger electron cloud called molecular orbital as shown below

s-Orbital   s-Orbital   s-s Overlap H_2 Molecule
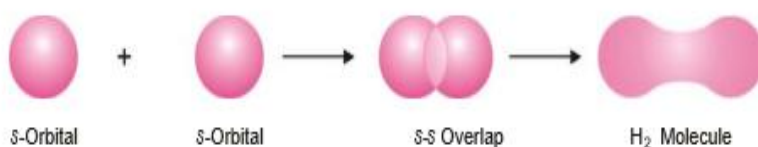
The newly form molecular orbital has energy lower than either of the two hydrogen atoms, it was formed from. Further explanation of the dependent

of the strength of covalent bond in hydrogen on distance of separation can be viewed in the potential energy surface shown in Fig. 1.
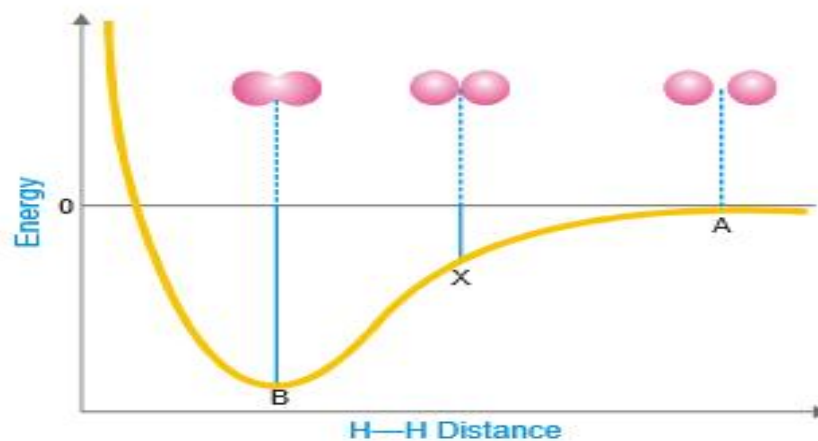

Fig. 1: Potential energy diagram of hydrogen molecule

In the diagram, at position A, the two hydrogen atoms are far from each other but as the atoms comes much closer, the energy drops until it gets to the minimum at B. After B, further decrease in distance destabilizes the molecule and leads to increase in repulsion (i.e. the energy increases). The minimum distance corresponds to the equilibrium bond length. It is at this point that maximum overlap occurs. The energy corresponding to the minimum of the curve is called dissociation energy. It is the maximum energy that stabilizes the molecule. Beyond the dissociation energy, the molecule will be destabilised.

Overlap in covalent bonded compounds can be due to sigma or pi bond depending on the molecular orbital and the orientation of the molecule before overlapping. Sigma bond can be from through one of the following overlaps

i.   s-s overlapping results from the combination of s orbital with one another. Example is the formation of hydrogen molecule

ii.   s-p overlapping occurs when an s-orbital from one atom overlap with a half-filled p-orbital from another atom. An example of molecule with s-p overlapping is in the formation of HCl and HF
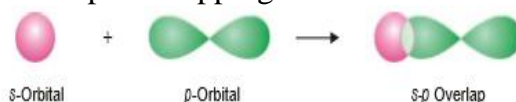

iii.   p-p overlapping can lead to sigma bond when one p-orbital from one atom overlaps with p-orbital from another orbital at the internuclear axis.
        Example is in the formation Cl_2, F_2, etc. (see diagram below)
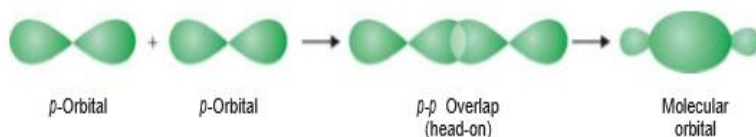
On the other hand, pi bond results from half-filled p-orbitals. The overlap occurs through lateral or sideward interaction (see diagram below). S orbital cannot form pi-bond no matter the manner they combine
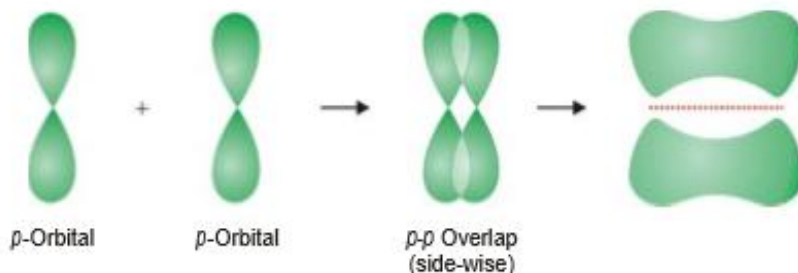
Generally, a sigma bond is stronger than a pi bond because the extent of overlap is greater during the formation of a sigma bond compared to the formation of a pi bond.

In-Text Question (ITQ)
(a)   Why is a sigma bond stronger than a pi bond?
(b)   State two conditions that are required before two orbitals can overlap
(c)   What is the different combination of orbitals that can lead to the formation of overlap in   sigma and pi bond. Give at least one example for each.

3.2   Hybridization theory

The valence bond theory (VBT) and the molecular orbital theory (MOT) cannot explain the formation of bonds in some atom or molecules such as carbon, helium etc. However, the concept of hybridization has been found to offer useful explanation for most cases that cannot be better explained by the VBT and MOT models. Hybridization combines atomic orbitals having comparable energies to form hybrid orbitals equal in number to the atomic orbitals from which they were formed. Some conditions required for hybridization to be feasible include the following,
i.   Only orbital of one single atom will undergoes hybridization.
ii.   The energy levels of the orbitals to be mixed must, be comparable
iii.   Number of hybrid orbitals generated is equal to the number of
             hybridizing orbitals.
iv.   The hybrid orbitals assume the direction of the dominating orbitals.

v.   For example, in sp hybridization, the s-orbital does not contribute towards the direction but it is the p orbitals   that determine the directional character of the hybrid orbitals.

vi.   Hybridization involves the orbitals and not the electrons.

vii.   The electron waves in hybrid orbitals repel each other and thus tend to be farthest apart.

3.2.1 Types of hybridization

3.2.3.1.1   Sp hybridization:

Sp hybridization involves the mixing of s and p orbitals to produce two hybrid orbitals in which the s-character and p-character are equal (i.e. 50 % each). This type of hybridization is sometimes called linear hybridization and the angle of separation is 180°. Diagrammatic representation of sp hybridization is shown below
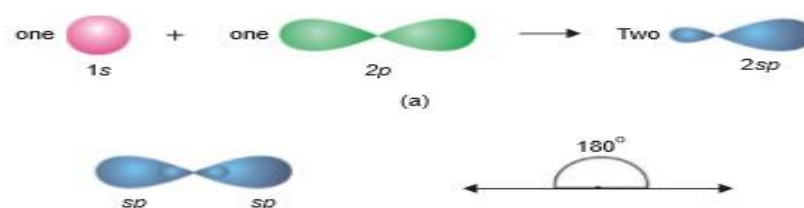
sp orbital has two lobes (a character of p orbital) one of which is farther than the corresponding s or p orbitals and also protrudes farther along the axis. It is this bigger lobe that involves itself in the process of an overlap with orbitals of other atoms to form bonds.

In-Text Question (ITQ)
Explain the theory of sp hybridization in BeF_2
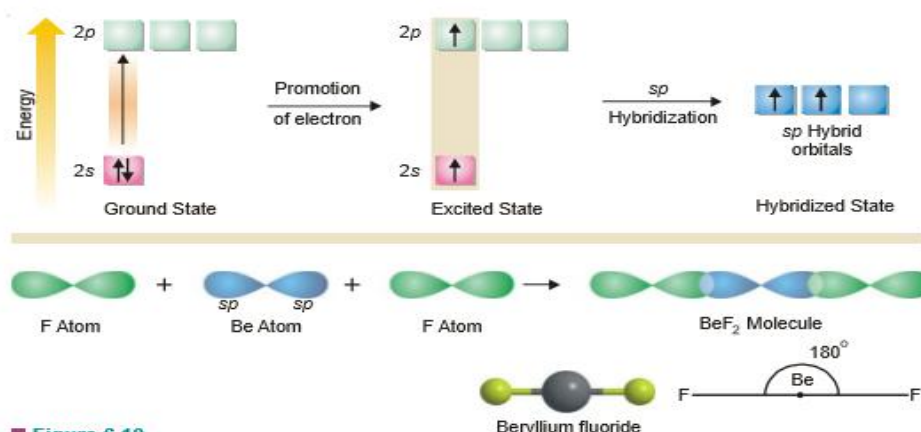

■ Figure 6.10

3.2.1.2   SP² hybridization

Sp^2 hybridization involves the mixing of one s-orbital with two p-orbitals resulting in the formation of three orbitals with 33 and 67 % s and p characters respectively. The hybrid orbitals lie on a plane father away from each other and at an angle of 120 ° as shown below. Example of compound formation that involves sp^3 hybridization is BeF$_3$. The ground state electronic configuration of Be is $1s^2 2s^2 2p_x^1 2p_y^0 2p_z^0$. From the electronic configuration, Be is expected to form only one bond since there is only one bonding electron but the existent of compound such as BF$_3$, BH$_3$, BCl$_3$ contradict this principle. However, the formation of such bond is achieved through hybridization.
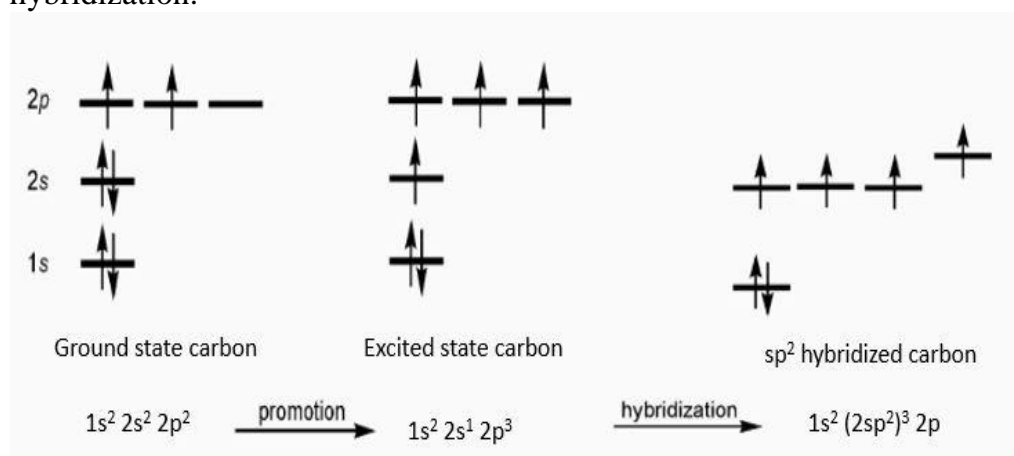
Scheme for sp² hybridization

When Be is excited, the one of the 2s electron is promoted to the 2P$_y$ level and the configuration becomes $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^0$. One s-orbital will then mix with 2p orbitals (P$_x$ and p$_y$) to form three hybrid orbitals by a process called sp^2 hybridization. The three sp^2 hybrid orbitals lies in one plane and subtends an angle of 120°. The three newly formed hybrid orbitals will overlap with three p-orbitals (each supply by one atom of fluorine) to form BeF$_3$. The shape of sp^2 molecules is trigonal explaining why sp^2 why sp^2 hybridization is sometime called trigonal hybridization.

Boron trifluoride
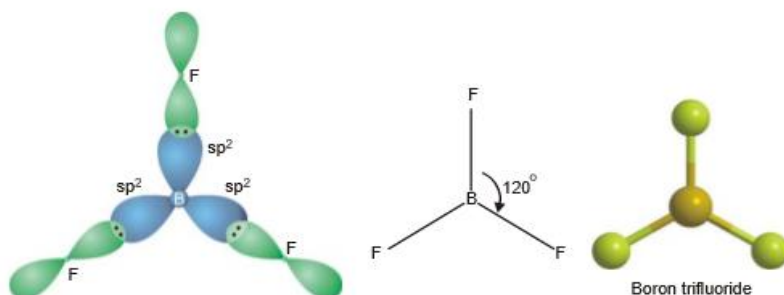
3.2.1.3   Sp³ hybridization

Sp³ hybridization has 25 % s0character and 75% p-character. It consists of four hybrid orbitals formed from one s and three p orbitals. The mixing of the four orbitals takes place in space, hence, the four hybrid orbitals would also lie in space. An arrangement in space that keeps them farthest apart is that of a tetrahedron. Consequently, each of the four hybrid orbitals are directed towards the four corners of a regular tetrahedron, sp³ hybridization is also called Tetrahedral hybridization. They are of the same shape as that of the previous two types but bigger in size. Example of molecule that can accommodate sp³ hybridization is methane (CH_4).

In-Text Question (ITQ)
Explain how carbon combine to form CH_4 in spite of the fact that its electronic configuration suggests that only two bonds can be formed.

In-Text Question (ITQ)
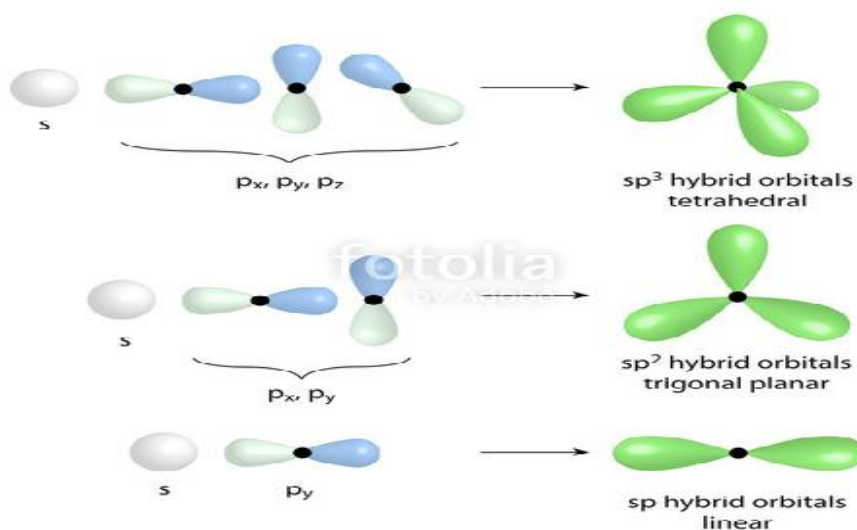What is the limitation of the valence bond theory?

Fig. 2: Summary of orbitals and orbital arrangement in the three basic types of hybridization

3.3   Molecular orbital theory (MOT)

The MOT was proposed by Hund and Mulliken in 1932 and explain the formation of molecular orbital through the combination of individual atomic orbitals with each other. The theory explains that the formation of molecule considers that the combining electrons in the atomic orbitals do not belong to a particular bond but spread throughout the entire molecule. According to

the MOT, a molecular orbital is a system constructed from linear combination of atomic orbitals. This combination give rise to two main types of orbitals (i.e. the bonding and anti-bonding molecular orbitals). The bonding molecular orbital arises from the constructive overlaps of neighbouring atomic orbitals while anti bonding molecular orbital arises from the destructive overlap of neighbouring atomic orbitals.

3.3.1 Linear combination of atomic orbital (LCAO)

Linear combination of atomic orbital provides a theoretical approach of using the wave function to represent the formation of molecular orbital through appropriate atomic orbitals. If a wave function for a 1S electron belonging to an atom, A is $\psi_{(1S)}(A)$ and $\psi_{(1S)}(B)$ describes the wave function for a 1s electron found in atom B. The overall wave function for the system must be written as a superposition of the two atomic orbitals (equation 2),

$$\psi = N[\psi_{(1S)}(A) + \psi_{(1S)}(B)] \qquad\qquad 2$$

where N is the normalization factor. The wave function resulting from superposition of different atomic wave function (as expressed in equation 2.1) is called linear combination of atomic orbital (LCAO). An approximate molecular orbital formed from a LCAO is called linear combination of atomic orbital-molecular orbital (LCAO-MO). According to the Schrodinger model, the square if the wave function (i.e., $|\psi|^2$) represents the probability density. Therefore, the probability density of the LCAO-MO of a 1s σ-orbital can be written as,

$$|\psi|^2 = N^2 \left[\psi_{(1S)}(A) + \psi_{(1S)}(B) \right]^2 \qquad\qquad 3$$

$$= N^2 \left[\psi_{(1S)}(A)^2 + \psi_{(1S)}(B)^2 + 2\psi_{(1S)}(A)\psi_{(1S)}(B) \right]$$

$$4$$

Equation 2.10 has three components which can be explained as follows.
i. $\psi_{(1S)}(A)^2$, which represent the probability density of electron confined to the orbital, A.
ii. $\psi_{(1S)}(B)^2$, which represents the probability density of electron confined to the orbital, B.
iii. $2\psi_{(1S)}(A)\psi_{(1S)}(B)$, which is the extra contribution to the density of electron and is called overlap density.

The overlap density also represents an enhancement of the probability of finding electrons in the internuclear region above what it would be if they were confined to one of the two atoms. This enhancement is also called constructive interference of the two atomic orbitals. Similar analogy can be extended to antibonding molecular orbital. The expression representing the

formation of antibonding molecular orbital arising from combination of atomic orbitals of atoms A and B can be written as,

$$\psi' = N[\psi_{(1S)}(A) - \psi_{(1S)}(B)] \qquad 2.4$$

LCAO-MO for the above wave function correspond to a molecular orbital having energy higher than any of the contributing orbitals. Therefore, antibonding molecular orbital increases the energy of a system Whereas bonding molecular orbital is associated with constructive interferences, antibonding molecular orbital is associated with destructive interference. The probability function of antibonding molecular orbital can also be derived as it was done for bonding molecular orbital, hence we have

$$|\psi'|^2 = N^2 \left[\psi_{(1S)}(A) - \psi_{(1S)}(B) \right]^2 \qquad 2.5$$
$$= N^2 \left[\psi_{(1S)}(A)^2 + \psi_{(1S)}(B)^2 - 2\psi_{(1S)}(A)\psi_{(1S)}(B) \right]$$
$$2.6$$

It can be seen that the first two terms in equation 2.6 are the same as in those obtained for bonding molecular orbital and their significant is the same. However, the difference is in the sign of the third term, which is positive for bonding molecular orbital and negative for antibonding molecular orbital. The negative value (i.e. $[-2\psi_{(1S)}(A)\psi_{(1S)}(B)]$ clearly signify the factor that contribute to reduce the probability of finding electron between the nuclei. Antibonding orbital raises the energy of the molecule relative to the separated atom and destabilizes the molecule relative to the separated atoms whereas bonding electron stabilizes the molecule.

A combination of N number of atomic orbitals will yield N number of molecular orbitals. There are two types of molecular orbitals, including binding and antibonding molecular orbitals. Several combinations of s or p electron can form bonding or antibonding molecular orbital. The formation of these molecular orbitals involves combination of valence electrons in the respective atomic orbitals. For example, combination of two hydrogen atoms to form hydrogen molecules involves two 1s-electrons combining with each other as shown below.
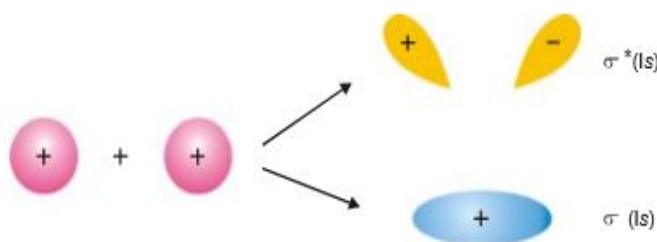
The wave functions either have (+) or (–) sign. The positive sign shown on 1s orbitals of hydrogen atoms reveals that these orbitals are spherically symmetrical and their wave functions are associated with +ve sign in all directions. In case of p-orbitals one lobe has +ve sign while other has –ve sign. The overlapping of atomic orbitals takes place if they have similar signs on their lobes

The combination generates two set of molecular orbitals. The first is called sigma bonding molecular orbital i.e. $\sigma(1s)$ and sigma antibonding molecular orbital, $\sigma^*(1s)$. As can be seen in the above diagram, $\sigma^*(1s)$ molecular orbital is positioned at a higher energy level than the $\sigma(1s)$ molecular orbital. This confirms that the bonding molecular orbital contributes to the lowering of the energy of a molecule and hence stabilizes the system while the antibonding molecular orbital increases the energy of the system and thus tend to destabilize the system. A sigma (σ) electron is an electron that occupies a sigma orbital. Sigma orbitals can also be formed from combination of p_z orbitals (z is assumed to be the internuclear axis) as shown in the diagram below,
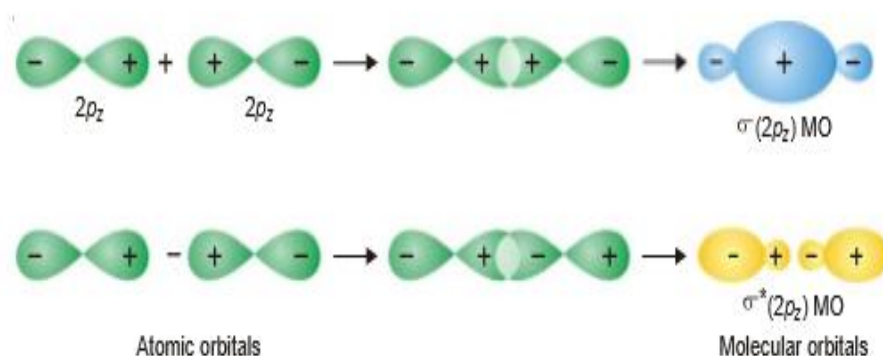

Apart from sigma orbitals, P_Y and P_X orbitals can combine to give pi-bonding and pi antibonding molecular orbitals as shown below,

2py   2py   Atomic orbitals   π(2py) Molecular orbital

2py   2py   Atomic orbitals   π*(2py) Molecular orbital
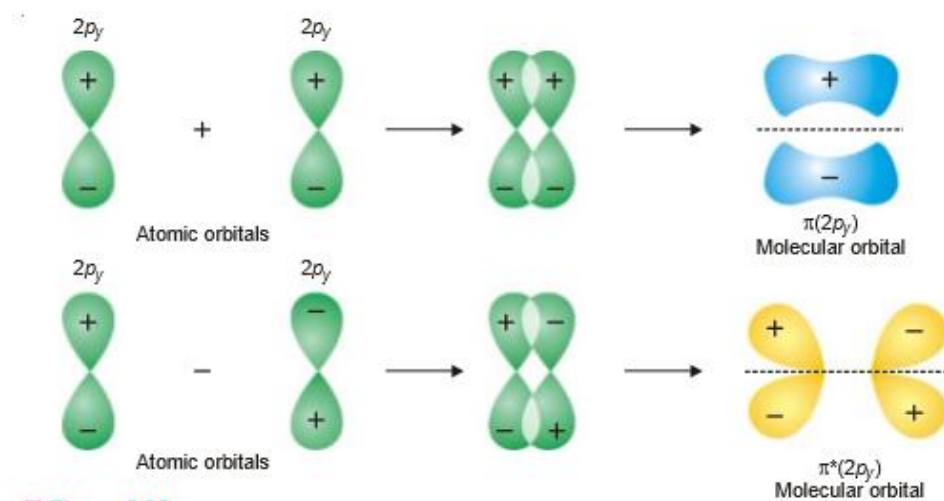
From the above, (2p$_y$) is pi bonding molecular orbital and is formed when similar charges on the 2p$_y$ orbitals meet side by side while *(2p$_y$) (that is the pi anti bonding molecular orbital) is formed when the adjacent charges are not similar. Since P$_x$ and P$_y$ sub orbitals are degenerate orbitals because they have similar energy, bot bonding or antibonding molecular orbitals arising from them will also be degenerate. The (2p$_y$) and (2p$_x$) bonding molecular orbitals have zero electron density on the plane that contain the nuclear axis but the electron density is concentrated above and below the nodal region. The * (2P$_y$) and * (2P$_x$) antibonding molecular orbitals have higher energy than their corresponding molecular and atomic orbitals.

It can be stated that different molecular orbitals have different energy level. For example, the energy of bonding molecular orbital varies in the following order, σ(1s) σ(2s) σ(2p$_Z$) (P$_y$) (P$_x$) while the order for the antibonding molecular orbital is σ*(1s)σ*(2s) σ*(2p$_Z$) (*P$_y$) *(P$_x$). However, (*P$_y$) and *(P$_x$) are degenerate orbitals just like (P$_y$) and (P$_x$) orbitals. The diagram below presents a pictorial trend for the variation of energy of the bonding and nonbonding molecular orbitals.
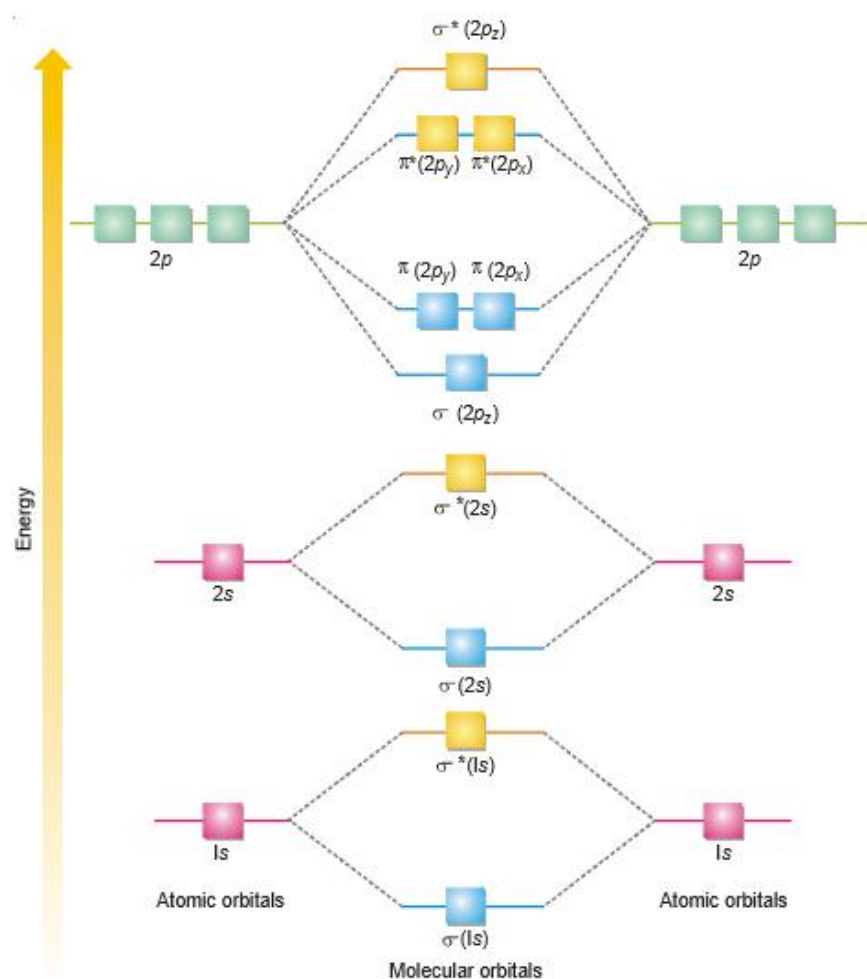
s and P_Z orbital can combine end to end to form sigma bonding and sigma antibonding molecular orbitals as shown below
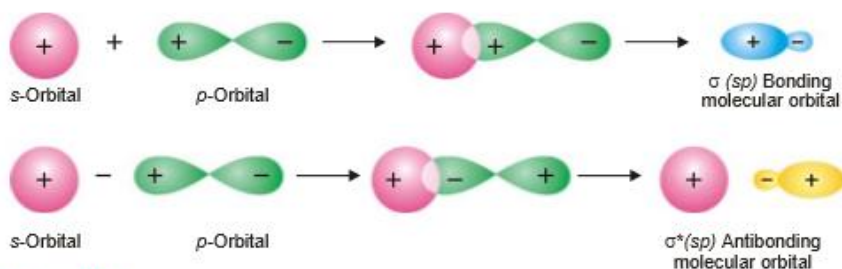
However, s-orbital cannot form a sigma molecular orbital with P_y or P_x because they do not have the same symmetry about the internuclear axis. Generally, the following conditions must be fulfilled before molecular orbitals can be formed,

(i)   The energies of the combining atomic orbitals should be comparable. For homonuclear diatomic molecules similar atomic orbitals combine

to form molecular orbitals. For example, 1s from one atom can combine with 1s atomic orbital from another atom to form molecular orbital. However, Is cannot combine with 2s because the energy is not comparable

(ii)   Overlap between atomic orbitals should be considerable significant. The greater the overlap between the atomic orbitals, greater is charge density between the nuclei.

(iii)   The symmetry of the combining atomic orbitals should be the same. The atomic orbitals should have the same symmetry about the internuclear axis. For example, 2s orbital of one atom can combine with 2s or $2P_z$ orbital of another atom but not with the $2P_y$ or $2P_x$ orbital. Molecular orbitals that can be formed from combination of possible atomic orbitals are presented in the Table 2.1 below,

Table 1: Combination of atomic orbitals and their corresponding molecular orbitals

Atomic orbital 1	Atomic orbital 2	Molecular orbital
s-orbital	s-orbital	σ (sigma) orbital
s-orbital	P_Z orbital	σ (sigma) orbital
P_Z orbital	P_Z orbital	σ (sigma) orbital
P_x orbital	P_x orbital	(pi) orbital
P_y orbital	P_y orbital	(pi) orbital

Bonding molecular orbital	Antibonding molecular orbital
The wave function $\psi = N[\psi_{(1S)}(_A) - \psi_{(1S)}(_B)]$	The wave function $\psi = N[\psi_{(1S)}(_A) - \psi_{(1S)}(_B)]$
Form from constructive (or addition) overlap of atomic orbitals	Formed from destructive(subtraction) overlap of atomic orbitals
Formed when the lobes of atomic orbitals have same signs	Formed when the lobes of atomic orbitals have different signs
Energy is lower than that of the combining atomic orbitals	Energy is higher than that of the combining atomic orbitals
The electron density is high in the region between the nuclei of bonded atoms	Electron density is low in the region between the nuclei and bonded atoms
Every electron in bonding MO contributes towards the attractive force	Electrons in antibonding molecular orbital contributes to repulsive force
Stabilizes the molecule	Destabilizes the molecule

In-Text Question (ITQ)

In a Tabular form, state five differences between bonding and antibonding molecular orbitals

SELF ASSESSMENT EXERCISE

Apply the molecular orbital theory to explain bonding in the following molecules
(i)   Hydrogen molecule
(ii)   Helium molecule
(iii)   Oxygen molecule

Solution
In each case, calculate the bond order and comment on the result obtained from the calculation

i.   Hydrogen molecule
Hydrogen molecule has two electrons, each contributed by 1s orbital. According to the Aufbau principle, the lowest level must first be filled before the higher level. The molecular orbitals formed between the two hydrogen atomic orbitals are sigma bonding and sigma antibonding molecular orbitals,

$$H(1s^1) + H(1s^1) \rightarrow H_2\sigma(1s^2), \sigma^*(1s^0)$$
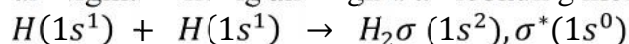
Consequently, the number of electrons in bonding molecular orbital is two while the number in antibonding molecular orbital is zero. Therefore, the bond order of hydrogen molecule is

$$b(H) = \frac{n - n^*}{2} = \frac{2 - 0}{2} = 1$$

The calculated bond order indicate that two hydrogen atoms are bonded together by only one bond to form hydrogen molecule. The formation process can be represented as shown in the diagram below,
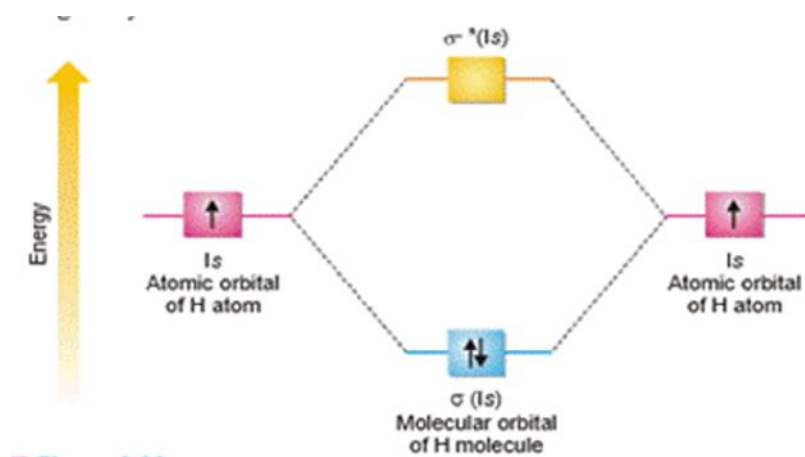
ii.   Helium

Helium has atomic number of two, hence two electrons. When two helium atoms combine, four electrons will be formed. The molecular orbital formed is developed from combination of two 1s atomic orbitals. That is a total of two molecular orbitals would be formed Thus

$$He\,(1s^2) \; + \; He\,(1s^2) \; \rightarrow \; He_2\sigma\,(1s^2), \sigma^*(1s^2)$$
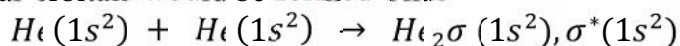
Therefore, the bond order for helium is

$$b\,(He) = \frac{n - n^*}{2} = \frac{2 - 2}{2} = 0$$

Calculated bond order of zero indicate that the molecule cannot exist.

ii.

(a)   In a Tabular form, state four differences between sigma and Pi molecular orbitals

(b)   What is common between pi and sigma molecular orbitals

Solution

(a)

| Sigma molecular orbital	Pi molecular orbital
Formed by head to head overlapping of atomic orbitals.	Formed by sideward overlapping of P_x or P_y atomic orbitals
The overlap is along internuclear axis.	Overlap is perpendicular to internuclear axis
This orbital is symmetrical to rotation about the line joining the two nuclei.	Orbital is not symmetrical to rotation about the line joining the two nuclei.
The region of overlap is greater leading to the formation of strong bond	Region of overlap is less resulting in the formation of weak bond.

(b)   The common feature is that they are both formed from proper combination of atomic orbitals, leading to the formation of overlap.
iii.

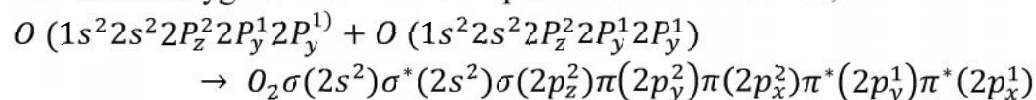What is bond order? Use oxygen atom to explain the concept
Solution
The term bond order (b) is often use to predict the stability of a molecule. Bond order, b is defined as half the difference between the number of electrons in the bonding molecular orbital (n) and the electrons in the antibonding molecular orbital (n*). That is b = ½ (n = n*). The greater the bond order, the more stable is the compound. Generally, bond order greater than unity points toward stability whereas bond order less than unity points toward instability. Let us calculate bond order of some molecules as shown below,
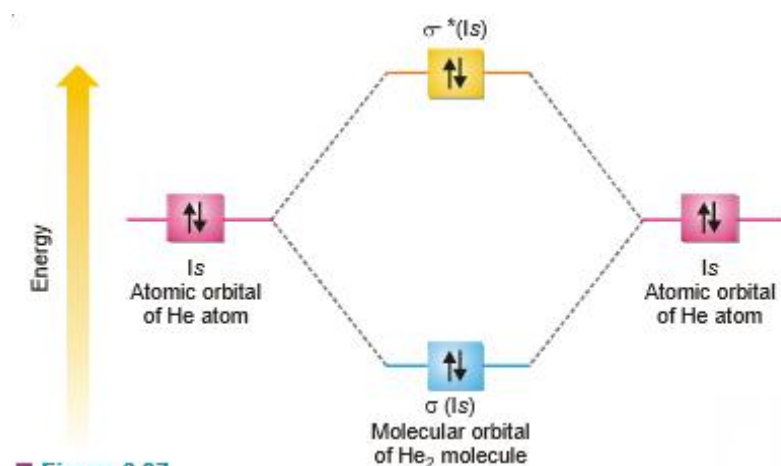
iv   Oxygen molecule
The electronic configuration of oxygen is $1s^2 2s^2 2P_z^1 2P_y^1 2P_y^1$. In this case, only the 2s and 2p orbitals would be involved in bonding (i.e. valence shell) giving a total of five electrons for each contributing oxygen atom and 6(2) =12 for the oxygen molecule. The equation can be written as,

$O\ (1s^2 2s^2 2P_z^2 2P_y^1 2P_y^{1)} + O\ (1s^2 2s^2 2P_z^2 2P_y^1 2P_y^1)$

$\rightarrow O_2\sigma(2s^2)\sigma^*(2s^2)\sigma(2p_z^2)\pi(2p_y^2)\pi(2p_x^2)\pi^*(2p_y^1)\pi^*(2p_x^1)$

From   the   molecular   orbital   configuration   is $\sigma(2s^2)\sigma^*(2s^2)\sigma(2p_z^2)\pi(2p_y^2)\pi(2p_x^2)\pi^*(2p_y^1)\pi^*(2p_x^1)$ indicating that the number of bonding electron is 8 while the number of antibonding electron is 4 (see diagram below). Therefore, the bond order is

$$b\ (O) = \frac{n - n^*}{2} = \frac{8 - 4}{2} = 0$$

The calculated bond order of 2 indicate that oxygen molecule is stable (n>n*) and from the above diagram, there are unpaired electrons hence it is paramagnetic.

4.0   CONCLUSION

Lewis structures are useful in handling valence bond theory while molecular orbital are functional parameters for molecular orbital theory. Mixing of atomic orbitals is called hybridization. The geometry of an organic molecule can be linked to the type of hybridization associated with its formation. Commonest types of hybridization are sp^3, sp^2 and sp hybridization and they give rise to different geometrics

5.0   SUMMARY

There are two major approaches that can be used to calculate molecular structure. These are the valence bond theory (VBT) and the molecular orbital theory (MOT). VBT assumes that all bonds are localized bonds formed between two atoms by the donation of an electron from each atom and that electrons occupy atomic orbitals of individual atoms within a molecule, and that the electrons of one atom are attracted to the nucleus of another atom. The basis of VB theory is the Lewis concept of the electron pair bond. On the other hand, the MOT relies on the combination of atomic orbitals to form bonding and antibonding molecular orbitals.

6.0   TUTOR MARK ASSIGNMENT

1.   Differentiate between valence bond theory and molecular orbital theory
2.   What are the short coming of the valence bond theory?
3.   Differentiate between bonding molecular and antibonding molecular orbital
4.   Calculate the bond order for neon

7.0   REFERENCES/FURTHER READINGS

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MODULE 2

Unit 1   Valence shell electron paired repulsion
Unit 2   Quantum Mechanics

UNIT 1   VALENCE   SHELL   ELECTRON   PAIR
                      REPULSION (VSEPR)

CONTENTS

1.0   Introduction
2.0   Objectives
3.0   Main Content
    3.1   VSEPR theory
    3.2   Electronic and molecular geometries
4.0   Conclusion
5.0   Summary
6.0   Tutor Mark assignments
7.0   References/Further Readings

1.0   INTRODUCTION

Lewis structure is used to represent the electrons in the valence shell of a molecule by using the concept of electron dot diagram through the addition of lines between valence electron in atoms to denote shared pairs in a chemical bond and also to represent nonbonding electrons with the dot
Lewis structure is a simplified model that accounts for the satisfaction of the octet requirement for the valence shell. It provides information in how electrons are arranged around individual atoms in a molecule. Electrons are shown as "dots" or for bonding electrons as a line between the two atoms. Addition of formal charges are also required in the Lewis structure representation of a molecule.

However, Lewis structure cannot help in presenting the picture of a geometry of a molecule neither can it give information on how bonds are formed and how electrons are shared between the combining atoms.
The limitation of the Lewis concept in predicting the geometry of a molecule is overcome through the valence shell electron repulsion (VSER) theory. VSER can predict the structure of most molecules and polyatomic ions when

the central atom is a nonmetal and for some cases where the central ion is a metal

VSEPR s developed from the Lewis electron dot structures. Lewis structures alone can only predict the connectivity of electrons (to form chemical bonds between atoms). However, combination of the Lewis structure and the VSEPR is informative on predicting the geometry of each atom in a molecule.

2.0   OBJECTIVES

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

- Know how to draw the Lewis structure of a molecule
- Know the assumptions of valence shell electron pair repulsion (VSEPR)
- Apply the VSEPR theory to predict the geometric of a molecule
- Understand what is steric number/factor and how to calculate the factor for a given molecule
- Know the influence of the number of bonding and non bonding electrons on the shape of molecule
- Differentiate between electronic and molecular geometrics

3.0   Main Content

3.1   VSEPR theory

According to the Lewis theory of bonding. The two types of electrons in a molecule are bonding electrons (which are electron involves in bonding) and non bonding electrons (which are electrons that are not involve in bonding and are also called lone pair electron). The VSEPR theory considers a pairs of bonding electrons and lone pair electrons having the tendency to repel each other (note, like charges repel while unlike charges attract). These pair of electrons are called groups. Due to electrostatic repulsion between electron pairs, the most stable arrangement of electron groups is the one with the lowest energy and this will correspond to the one that minimize repulsion (Since repulsion leads to increase in energy). Consequently, achievement of a stable structure is achieved by orientation that position the groups around the central atom in a way that produces the molecular structure with the lowest energy. This implies that the favourable geometry would be the one in which the groups are as far apart from each other as possible.

The VSER can be summarized as follows, Atoms are bonded together by electron pairs in valence orbitals. Electrons are all negatively charged and tend to repel other electrons. Bonding pairs of shared electrons tend to repel other bonding pairs of electrons in the valence orbital. The best spatial arrangement of the bonding pairs of electrons in the valence orbitals is one in which the repulsions are minimized. Let us consider some simple compound

(i)   The Lewis structure of ammonia can be written as follows,

$$H-\overset{\displaystyle \cdot\cdot}{N}-H$$
$$|$$
$$H$$
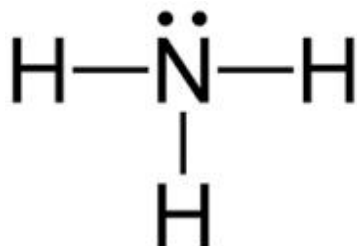
It can be seen that there are four electrons pairs in ammonia. This consist of three bonding pair of electrons and one lone pair. Each of this pair will repel each other, Consequently, the electron shell repulsion between these four electron pairs is minimized in a tetrahedral arrangement (i.e. the electron pair geometry is tetrahedral for ammonia molecule) as shown below

The molecular geometry is the location of the atoms of a compound in space. We can predict the molecular geometry from the electron pair geometry. In the above example (ammonia), it is predicted that the three hydrogens would form the vertices of a tetrahedron, and the nonbonding electron pair the fourth. Thus, ammonia would have a trigonal pyramid arrangement of its H atoms Steps involved in determining the VSEPR model are

(i)   Drawing of the Lewis structure
(ii)   Determination of the total number of electron pairs around the central atom.
(iii)   Arrangement of the atoms to minimize the electron shell repulsion
(iv)   Description of the molecular geometry in terms of the angular arrangement of the bonding pairs

Generally, the following rules may apply for geometry arrangement based on the number of electron pair:

(i)   Two electron pairs in the valence orbital are arranged linearly
(ii)   Three electron pairs are organized in a trigonal planar arrangement
(iii)   Four electron pairs are organized in a tetrahedral arrangement
(iv)   Five electron pairs are arranged in a trigonal bipyramid
(v)   Six electron pairs are organized in an octahedral arrangement

In-Text Question (ITQ)
Predict (with example) the geometry of molecules that have two and three electrons pairs respectively
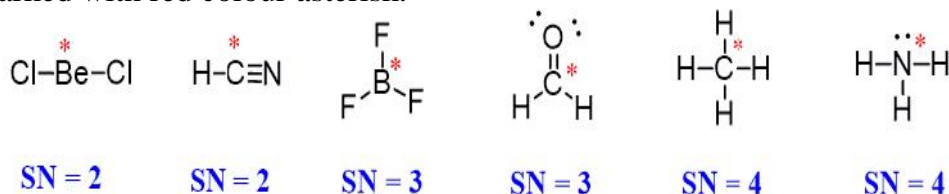
3.2.1 Steric number

Consideration of the Lewis structure of water indicates that it has bonding pairs and two lone pairs of electrons as shown below
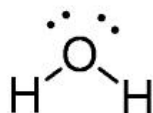
Therefore, there are four units around the central atom (i.e oxygen) including two hydrogen atom and two lone pairs as shown below
Steric number is the sum of the number of atom and the lone pairs deduced from the Lewis structure of the molecule. Therefore, the steric number of water molecule is 2(two hydrogen atoms) +2 (two lone pairs) =4.
Further demonstration can be ascertained by calculating the steric number of the following compounds). In the underlisted examples, the central atom is marked with red colour asterisk.

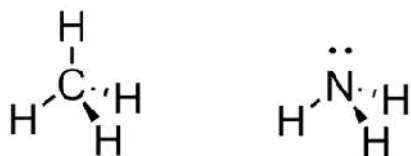

3.2   Electronic and molecular geometries

The steric numbers of water and methane are equal. Methane has no lone pair of electron (unlike water). The observed similarity and expected geometries for the two molecules can be explained in of electronic and molecular geometries. terms Some molecules may have similar electronic and molecular geometries

For the Electron Geometry, we treat the atoms and electrons equally for example, CH_4 and NH_3 are both tetrahedral.

SN (C) = 4 atoms + 0 lone pairs = 4

SN (N) = 3 atoms + 1 lone pair = 4

This corresponds to a tetrahedral electron geometry:

Tetrahedral electron geometry

However, their molecular geometries are different. For **methane** (CH_4), it is **tetrahedral** and for **ammonia** (NH_3), it is **trigonal pyramidal**. The lone pair on the ammonia nitrogen is significant and if it wasn't there, we would have a hypothetic molecule with a flat/planar geometry:
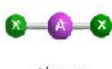

Lone pair pushes the H's down
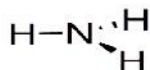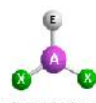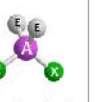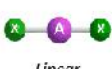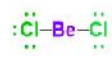
Without the lone pair

In-Text Question (ITQ)

Why do we ignore the lone pair for naming the molecular geometry?

The Figure below provide a guide in classification of molecules and their expected geometry based on the number of atom and lone pair electrons

A summary of Electron and Molecular Geometries

Steric Number	2	3		4		
Type	AX_2	AX_3	AX_2E	AX_4	AX_3E	AX_2E_2
Electron Geometry	Linear	Trigonal planar	Trigonal planar	Tetrahedral	Tetrahedral	Tetrahedral
Molecular Geometry	Linear	Trigonal planar	Bent	Tetrahedral	Trigonal pyramidal	Bent
Bond Angle	180°	120°		109.5°		
Example	$:Cl—Be—Cl:$	$H-B(H)-H$	$H_2C=N-H$	$H-C(H)(H)-H$	$H-N(H)-H$	$H-O-H$

A = central atom, *X* = an atom or a group, *E* = a lone pair of electrons   ChemistrySteps.com

Lewis structure, steric number and classes of more molecules are presented below

(i) $BeCl_2$

The Lewis structure is

$$:\overset{..}{C}l—Be—\overset{..}{C}l:$$
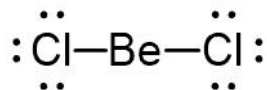
The steric number with respect to the central atom(Be) = **2 atoms + 0 lone pairs = 2**. Therefore, $BeCl_2$ is a AX_2 type. The angle of separation is 180° as shown below

$$:\overset{..}{C}l—Be—\overset{..}{C}l:$$
180°
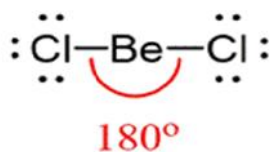
Therefore, the compound is linear for both electron and molecular geometry since it does not have a lone pair

(ii) BH_3

The Lewis structure is

$$H-B(-H)-H$$
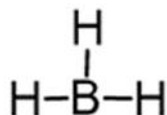
The steric number of boron is **S.N. (B) = 3 atoms + 0 lone pairs = 3**. Therefore, BH_3 is a AX_3 type and the boron must be at 120° to minimize the

repulsion giving rise to trigonal planar geometry with all the atoms in the same plane
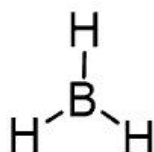
(iii) CH$_2$NH has the following Lewis structure
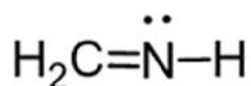
S.N (N) = 2 atoms + 1 lone pair = 3 giving rise to AX$_2$E type. The atoms and electrons around the nitrogen are at about 120°
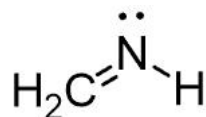
The geometry is said to be **bent geometry** since the molecule looks bent if we ignore the lone pairs. The lone pairs in NHCH$_2$ have stronger repulsion than atoms. Therefore, the expected angles are not always 100% in agreement with what they actually are:
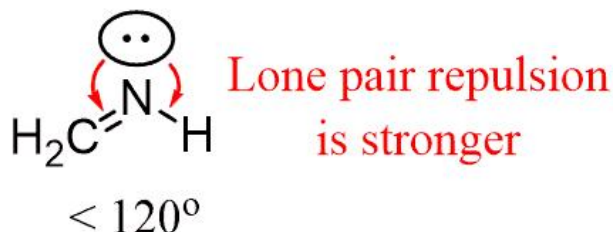
(iv) CH$_4$ has the following Lewis structure,
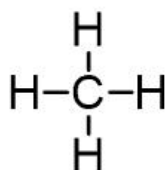
S.N. (C) = 4 atoms + 0 lone pairs = 4. This is an AX$_4$ type. The atoms are at 109.5° and molecular is **tetrahedral** for electron and molecular geometry
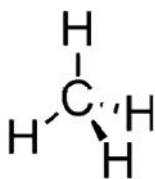
(vi)   NH₃ has the following Lewis structure
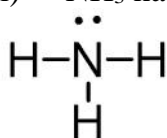
The **S.N. (N) = 3 atoms + 1 lone pair = 4** and it is an AX₃E type molecule. The atoms at the lone pair are expected to be at 109.5°, however, because the revulsion from the lone pair is stronger, the angle between the hydrogens is about 107° and the geometry is called a **trigonal pyramidal** geometry.

107°
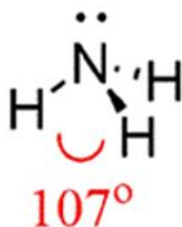
(vi)   H₂O
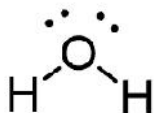
The **S.N. (O) = 2 atoms + 2 lone pairs = 4**. This is under the AX₂E₂ type molecule. The atoms at the lone pair are expected to be at 109.5°, however, because the revulsion from the lone pair is stronger, the angle between the hydrogens is about 104.5°:

104.5°
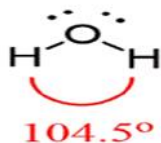
This resulting geometry is called a **bent geometry**. It can be observed that the angles in water and molecule C (CH₂NH) are different even if they are both bent. This is because the angle is defined based on the electron geometry.

SELF ASSESSMENT EXERCISE

i.   Justify the reasons for the steric numbers of methane, water, ammonia, ethylene, acetylene and carbon dioxide

Solution

Methane (CH₄) – Methane consists of carbon bonded to 4 hydrogen atoms and 0 lone pairs. SN is 4.

Water (H₂O) – Water has two hydrogen atoms bonded to oxygen and also 2 lone pairs, so its SN is 4.

Ammonia (NH₃) – Ammonia also has a steric number of 4 because it has 3 hydrogen atoms bonded to nitrogen and 1 lone electron pair.

Ethylene (C₂H₄) – Ethylene has 3 bonded atoms and no lone pairs. Note the carbon double bond. SN = 3.

Acetylene (C₂H₂) – The carbons are bonded by a triple bond. There are 2 bonded atoms and no lone pairs. SN = 2.

Carbon Dioxide (CO₂) – Carbon dioxide is an example of a compound that contains 2 sets of double bonds. There are 2 oxygen atoms bonded to carbon, with no lone pairs, so the SN is 2.

ii   Use the VSEPR to explain bonding, lone pair and expected geometry of formaldehyde. Based on this model, how will you classify this molecule?

Solution
The VSEPR model predicts that CH_2O is trigonal planar with bond angles of about 120 °.The Lewis structure of formaldehyde (CH_2O) is
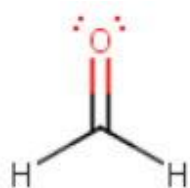
There are three electron regions around the central carbon atom. The VSEPR model states that the electron regions around an atom spread out to make each one as far from the others as possible.

In formaldehyde, the central atom has three electron clouds emanating from it. The carbon atom has two single bonds to hydrogen and a double bond to oxygen. For these clouds to be as far as possible from one another, they will form a plane containing the central atom. The bonds will emanate from the central atom at angles of about 120° to each other. The structure will be trigonal planar.

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The central atom is in the centre of the triangle, with the ends of the electron clouds at the corners of the triangle. Therefore CH_2O is classified as an AX_3 molecule

4.0   CONCLUSION

VESPR stands for valence shell electron pair repulsion. This theory basically says that bonding and non-bonding electron pairs of the central atom in a molecule will repel (push away from) each other in three dimensional space and this gives the molecules their shape.

We can use the following notations when examining a Lewis structure of a molecule.

A = central atom
X = peripheral atoms
E = non-bonding electron pairs of the central atom
AX2 = linear molecule (example CO2)
AX3 = trigonal planar (example, AlH3)
AX3E = trigonal pyrimidal (example, NH3)
AX2E2 = bent (example. H2O)
AX4 = tetrahedral molecule (example, CH4)

5.0   SUMMARY

VSEPR is a strong model in structure and bonding because it can be used to predict the geometry of a molecule based on number of bonding and nonbonding electrons. The model has been successfully used to successfully analyse geometrics of several compounds with central atoms.

6.0   TUTOR MARK ASSIGNMENTS

(1)   Complete the following Table

No of attach atom	Molecular Geometry	Examples of compounds
1		
2		
3		
4		

(2)   Determine the molecular geometry of XeF_2

(3)   What is the relationship between Lewis structure and VSEPR?
(4)   State the principles of VSEPR, advantage and disadvantages

7.0   REFERENCES/FURTHER READINGS

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UNIT 2   QUANTUM THEORY OF BONDING

1.0   INTRODUCTION

Quantum chemistry applies the principles of quantum mechanics to solved problems in chemistry. Quantum chemistry is widely applied in several branches of chemistry including the following,

i.   Physical chemists apply quantum mechanics (together with statistical mechanics) to calculate thermodynamic properties of a system, interpret molecular spectra (refer to the chapter on molecular spectroscopy), calculation of molecular properties (such as bond length, bond angle, dipole moment), calculations of transition state, rate constant, intermolecular forces, etc.

ii.   In organic chemistry, quantum mechanics can be used to predict the relative stability and reactivity of a compound, investigation of mechanism of a compound, interpretation of spectra and to calculate electronic and molecular properties of molecules such as the frontier molecular orbital energies (the energy of the highest occupied molecular orbital, the energy of the lowest occupied molecular orbital, the energy gap), polizability, Hemet constant, etc.

iii.   In Analytical chemistry, the major application of quantum mechanics is in the interpretation of frequencies and intensities of spectra lines.

iv.   In inorganic chemistry, quantum mechanics is used in ligand field theory, which is an approximate quantum approach in predicting and explaining the properties of transition metal complex.

v.   In pharmaceutical chemistry, quantum mechanics is used in drug discovery through the calculation of quantitative structure activity relation (QSAR) parameters, which are mostly quantum chemical parameters.

vi.   In polymer and biological chemistry also apply quantum mechanics to study macromolecules, since macromolecules can be considered as a composite of micro molecules.

In recent times, several softwares have been produced for used in quantum chemical calculations. Most of them are designed for used, even with user inadequate theoretical knowledge.

2.0   OBJECTIVES

When you have studied this section, you should be able to

- understand the concept of quantum chemistry of bonding
- historical development of quantum mechanics
- derive the Schrodinger equation
- how orbitals are formed
- relate wave function with orbitals
- different types of orbitals

3.0   MAIN CONTENT

3.1   Historical development of quantum mechanics

The beginning of quantum mechanics was in 1980 when Planck discovered that a heated solid gives out light. However, detail information on the nature of light giving out was not provided by Planck.

In 1800, Thomas Young provided experimental evidences on the wave nature of light, when he observed diffraction and interferences of light as it passes through two adjacent pinholes. Diffraction described the bending of light around an obstacle while interferences defines the algebraic or vector sum of different light of similar or closely similar frequencies.

Further exploration into the science of electromagnetic radiation by James Clark Maxwell in 1860, who developed a set of equations called Maxwell

equations. These equation bridges the gap between the laws of electricity and magnetism by providing evidences that an accelerating electric charge will radiate energy similar to electromagnetic waves consisting of oscillating electric and magnetic fields. Fortunately, the speed, predicted by Maxwell coincided with the speed of light.

In 1888, Heinrich Hertz discovered that an electromagnetic light was produced by an accelerating electric charge in a spark. This findings also supported Maxwell's work and confirmed that light is an electromagnetic radiation. Generally, an electromagnetic waves travels at a speed of 2.998 x 10^8 m/s in a vacuum. The frequency and wavelength are related by the equation, $\lambda v = c$, where c is the speed of light, λ is the wavelength and v is the frequency of the light.

In the late 18th century, studies were conducted on the emission of radiation by a black body. A black body is an object that absorbed all the light that falls on it. A good example of a black body is a cavity with a tiny hole. The surprising feature of the black body radiation was that curves developed for variation of intensity with frequency using classical approaches (statistical mechanics and electromagnetic wave model) were at variance with curves obtained from experiments. It was Planck, in 1900 that gave explanation to this phenomenon. Planck concluded that the atom of the black body could emit light energy only in an amount given by hv. where h (h = 6.625 x 10^{-34} J.s) is the Planck constant and v is the frequency of radiation. In view of its importance in the history of quantum mechanics, black body radiation is single out for more discussion as follows.

3.2   Structure of atom and quantization

Atom consist of proton, electron and neutron. The proton is positively charged and is about 1836 times heavier than the negatively charged electron. Neutron, which was discovered in 1932 has no charge and is slightly heavier than the proton. The first set of investigation on the structure of atom started between 1908 and 1913, when Rutherford, Hans Geiger and Ernest Marsden repeatedly passed a beam of alpha particle through a thin metal foil in the Physical Laboratories of the University of Manchester and observed the deflection of the particle through a fluorescence screen. In their experiment, they discovered that most of the alpha particle passed through the foil undeflected, few were strongly deflected and others were deflected backward. From the findings of their experiment, they noted that such large deflection is possible if the positive charge was concentrated in a tiny heavy nucleus and concluded that every atom contains a nucleus where its positive charge and most of its mass are concentrated. In 1904, J. J. Thompson

suggested that the positive charges were spread throughout the atom but Rutherford and co-workers refuted this fact on the grounds that if it were so, then once the high energy atom penetrates the atoms, the repulsive forces would have fallen off and eventually become zero.

Nowadays, it is known that atom contain Z number of proton and number of Z electrons (where Z is the atomic number). The mass of the atom is concentrated in the central nucleus (which contains proton and neutron, collectively called nucleons). The nucleus is held together by strong nuclear forces while the nucleus and the electrons are held together by columbic force of attraction. In 1911, Rutherford proposed the planetary model of the atom, which stated that electron revolves around the nucleus. However, this model was exposed to several criticism. Classically, electromagnetic theory expects an accelerating ally charge particle to radiate electromagnetic waves. Also, a rotating charge radiating electromagnetic waves with changing velocity and direction will gradually lose energy and the atom will be unstable and eventually collapse.

In 1913, Niels Bohr offered explanation to the Rutherford theory through the concept of quantization of energy in the hydrogen atom. Bohr stated the energy of electron in hydrogen is quantized with electron allowed to move only in a number of allowed circle.
Bohr found that when hydrogen gas is heated, it emits electromagnetic radiation, characterised by certain distinct frequencies. Such spectral frequencies were explained according to equation 1

$$\frac{v}{c} = \frac{1}{\lambda} = \left(\frac{1}{n_b^2} - \frac{1}{n_a^2} \right) \qquad (1)$$

where n_b = 1, 2, 3 ......, n_a = 2, 3 .... $n_a > n_b$ and R is the Rydberg constant = 1.096776 x 10^5cm^{-1}

Classically, all frequencies of light ought to have been emitted but this is not true hence Einstein equation implies that the hydrogen atom exist in certain energy states. Indeed, an atom can has only certain energies, E_1, E_2, E_3 .... These allowed states of constant energy are called the stationary states. An atom in a stationary state can only emit radiation when its makes transition from a stationary state of higher level to the stationary states of lower energy and will therefore satisfyy equations 2 and 3;

$$E_{Higher} - E_{Lower} = hv \qquad (2)$$
$$E_a - E_b = hv \qquad (3)$$

Combination of equations 2 and 3, yields equation 4

$$E_a - E_b = Rhc \left(\frac{1}{n_b^2} - \frac{1}{n_a^2} \right) \qquad (4)$$

The implication of equation 4 is that the energies of the H-atom stationary states can be written as

$$E = -\frac{Rhc}{n^2} \qquad (5)$$

The major limitation of the Bohr theory arises from the use of classical mechanics to describe the motion of an electron in an atom. Evidence obtained from spectra of atoms reveals discrete frequencies which indicates that only certain energies of motion is allowed and that the electronic energy is quantized. Classically, continuous range of energies are possible but quantum mechanically, the energy is restricted to certain permissible values. Although Bohr model was satisfactory in explaining the hydrogen atom, it fails to explain poly-electron systems. In order to extend quantization to systems with two or more electrons, Louis de Broglie in 1923 found that just as light shows both wave and particle aspect, matter also has a dual nature, as well as showing particle like behaviour, electron could also show wave like behaviour, which manifest itself in the quantized energy levels of electrons in atoms and molecules. For photons, we have, $E_{photon} = h\nu$. Einstein special theory of relativity gives the energy of a photon as $E_{photon} = Pc$, where P is the momentum of the photon and c is the speed of light. Equating the two equations, we have $h\nu = pc$ and since $\nu = \frac{c}{h}$, we have

$$\frac{hc}{\lambda} = pc \text{ or } \lambda = \frac{hc}{p} = \frac{h}{mv} \qquad (6)$$

In 1927, the German physicist, Werner Heisenberg stated that the more precise the position of some particle is determine, the less precisely the momentum can be known and vice versa. However,, Earle Hesse Kennard and Hermann Wey in 1928 were able to derived the formal inequality that relates the standard deviation of position, a_x and that of momentum a_p as follows,

$$a_x . a_p \geq \frac{\hbar}{2} \qquad (7)$$

In quantum mechanics, uncertainty principle is any of the variety mathematical inequalities that sustain a fundamental limit to the precision with which certain pairs of complementary physical properties can be known. Uncertainty principle is inherent in the properties of all wave like systems and its originate from the de Broglie wave matter duality principle. In quantum chemistry, the uncertainty principle is mostly use to explore the relationship between simultaneous measurement of position and momentum. Therefore, the principle can be restated as, the product of the uncertainties in position and in momentum is in the order of magnitude of Planck constant or greater i.e.

$$\Delta x . \Delta p \geq \frac{\hbar}{2} \tag{8}$$

where $\hbar$ is the reduced Planck constant. $\hbar = \frac{h}{2\pi}$

3.3   The time independent Schrödinger equation

The Schrödinger equation is like the Newton's law and the law of conservation of energy in classical physics because it aids in predicting the future behaviour of dynamic system. This work of Schrödinger was initiated by Einstein in 1925, when he published a paper on quantum theory of ideal gas, and the de Broglie theory of matter waves. However, in 1926 Erwin Schrödinger proposed an equation that describes the evolution of a quantum mechanical system è SWE which represents quantum equations of motion in the following forms :

$$\frac{-\hbar \partial^2 \psi}{2m\partial x^2} + V(x)\psi(x,t) = i\hbar \frac{\partial \psi}{dt}$$

$$\left[\frac{-\hbar \partial^2}{2m\partial x^2} + V(x)\right]\psi(x,t) = i\hbar \frac{\partial \psi}{dt}$$

This is an equation that describes how the quantum state of a system changes with time. We can derive, the Schrödinger equation using the unique equation,

$$\Psi = A\frac{\sin 2\pi x}{\lambda} \tag{9}$$

Differentiating equation 13 with respect to x, we have;

$$\frac{d\Psi}{dx} = \frac{2\pi}{\lambda}A\cos\frac{2\pi x}{\lambda} \tag{10}$$

Taking a second derivative of equation 9 with respect to x yields equation11;

$$\frac{d^2\Psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}A\sin\frac{2\pi x}{\lambda} \tag{11}$$

Since $\psi = \frac{\sin 2\pi x}{\lambda}$, equation 11 can be simplified to the form given by equation 12

$$\frac{d^2\Psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi \tag{12}$$

Equation 16 can be simplified by applying the de Broglie equation, which relates particle momentum to wavelength as, $\lambda = \frac{h}{mv}$. Therefore, $\lambda^2 = \frac{h^2}{m^2 v^2}$ and substituting for λ^2 in equation16, equation 13 is obtained

$$\frac{d^2\varphi}{dx^2} = \frac{4\pi^2}{\left(\frac{h^2}{m^2.v^2}\right)}\psi = \frac{-4m^2v^2\pi^2}{h^2}\psi \tag{13}$$

The total energy of a system is the sum of the kinetic energy (KE = ½ mv^2) and the potential energy (U), i. e E = KE + U = ½ mv^2 + U and v^2 = 2/m (E – U). Modification of equation 13 through substituting the value of v^2 by 2/m (E – U) leads to equation 14

$$\frac{d^2\varphi}{dx^2} = \frac{-8m\pi^2}{h^2}(E - U)\psi \tag{14}$$

Introducing the reduced Planck constant, $= h/2$, equation 14 becomes,

$$\frac{d^2\varphi}{dx^2} = \frac{-2m}{\hbar^2}(E - U)\psi \tag{15}$$

Equations 14 and 15 are the various differential forms of the time independent Schrödinger equation for a one dimensional system. For a three dimensional system, the following equations are obtained,

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} = \frac{-8m\pi^2}{h^2}(E - u)\varphi \tag{16}$$

$$= (\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2})\psi = \frac{-8m\pi^2}{h^2}(E - u)\psi \tag{17}$$

$$= \nabla^2 \quad = \frac{-8m\pi^2}{h^2}(E - u)\psi \tag{18}$$

$$= \nabla^2 \quad = \frac{-2m}{\hbar^2}(E - u)\psi \tag{19}$$

where ∇^2 is called Laplacian operator, $\nabla = \partial/dx + \partial/dy + \partial/dz$. The Schrödinger equation can be re-arranged by collecting like terms as follows,

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U\psi = E\psi \quad or \quad \left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + U\right)\psi = E\psi \tag{20}$$

The first term $\left(\frac{-h^2}{2m}\frac{\partial^2}{dx^2} + U\right)$ is called the Hamiltonian operator,   which operates on   to give the energy E and the wave function. Therefore, the general form of the Schrödinger equation can be written as   = E . The Schrödinger equation is on eigen equation or eigen function of the form (operator) (function) = (numerical value) x (function). The numerical function in this case is the energy and is called an eigen value. Solving the Schrödinger equation involves finding the value of the eigen value. The importance of eigen value equation is that it is consistent with the following patterns,
(Energy operator) (wave function) = (Energy) (wave function)
(operator)(wave function) = (observable)(wave function)
From the above, if we know both   and the operator corresponding to the observable of interest, we can predict the outcome of an observation of that property.

3.3.1 The wave function

The Schrödinger equation is the fundamental equation in quantum mechanics. The wave function does not has any physical significant but the square of the wave function represent the probability density of finding a system in a given time. . This assertion was proposed by Max Born. Max, also proposed four conditions that must be fulfilled when the solution to the Schrödinger equation is sought for. Born's conditions to be imposed on the wave function, ψ are:

i.   The wave function must be single valued. This means that for any given values of x and t ψ, must have a unique value. This is a way of guaranteeing that there is only a single value for the probability of the system being in a given state. Actually, if ψ is a proper mathematical function, it will satisfy this requirement automatically, since one condition all functions must satisfy is that they are single-valued.

ii.   The wave function must be quadratically integratable. This implies that, the integral of $|\psi|^2$ over all space must be finite. This is another way of saying that it must be possible to use $|\psi|^2$ as a probability density, since any probability density must integrate over all space to give a value of 1, which is clearly not possible if the integral of $|\psi|^2$ is infinite. One consequence of this proposal is that the wave function must tend to 0 for infinite distances.

iii.   The wave function must be continuous at all points, indicating that there should not be a sudden jump in the probability density when moving through space. If a function has a discontinuity such as a sharp step upwards or downwards, this can be seen as a limiting case of a very rapid change in the function. Such a rapid change would mean that the derivative of the function was very large (either a very large positive or negative number). In the limit of a step function, this would imply an infinite derivative. Since the momentum of the system is found using the momentum operator, which is a first order derivative, this would imply an infinite momentum, which is not possible in a physically realistic system.

iv.   All first-order derivatives of the wave function must be continuous.

Following the same reasoning as in condition iii, a discontinuous first derivative would imply an infinite second derivative, and since the energy of the system is found using the second derivative, a discontinuous first derivative would imply an infinite energy, which is not physically realistic.

3.3.2 The Operator

An operator is an instruction, a symbol which tells us to perform one or more mathematical acts on a function, say *f(x)*. The essential point is that they act on a function. Operators act on everything to the right, unless the action is constrained by brackets.

i.   Addition and subtraction rule for operators:
$$(\hat{A}_1 \pm \hat{A}_2)f(x) = \hat{A}_1 f(x) \pm \hat{A}_2 f(x)$$
(21)

ii.   The product of two operators requires successive operation. For

example,
$$\hat{A}_1 . \hat{A}_2 f(x) = \hat{A}_1 [\hat{A}_2 . f(x)]$$ (22)
It should be noted that the product of two operators is the third operator, i.e,
$$\hat{A}_3 = \hat{A}_1 . \hat{A}_2$$

iii.   Two operators are said to commute if the obey the simple operator expression
$$[\hat{A}_1 . \hat{A}_2] = \hat{A}_1 . \hat{A}_2 - \hat{A}_2 . \hat{A}_1 = 0 .$$ This indicate that $\hat{A}_1 . \hat{A}_2 = \hat{A}_2 . \hat{A}_1$

3.3.3 Schrödinger equation and orbital

The solution of the Schrödinger equation involves finding the eigen value through the eigen function. Several wave functions such as $\psi_1, \psi_2, \psi_3, \psi_4, \ldots$ may satisfy the requirements for the Schrödinger equation and each of them has corresponding eigen value such as the energy, $E_1, E_2, E_3, E_4 \ldots$ respectively. Each of these wave function is called an orbital and the square of each of them represent the probability of finding electron within a given volume element. For example, ψ_1 can be used to represent the ground state orbital of hydrogen atom because its single electron will first occupied the first orbital. The energy of this orbital will be E_1.

Each atom has a number of acceptable solutions to the Schrödinger wave equation and each orbital may be described by a set of three quantum numbers namely,
i.   The Principal quantum number, n: describes the energy level of electron
ii.   The subsidiary quantum number, l: describes the shape of orbital occupied by electrons. Values of l includes the integers and zero, i.e 0, 1, 2, 3, 4…. When l = 0, 1, 2,3.. the orbitals are s-orbital, the p-orbital, the d-orbital and the f-orbital respectively. The letter s, p, d and f originates from spectroscopy and are sharp, principal, diffuse and fundamental respectively
iii.   The magnetic quantum number, m: describes the paramagnetic or diamagnetic properties of electron. When l = 0, m = 0

Based on allowed solutions to the Schrödinger equation, orbitals can generally be classified into three groups. These are
i.   Those whose probability of finding electrons is a function of distance, r from the nucleus and the probability, $|\psi|^2$ is the same in all direction. The s-orbital is the only orbital in this group

ii.   Those whose wave function depends on the distant from the nucleus and on the direction in space (x, y, z). Orbitals in this group are characterised by subsidiary quantum number equal to 1 and are called p-orbital. There are three possible values of the magnetic quantum number, i.e m = -1, 0, +1, indicating that there are three sub orbitals for orbital in this group. These are,

- $\psi_x = f(r).f(x)$
- $\psi_y = f(r).f(y)$
- $\psi_z = f(r).f(z)$

These sub orbitals have the same energy. Therefore, there are three degenerate orbital for each of the value of n = 2, 3, 4

iii.   The third group consist of orbitals whose wave function depends on distance from the nucleus, r and also on two directions in space. For example the d and f orbitals. For the d-orbital, the subsidiary quantum number, is 2 and the magnetic quantum number, m = 4, i.e,   -2, -1, 0, +1, +2. Therefore, there are four degenerate sub orbitals for the d-orbital formed when n = 3, 4, 5. These are,

i. ψ_{x-y} = $f(r).f(x).f(y)$
ii. ψ_{x-z} = $f(r).f(x).f(z)$
iii. ψ_{y-z} =- $f(r).f(y).f(z)$
iv. ψ_{z^2} = $f(r).f(z).f(z)$
v. $\psi_{z^2-y^2}$ = $f(r).f(z^2).f(y^2)$

The subsidiary quantum number for the f-orbital, l is 3 indicating that the magnetic quantum number m = 7, i.e -3,-2, -1, 0, +1, +2, +3. Therefore there are seven degenerates sub orbitals for the f- orbital, which are formed when n = 4, 5, 6.

3.4   Atomic Orbitals

An orbital is the quantum mechanical refinement of Bohr's orbit. In contrast to his concept of a simple circular orbit with a fixed radius, orbitals are mathematically derived regions of space with different *probabilities* of having an electron. Because ^{2} gives the probability of finding an electron in a given volume of space (such as a cubic picometer), a plot of ^{2} versus distance from the nucleus (*r*) is a plot of the *probability density*. The 1*s* orbital is spherically symmetrical, so the probability of finding a 1*s* electron at any given point depends *only* on its distance from the nucleus. The probability density is greatest at *r* = 0 (at the nucleus) and decreases steadily with increasing distance. At very large values of *r*, the electron probability density is very small but *not* zero.

The *radial probability* (the probability of finding a 1s electron at a distance r from the nucleus) can be calculated by adding together the probabilities of an electron being at all points on a series of x spherical shells of radius r_1, r_2, r_3,…, r_{x-1}, r_x. The approach divides the atom into different shells and calculate the probability for each of the shell beore adding them together (**consider different layers of onions and think of calculating the probability for the different layers and obtain the overall probability by adding the individual probability**) .

The greatest probability is found when r = 0 and the surface area of each spherical shells is $4\pi r^2$. Since the surface area is a function of r, it will increase with increase in r even at a rate greater than the increase in electron density. Consequently, a plot of radial probability has a maximum at a maximum at a particular distance (Fig. 1).
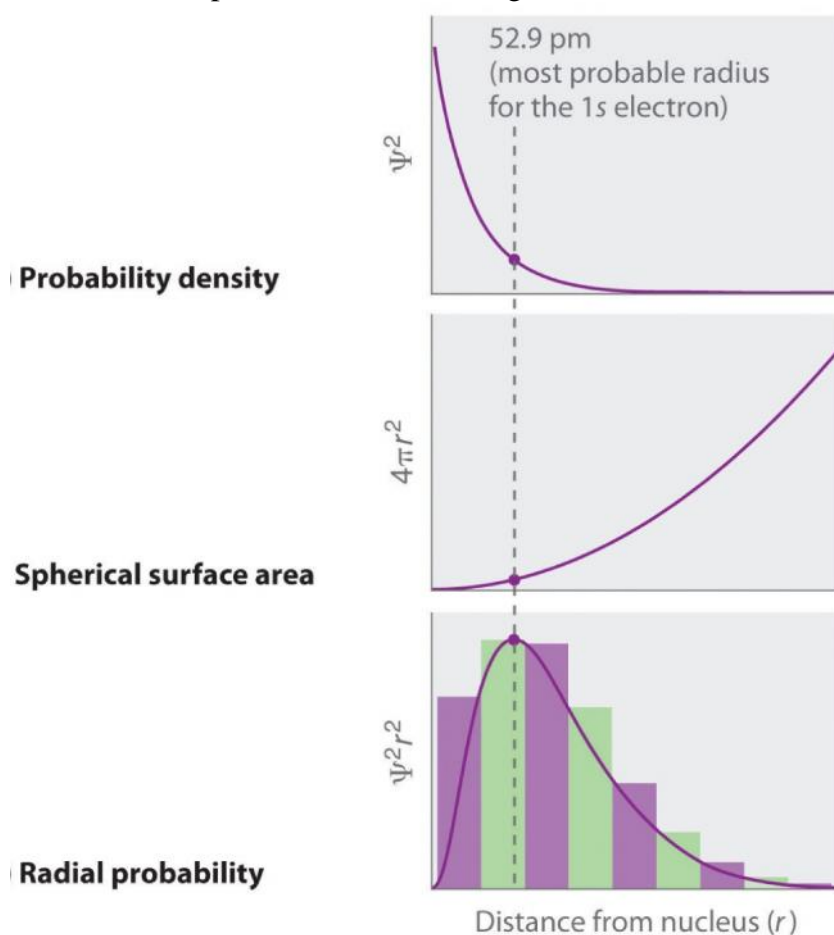
Fig. 1 Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom.

The first plot is a plot of electron probability density ^{2} versus r , which reveals that that the electron probability density is greatest at $r = 0$ and falls off smoothly with increasing r. The density of the dots is therefore greatest in the innermost shells. The second plot shows the plot of spherical surface ($4\pi r^2$) versus the radius, and it increases that the surface area increases increases rapidly with increasing radius. r. The last diagram is a radial probability plots which represents a plot of the product of the square of the atomic orbital function and the r^2. Since the surface area of each shell increases more rapidly with increasing r than the electron probability density decreases, a plot of electron probability versus r (the *radial probability*) shows a peak. This peak corresponds to the most probable radius for the electron, 52.9 pm, which is exactly the radius predicted by Bohr's model of the hydrogen atom.

For the hydrogen atom, the peak in the radial probability plot occurs at $r =$ 0.529 Å (52.9 pm), which agrees with the radius calculated by Bohr for the $n = 1$ orbit. Therefore, the *most probable radius* obtained from quantum mechanics is identical to the radius calculated by classical mechanics. In Bohr's model, however, the electron was assumed to be at this distance 100% of the time, whereas in the quantum mechanical Schrödinger model, it is at this distance only some of the time. The difference between the two models is attributable to the wavelike behavior of the electron and the Heisenberg uncertainty principle.

Fig. 2 compares the electron probability densities for the hydrogen 1s, 2s, and 3s orbitals. Note that all three are spherically symmetrical. For the 2s and 3s orbitals, however (and for all other s orbitals as well), the electron probability density does not fall off smoothly with increasing r. Instead, a series of minima and maxima are observed in the radial probability plots). The minima correspond to spherical nodes (regions of zero electron probability), which alternate with spherical regions of nonzero electron probability.
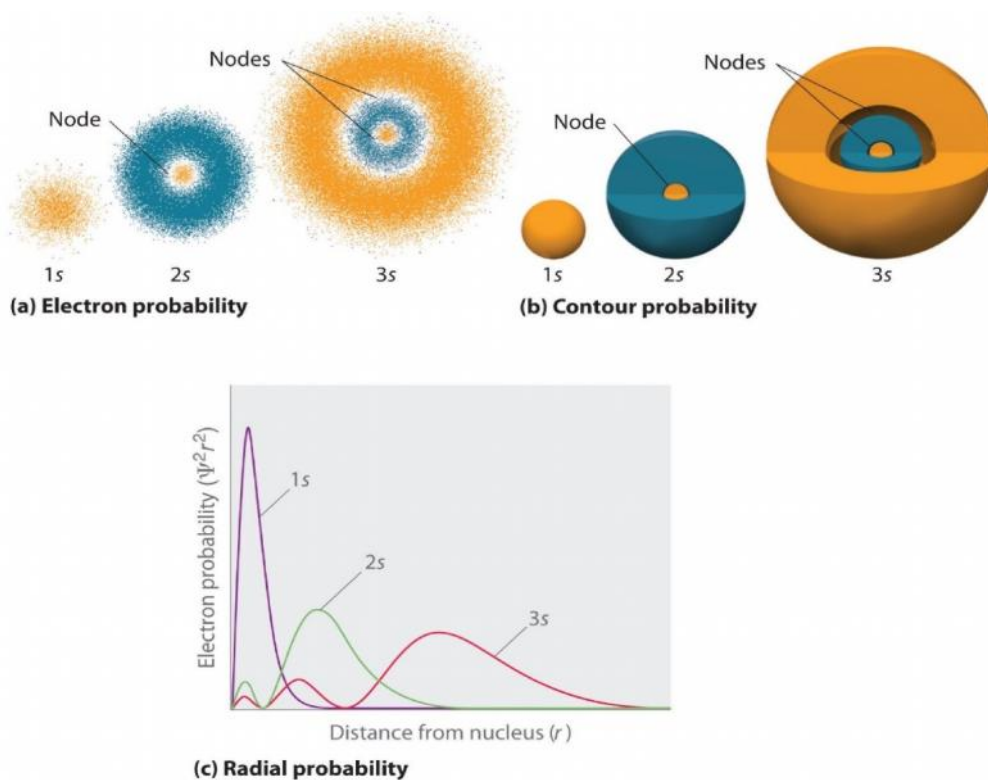
Fig. 2: Probability Densities for the 1*s*, 2*s*, and 3*s* Orbitals of the Hydrogen Atom.

In-Text Question (ITQ)

(1)   What Kind of orbital is show below?
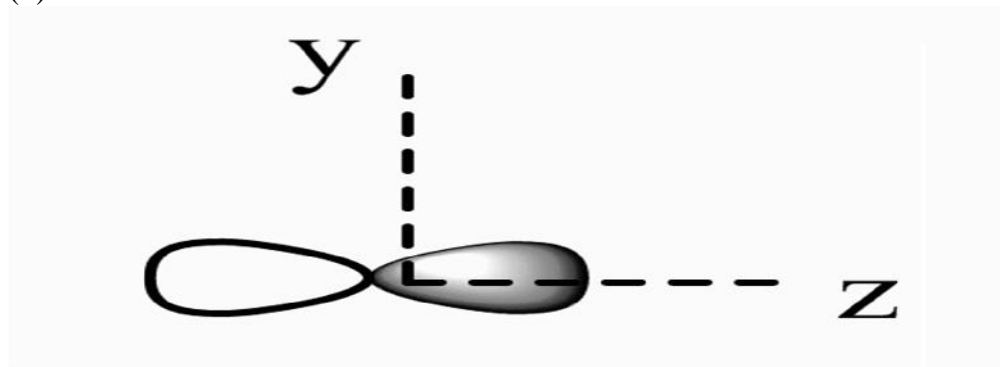
(2)   Which of the following is furthest from the nucleus: 2s, 3s, or 4s?

(3)   Which of the following orbital has the lowest energy : 2s, 3s, or 4s?

(4)   What is the *l* value for a 3p orbital?

3.5   Types of Orbitals

(i)   s-Orbitals

Three things happen to *s* orbitals as *n* increases

       (i)   They become larger, extending farther from the nucleus.

(ii)   They contain more nodes. This is similar to a standing wave that has regions of significant amplitude separated by nodes, points with zero amplitude.

(iii) For a given atom, the s orbitals also become higher in energy as n increases because of their increased distance from the nucleus.

Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron density, Such diagram should show the relative sizes of the orbitals, they do not normally show the spherical nodes in the 2s and 3s orbitals because the spherical nodes lie inside the 90% surface. This is insignificant since, the positions of the spherical nodes are not important for chemical bonding.

(ii)   p Orbitals

Only s orbitals are spherically symmetrical. As the value of l increases, the number of orbitals in a given subshell increases, and the shapes of the orbitals become more complex. Because the 2p subshell has $l = 1$, with three values of m_l (−1, 0, and +1), there are three 2p orbitals.
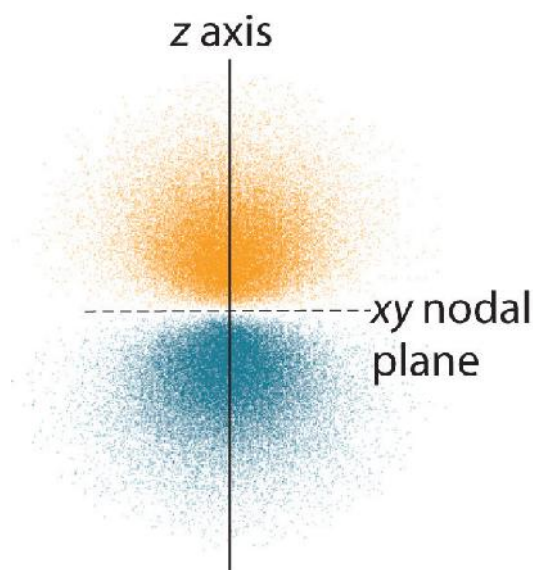
The colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

The electron probability distribution for one of the hydrogen 2p orbitals is shown in Fig 3.. Because this orbital has two lobes of electron density arranged along the z axis, with an electron density of zero in the xy plane (i.e., the xy plane is a nodal plane), it is a $2p_z$ orbital. The other two 2p orbitals have identical shapes, but they lie along the x axis ($2p_x$) and y axis ($2p_y$), respectively. Each p orbital has one nodal plane. In each case, the phase of the wave function for each of the 2p orbitals is positive for the lobe that

points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the *phase* of the wave that describes the electron motion, *not* to positive or negative charges.
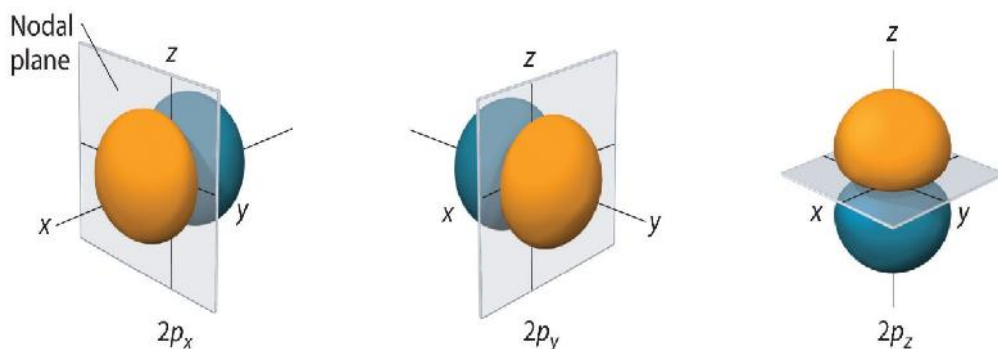
Fig. 2: The Three Equivalent *2p* Orbitals of the Hydrogen Atom

The surfaces shown enclose 90% of the total electron probability for the $2p_x$, $2p_y$, and $2p_z$ orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each $2p$ orbital. The phase of the wave function is positive (orange) in the region of space where x, y, or z is positive and negative (blue) where x, y, or z is negative.

The size and complexity of the p orbitals for any atom increase as the principal quantum number n increases. The shapes of the 90% probability surfaces of the $3p$, $4p$, and higher-energy p orbitals are, however, essentially the same as those shown in Fig. 2

The electron configuration of an atom is the representation of the arrangement of electrons distributed among the orbital shells and subshells. Commonly, the electron configuration is used to describe the orbitals of an atom in its ground state, but it can also be used to represent an atom that has ionized into a cation or anion by compensating with the loss of or gain of electrons in their subsequent orbitals. Many of the physical and chemical properties of elements can be correlated to their unique electron configurations. The valence electrons, electrons in the outermost shell, are the determining factor for the unique chemistry of the element.

In-Text Question (ITQ)
Identify all the possibilities of the four quantum numbers for principal quantum number equal to 5

In-Text Question (ITQ)
Given 6s and $m_L= +1$, identify all the possibilities of the four quantum numbers.

In-Text Question (ITQ)
Given 4d and $m_s = +1/2$, identify all the possibilities of the four quantum numbers.

3.6   Pauli Exclusion Principle

The Pauli exclusion principle states that there can only be a maximum of two electrons for every one orientation, and the two electrons must be opposite in spin direction; meaning one electron has $m_s=+1/2$ and the other electron has $m_s=-1/2$. This implies that the spin must be opposed when the electrons are paired.

3.7   Hund's Rule

Hund's rule states that the electrons in the orbital are filled up first by the +1/2 spin. Once all the orbitals are filled with unpaired +1/2 spins, the orbitals are then filled with the -1/2 spin (as shown in the diagram below).
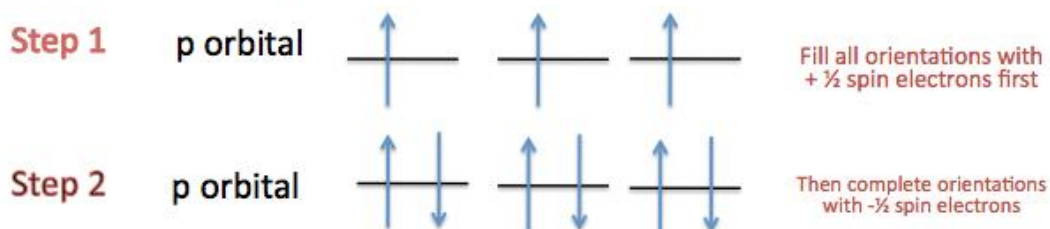
3.8   Atomic spectra

When atoms are excited they emit light of certain wavelengths which correspond to different colors. The emitted light can be observed as a series of colored lines with dark spaces in between. These series of colored lines is called a line or atomic spectra. Each element produces a unique set of spectral lines. Since no two elements emit the same spectral lines, elements can be identified by their line spectrum.

The emission spectrum of a chemical element or chemical compound is the spectrum of frequencies of electromagnetic radiation emitted due to an atom

or molecule making a transition from a high energy state to a lower energy state

The emission spectrum of a chemical element or chemical compound is the spectrum of frequencies of electromagnetic radiation emitted due to an atom or molecule making a transition from a high energy state to a lower energy state

Spectra can be generated through one of the following means:

(1)   In most cases the spectra arise from single-electron excitations. For spectra in or near the visible region a transition of one of the outermost electrons is responsible for the spectrum; in the x-ray region an inner shell electron is involved.

(2)   Most of the atomic spectra are of the electric dipole type with transition probabilities in the range of 10^7 to 10^9 sec^{-1}. Magnetic dipole and electric quadrupole transitions are less probable by a factor of 10^5 but may nevertheless be observed in special situations.

(3)   Very few spectra conform to pure *LS* or *jj* coupling. In passing from light to heavy atoms there is a continuous transition from predominantly *LS* to predominantly *jj* coupling.

(4)   As the departure from *LS* coupling increases, intercombination lines (S 0) become more probable. Such lines are weak in the spectra of the light atoms and become fairly strong in heavy atoms.

The classification of spectra is achieved by separating the atoms into groups based on the number and type of electrons that are excitable. The most commonly studied spectrum is that of hydrogen whose main features are contained in the expression,

$$\frac{1}{\jmath} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] m$$

$$R_H = \frac{R_\infty}{1(m/M)} = \frac{\mu e^4}{2\hbar^2} = 109\ 678.758\ cm^{-1} = 13\ 595\ eV$$

$$R_\infty = \frac{m e^4}{2\hbar^2} \simeq 109\ 737.311\ cm^{-1} = 13.605\ eV$$

and *m* is the mass of electron, *M* the mass of proton, μ is the reduced mass = *mM/(m + M)*, R_H, which is based on the reduced mass of the electron–proton system, is the ionization potential of hydrogen, and R the Rydberg constant. Spectra can be classified based on the transition from one principal quantum number to another as shown in Table 1..

Table 1: Classification of spectra based on the transition quantum number

Series	n_1	n_2	Longest wavelength (A^0)
Lyman	1	2,3, …	1215.68
Balmer	2	3,4, …	6562.79
Ritz-Paschen	3	4,5, …	18,751
Brackett	4	5,6, …	40,510
Pfund	5	6,7, …	74,560

Another classification method is based on angular momentum quantum number (Table 2)

Table 2: Classification of spectra based on angular momentum quantum number

Series	Transition	n	Number of lines
Principal	1 2S1/2−n 2P1/2,3/2	2,3, …	2
Sharp	22P1/2,3/2−n2S1/2	3,4, …	2
Diffuse	22P1/2−n 2D3/222P3/2−n 2D3/2,5/2	3,4, …	3
Fundamental	32D3/2−n 2F5/232D5/2−n 2F5/2,7/2	4,5, …	3

The alkali elements (Li, Na, K, Rb, Cs, Fr) have a single electron outside of a filled s or p shell; the ground state is $^2S_{1/2}$. Because of the spherical symmetry of the filled shells, the outer electron moves in a central field as in hydrogen. Therefore, the spectra of these elements resemble the spectrum of hydrogen and consist of analogous series. In the ground state, the outer s electron is more loosely bound than any of the other electrons in the filled shells and is also more loosely bound than the s electron in hydrogen. Hence the ionization potentials of these elements are lower; however, the doublet splitting due to spin-orbit interaction is much larger than in hydrogen.

Cu, Ag, and Au in their ground states have an s electron outside of a filled d shell. However, the binding energies of the s and d electrons are comparable so that the spectra of these elements and can be interpreted on the basis of either s or d excitation.

Elements with a single p electron outside of closed shells are B, Al, Ga, In, and T1. In boron, for example, the ground state configuration is $1s^22s^22p$; the

spectrum therefore resembles that of an alkali atom but with the lowest ^{2}S missing. In the same category are the elements F, C1, Br, I, and At whose ground state configurations are np^5 which gives rise to the single term ^{2}P as in the case of np but the multiplet structure is inverted because the shell is more than half-full.

Helium, the lightest element with a closed shell configuration in the ground state can produce two-term systems including singlets (parahelium) and triplets (orthohelium); however, both singlet and triplet S states must remain single. In the ground state the configuration is 1s^2; hence the only possible term consistent with the Pauli principle is ^{1}S$_0$. The lowest triplet ^{3}S$_1$ arises from the configuration 1s^{2}s and each triplet term is lower than the singlet term with the same values of n. The two-term systems do not mix since transitions between singlets and triplets are forbidden in the *LS* coupling approximation, and as a result there are two separate spectral systems, one associated with singlet states and the other with triplet states. The lowest triplet state ls2s ^{3}S$_1$ is metastable since there is no allowed transition to a lower state. There is a curious anomaly in the 2 ^{3}P term which shows a reversal in the order of the levels, i.e., the levels increase in energy in the order 2 ^{3}P$_2$, 2 ^{3}P$_1$, 2 ^{3}P$_0$. This is surprising since *LS* coupling predicts the opposite order. An explanation of this phenomenon has been given on the basis of spin-spin interactions and relativistic corrections.

The alkaline earth elements, Be, Mg, Ca, Sr, Ba, Ra, Zn, Cd, and Hg, contain two electrons (ns^2) outside of closed shells. Hence there are singlet and triplet terms as in helium with the triplet terms lying lower than the corresponding singlets. However, the selection rule $S = 0$ is not as strict as in helium so the spectra contain intercombination lines which increase in strength as one progresses from the lighter to the heavier elements due to increasing departure from *LS* coupling. Also, the ionization potentials are smaller than in helium. These elements also provide examples in which it is necessary to consider configuration interaction. Thus, in calcium, 3d5s ^{3}D lies in the same energy region as 4s8d ^{3}D and 4s9d ^{3}D and the states are all of the same type, that is, in regard to *L, S,* and the parity; hence each of these states are properly regarded as a mixture of configurations.

For the elements C, Si, Ge, Sn, and Pb the ground state configuration is np^2 and the ground term is ^{3}P$_0$ as required by Hund–s rule for a shell that is less than half-full. In configurations of the type np$(n + 1)$s like 2p3s in C, 3p4s in Si, etc., there is a gradual transition from *LS* coupling in the light elements to *jj* coupling in the heavier elements. O, S, Se, Te, Po have the configuration np^4 which produces the same terms as those arising from np^2 but with an inverted multiplet structure. A half-full shell np^3 is

found in the ground states of N, P, As, Sb, and Bi. The lowest term is ^4S while the other terms from np^3—^2P, ^2D—are metastable because of the selection rule $S = 0$, but some intercombinations are observed in the heavier elements. The closed shell configuration np^6 occurs in Ne, Ar, Kr, Xe, and Rn; in each case the lowest term is $^1S_0$.

There are several groups of elements in which the occupation of s orbitals competes with the occupation of d orbitals. As a result, these elements have one or two s electrons outside of *partially* filled d shells. The groups are classified according to their unfilled d shells: the 3d (iron) group (Sc, Ti, V, Cr, Mn, Fe, Co, Ni), the 4d (palladium) group (Y, Zr, Nb, Mo, Tc, Ru, Rb, Pd), and the 5d (platinum) group (Lu, Hf, Ta, W, Re, Os, Ir, Pt). In view of the large number of terms that are produced by several d electrons, these elements have rich spectra in the visible and ultraviolet. These elements include those with significant magnetic properties also are attributable to the unfilled d shells.

Finally we have the elements whose properties are mainly determined by their f electrons. These are the lanthanides (4f) group (Ce, Pr, Nd, Pn, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb) and the actinides (5f) group (Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf). Here too there are numerous terms arising from f electron configurations and consequently many lines in the spectra. The magnetic properties of the lanthanides are also determined by the partially filled 4f shell which is shielded by the outer 5s and 5p shells.

Spectra which originate from transitions by inner shell (core) electrons are known as X-ray spectra. In order to produce X-ray spectra it is necessary to remove (ionize) an electron from an inner shell thus creating a vacancy or hole. This can be accomplished by electron bombardment or by other means depending on the depth of the shell. Upon reverting to its ground state the atom may undergo a transition whereby the vacancy is filled by an electron from an outer shell with the release of an X-ray photon.

SELF ASSESSMENT EXERCISE

i.   a.   State and use appropriate conditions needed for an atom in a stationary state to emit radiation. Hence write an expression for the energy of the hydrogen atom stationary states.

            b.   Discuss the limitation of the Bohr's theory

ii.   What are the shortcoming of the Bohr's model of atom

a.   The Bohr theory cannot explain the spectra of atoms containing more than one electron.
b.   Even for the atoms with one electron, the theory does not predict the relative intensities of the lines or the splitting of the lines observed when the atoms are excited in a magnetic field (the Zeeman effect). Even in the absence of external fields, the spectral lines were found to be more complex when examined with high resolution equipments. (The theory could not explain the fine details of the spectra).
c.   The theory ignores the wave nature of the electron.
d.   It violates the Heisenberg's Uncertainty Principle – Bohr claims it is possible to know exactly the position and study the motion of the electron at the same time.
e.   It regards the electron as being stationary, with a specific position and distance from the nucleus.
f.   It does not explain molecular bonds.
g.   It does not predict the relative intensities of spectral lines.
h.   The Bohr model does not explain fine structure and hyperfine structure in spectral lines

iii.

a.   What is a quantum of energy?
b.   Explain the significance of the photoelectric effect.
c.   If an atom has a frequency of 5.357×10^{14} s^{-1}, using Planck's equation, what is the energy of a single photon?
d.   Using the answer from number 3, calculate the energy of a mole of photons.
e.   Assume you have light at a wavelength of 640 nm. Calculate the energy of one photon of light at that wavelength. Remember that c= 3.00×10^8 m s^{-1} and   is wavelength in meters.

5.0   CONCLUSION

Quantum mechanics can be used to explain intrinsic properties associated with structure and bonding in atoms. The major functional parameter of quantum mechanics is the Schrodinger equation, which defines atomic orbital as the wave function and molecular orbital as a combination of atomic orbitals through the square of the wave function.

5.0   SUMMARY

Models of addressing structure and bonding can not be completed without quantum approach. Quantum mechanics can explain the intrinsic properties that can not be easily handled by experiments. The major contribution of quantum mechanics in structure and bonding is the explanation of atomic and molecular orbital, spin and angular momentum, transition dipole and spectra emission.

6.0   TUTOR MARK ASSIGNMENTS

(1)   Given that the spectral frequencies for emission of radiation is expressed as follow

1. $\frac{v}{c} = \frac{1}{\lambda} = \left(\frac{1}{n_b^2} - \frac{1}{n_a^2}\right)$ 1

where $n_b = 1, 2, 3$ ......, $n_a \equiv 2, 3$ .... $n_a > n_b$ and R is the Rydberg constant = 1.096776 x $10^5 cm^{-1}$

Calculate the frequencies associated with transitions from

      (i)   n = 1 to $n = 2$
      (ii)   n = 2 to n = 3
      (iii)   n = 3 to $n = 4$

(2)   Use the Einstein equation to show that $\frac{hc}{\lambda} = pc$

(3)   Given that the wave function is defined as $\Psi = A \frac{\sin 2\pi x}{\lambda}$, derive the Schrodinger equation

(4)   From the derived Schrodinger equation, define atomic and molecular orbitals using the wave function.

(5)   State three properties of Hamiltonian operators

(6)   State Pauli exclusion principle and Hund's law

(7)   Identify the spin direction (e.g. $m_s = -\frac{1}{2}$ or $+\frac{1}{2}$ or $\pm\pm\frac{1}{2}$) of the outermost electron in a Sodium (Na) atom.

(8)   Identify the spin direction of the outermost electron in a Chlorine (Cl) atom.

(9)   Identify the spin direction of the outermost electron in a Calcium (Ca) atom.

(10)   Given 5p and $m_s = +\frac{1}{2}$, identify all the possibilities of the four quantum numbers.

(11)   Given 6f, identify all the possibilities of the four quantum numbers.

(12)   How many electrons can have n = 4 and L = 1?

(13)   How many electrons can have n = 4, L = 1, $m_L = -2$ and $m_s = +\frac{1}{2}$?

(14)   How many electrons can have n = 5, L = 3, $m_L = \pm\pm 2$ and $m_s = +\frac{1}{2}$?

(15)   How many electrons can have n = 5, L = 4, $m_L = +3$ and $m_s = -\frac{1}{2}$?

(16)   How many electrons can have n = 4, L = 2, $m_L = \pm\pm1$ and $m_s = -1212$?
(17)   How many electrons can have n = 3, L = 3, $m_L = +2$?

7.0   REFERENCES/FURTHER READINGS

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MODULE 3

Unit 1   Chemistry of the main group element
Unit 2   Second and higher main group elements

UNIT 1   CHEMISTRY OF MAIN GROUP ELEMENT

1.0   Introduction
2.0   Learning Outcome
3.0   Main Text
         3.1   Periodic trend for Main Group Element
         3.2   Hydrogen in the periodic table
                  3.2.1   Properties of hydrogen
                  3.2.2   Reactions of hydrogen
                  3.3.3   Reaction with active metals
                  3.3.4   Reactions with non-metals
         3.4   The Alkali metals
4.0   Conclusion
5.0   Summary
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1.0   INTRODUCTION

The main group is the group of elements (representative elements) whose lightest members are represented by helium, lithium, beryllium, boron, oxygen and flourine as arranged in the periodic table of the elements. The main group includes the elements (except hydrogen, which is sometimes not included) in groups 1 and 2 (s-block), and groups 13 to 18 (p-block). The s-block elements are primarily characterised by one main oxidation state, and the p-block elements, when they have multiple oxidation states, often have common oxidation states separated by two units.

Fig. 1 : Periodic table of elements (main group elements are groups 1, 2, 13 to 18)

The chemistry of the main group depends on the number of valence electron which also correspond to the group number
Compounds formed by main group elements always strive to satisfy the octet rule in order to attain the noble gas like electronic configurations

2.0   OBJECTIVES

When you have study this section, you should be able to:

• Know those elements in the periodic table that constitute main group elements
• Know periodic trend for main group element
• Know the controversial positioning of hydrogen in the periodic table, their properties and reactions
• Understand the chemistry of the alkali metals

3.0   MAIN CONTENT

3.1   Periodic trend for Main Group Element

There are trends in the periodic table that are pretty much determined by the effective nuclear charge and overall number of electrons in an atom. These include

(i)   Atomic radius decreases as we move from left to right and up the periodic table. Movement to the right does not increase the number of electronic orbital or shell but increase the number of electrons added to the same shell. Addition of more electrons tend to contract the electronic shell due to increase attraction between electrons and proton in the nucleus (i.e effective nuclear charge increases). Hence atomic radius decreases as we move from lower group to higher group. On the other hand, movement down the group (i.e from lower row to higher row) is accompanied by additional orbital indicating increase in atomic radius.

(ii)   Ionization energy increases as we move from the left to the right and up the periodic table. Ionization energy is the energy needed to remove valence electron from an atom. The first ionization energy is the energy needed to remove the most loosely bound electron. This is because as we move from left to right, there is increasing number of electrons in the valence shell and the strength of the force between electron and nucleus becomes more stable making it difficult to remove electron as we move towards the right. Also, as we move down the group, new electronic orbital is added. The removal of electron (ionization) becomes more easier as the distance from the nucleus increases because of decrease in effective nuclear charge (i.e, less attraction between the nucleus and the outermost electrons)

(iii)   Electronegativity increases to the right and up the periodic table. Electronegativity defines the tendency of an atom to accept electron. The ability to attend the nearest noble gas like configuration increases (i.e octet configuration) as the number of valence electron increases, which is signified by movement from left to right of the periodic table. On the other hand, since movement down the group is effective in increasing the ability to lose electron, it leads to decrease in electronegativity and vice versa.

(iv)   Polarizability increases to the right and down the periodic table. Polarizability is a measure of the ease of distorting an electron cloud by an electric field. The electron cloud may belong to an atom or molecule or ion while the electric field could be caused by an electrode or a nearby cation or anion. Polarizability is related to dipole moment which can be defined as $\mu = \alpha E$ (where α and E are polarizability and electric field respectively). Generally, polarizability increases as the volume occupied by electrons increases. Polarizability therefore decreases from left to right. Polarizability increases down on columns of the periodic table. Likewise, larger molecules are generally more polarizable than smaller ones. Different compounds also tend to response to effect of electric field differently. For example, Water is a very polar molecule

while alkanes and other hydrophobic molecules are more polarizable. Water with its permanent dipole is less likely to change shape due to an external electric field. Also, alkanes are the most polarizable molecules than alkenes and arenes (although alkenes and arenes are expected to have larger polarizability than alkanes) because of their higher reactivity compared to alkanes. Trend in the variability of polarizability has significant impact on properties of elements. Choundhary *et al*. (2019), atomic polarizability is an essential theoretical construct to define and correlate many physicochemical properties. It exhibits periodicity and has a relationship with other periodic descriptors.

(v)   Non-metallic character increases to the right and up the periodic table 4. Metals are generally identify as those element that ionizes by losing electron while non metals ionizes by gaining electron. Therefore, since the ability to lose electron increases across the period and up the group, metallic character will decrease in that same trend. Fig. 1 below shoes the periodic table reflecting metals, metalloid and non metals

Fig.1: Location of metals (blue colour), metalloid (red colour) and non metals (yellow colour) in the periodic table.

Some general properties of main group elements are:

(i)   The second row of the periodic table is unique because overlap of adjacent 2p orbitals creates bonding and because the significance of intermolecular hydrogen bonding forces. In contrast, third and higher rows create expanded orbitals to accommodate additional electrons with low energy bonds.

(ii)   Most elements except the noble gases form very stable compounds with itself, whether through metallic bonding, network solids like C, or small covalent molecules like N_2 or P_4.

(iii)   Also, most elements forms hydrides by reacting with hydrogen. Basic ionic hydrides like NaH are found to the left on the periodic table and increasingly covalent acidic hydrides like HCl are found to the right on the periodic table

3.2   Hydrogen in the periodic table

Hydrogen was first isolated and identified as an element by Cavendish in 1766. The element was believed to be many different things. Cavendish himself thought that it was "inflammable air from metals", owing to its production by the action of acids on metals. Prior to Cavendish observation, Robert Boyle and Paracelsus produced hydrogen from the reactions between iron and acids while the name, hydrogen was given by Antoine Lavoisier, meaning water producer. (when when ignited in air). Others thought it was pure phlogiston because of its flammability. Hydrogen is among the ten most abundant elements on the planet, but very little is found in elemental form due to its low density and reactivity. Much of the terrestrial hydrogen is stocked up in water molecules and organic compounds such as hydrocarbons. Hydrogen is a colorless, odorless and tasteless gas that is the most abundant and lightest (with respect to atomic mass) element in the universe. It is also the simplest element because it has only one proton and one electron (and no neutrons in its most common isotope. Some properties of hydrogen are presented in Table 1.

Table 1 : Properties of hydrogen

Property	Value
Atomic number	1
Atomic weight	1.0079
Electronic configuration	$1S^1$
Oxidation state	+1 or -1
Atomic radius	78 pm

Hydrogen has three isotopes whose properties are presented in Table 2 below

Table 2: Characteristics of isotopes of hydrogen

Characteristics	Hydrogen	Deuterium	Tritium
Symbol	H	^{2}H or D	^{3}H or T
Molar mass (g/mol)	1.008	2.014	3.016
Abundance (%)	99.98	0.02	radioactive
Melting point (K)	14	19	21
Boiling point (K)	20	24	25
Density (g/L)	0.089	0.18	0.27

3.2.1 Properties of hydrogen

Hydrogen can be seen as a metal because it has ns^1 electron configuration like the alkali metals. However, it varies greatly from the alkali metals as it forms cations (H^+) more reluctantly than the other alkali metals. Hydrogen's ionization energy is 1312 kJ/mol, while lithium (the alkali metal with the highest ionization energy) has an ionization energy of 520 kJ/mol.

The ability of hydrogen to accept electron from metals or shared electron with non metals also sort hydrogen as a non metal. It can form hydride (in -1 oxidation state, i.e hydride anions). Consequently, it is some times placed above halogen in the periodic table. It is sometimes placed above the halogens in the periodic table. Hydrogen also forms H_2 dihydrogen like halogens. However, hydrogen is very different from the halogens because it has a much smaller electron affinity than the halogens.

H_2 dihydrogen or molecular hydrogen is non-polar with two electrons. There are weak attractive forces between H_2 molecules, resulting in low boiling and melting points. However, H_2 has very strong intramolecular forces; Reactions involving H_2 are generally slow at room temperature due to strong H—H bond. Hoever, H_2 is easily activated by heat, irradiation, or catalysis. Once activated, it can reacts exothermically with many substances at a fast rate.

Hydrogen also has an ability to form covalent bonds with a large variety of substances due to its ability to form hydroxyl bonds. It is a good reducing agent for metal oxides that is below it in the reactivity series (shown in Fig.2).

For example,

$CuO_{(s)} + H_{2\,(g)}$ $Cu_{(s)} + H_2O_{\,(g)}$

Reactivity Series
Element
Lithium (Li)
Potassium (K)
Barium (Ba)
Ca (Ca)
Sodium (Na)
Magnesium (Mg)
Aluminum (Al)
Carbon (C)
Zinc (Zn)
Iron (Fe)
Nickel (Ni)
Tin (Sn)
Lead (Pb)
Hydrogen (H)
Copper (Cu)
Tungsten (W)
Mercury (Hg)
Silver (Ag)
Gold (Au)
Platinum (Pt)

Decreasing reactivity

Fig. 2: Reactivity series for metal oxides

3.2.2 Reactions of hydrogen

The low ionization potential of Hydrogen enables it to act as an alkali metal:

$$H_{(g)} \rightarrow H_{(g)}^+ + e^-$$
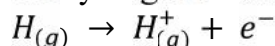
However, it half-filled valence shell (with a $1s^1$ configuration) with one also causes hydrogen to act like a halogen (non-metal) to gain noble gas configuration (duplet configuration) by accepting electron

$$H_{(g)} + e^- \rightarrow H_{(g)}^-$$
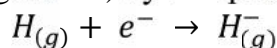
3.3.3 Reaction with active metals

Hydrogen accepts e- from an active metal to form ionic hydrides such as LiH. In such reactions, hydrogen accept electron from the metal and its oxidation number changes from 0 to -1. This reaction is similar to the behaviour of halogen,

$Li + H \rightarrow LiH$
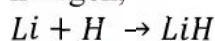
Generally, reactions of hydrogen with group 1 metals can be represented as

$2M_{(s)} + H_{2(g)} \rightarrow 2MH_{(s)}$

For example

$$2K_{(s)} + H_{2(g)} \rightarrow 2KH_{(s)}$$
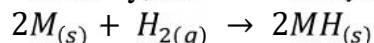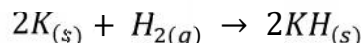
The above reaction can be compared with reactions with halogen, for example,

$2K_{(s)} + Cl_{2(g)} \rightarrow 2KCl_{(s)}$
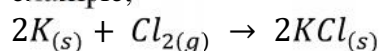
Hydrogen also reacts with group two (alkali earth metals) to form hydrides according to the following equation (which is also comparable with the reaction of these metals with halogen).

$$Ca_{(s)} + H_{2(g)} \rightarrow CaH_{2(s)}$$
$$Ca_{(s)} + Cl_{2(g)} \rightarrow CaCl_{2(s)}$$
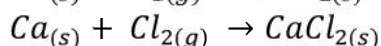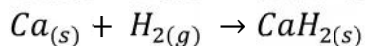
3.3. 4 Reactions with non-metals

Hydrogen forms polar covalent bonds with non metals (unlike metals that forms ionic bond). This is because the active metals are more electropositive than hydrogen. Some reactions with non metals are presented below,

(i)   With halogen

$$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCk_{s(g)}$$

(ii)   With oxygen

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g}0$$
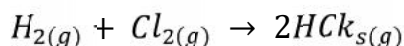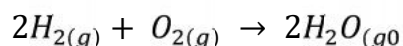
The reaction of hydrogen with oxygen generates upto 47 kJmol of heat energy. Hydrogen is produced commercially by reforming reaction, using nickel catalyst (see equation below)

$$CH_{4(g)} + H_2O \xrightarrow{\text{nickel catalyst}} CO_{2(g)} + 3H_2$$

However, one of the most efficient synthetic route for hydrogen is by photochemical decomposition of water] which is a chemical reaction in which water is broke down into hydrogen and oxygen,

$$H_2O \rightarrow H_{2(g)} + O_{2(g)}$$
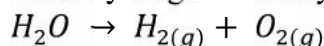
Usefulness of hydrogen include fuel, for the reduction of metal oxide (when the reaction has negative free energy change) and as a feed stock for the production of ammonia through Haber process.

3.4   The Akali metals

The electronic configurations of the alkaline metals are presented in Table 3 . From the Table, it can be seen that the general formula for the electronic configuration of the alkali metals is ns^1, where n is the highest occupied principal energy level

Table 3: Atomic number and electronic configuration of alkaline metals

Alkali metal	Atomic number	Electronic configuration	In terms of noble gas
Li	3	Is^22s^1	$He2S^1$
Na	11	$Is^22s^22p^63s^1$	$Ne3s^1$
K	19	$Is^22s^22p^63s^23p^64s^1$	$Ar4s^1$
Rb	37	$Is^22s^22p^63s^23p^64s^24p^65s^1$	$Kr5s^1$
Cs	55	$Is^22s^22p^63s^23p^64s^24p^65s^24d^{10}5p^66s^1$	$Xe6s^1$
Fr	87	$Is^22s^22p^63s^23p^64s^24p^65s^24d^{10}5p^66s^24f^{14}5d^{10}6p^67s^1$	$Rn7s^1$

The general properties of the alkaline metals include:

(i)   They have a $1s^1$ electronic configuration such that their configuration differ from that of the nearest rare gas by additional one electron

(ii)   The metals have low ionization energy indicating that they can readily lose one electron (which is the only electron in their valence shell)

(iii)   The exhibit metallic properties and can easily oxidised by donating an electron to form a mono-cation that are always in +1 oxidation state no matter the compound

(iv)   They have low boiling and melting points and weak bonding as shown in the table below

(v)   The react readily with water and with most substances

(vi)   They form basic hydrides and oxides.

In-Text Question (ITQ)
State the electronic configuration of Cs which has atomic number of 55

SELF ASSESSMENT EXERCISE

i.   What are the properties of the alkali metal?

ii   Write equations to show the following reactions
    a.   hydrogen with halogen
    b.   Hydrogen with oxygen
    c.   Production of hydrogen by reforming reaction

     d.   Production of hydrogen by photochemical decomposition of water
     e.   State the usefulness of hydrogen

(i)   With halogen

$$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCk_{s(g)}$$

(ii)   *With oxygen*

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g0}$$

The reaction of hydrogen with oxygen generates upto 47 kJmol of heat energy.

(iii)   Hydrogen is produced commercially by reforming reaction, using nickel catalyst (see equation below)

$$CH_{4(g)} + H_2O \xrightarrow{nickel\ catalyst} CO_{2(g)} + 3H_2$$

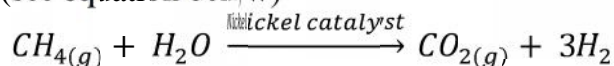(iv)   However, one of the most efficient synthetic route for hydrogen is by photochemical decomposition of water which is a chemical reaction in which water is broke down into hydrogen and oxygen,

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

(v)   Usefulness of hydrogen include fuel, for the reduction of metal oxide (when the reaction has negative free energy change) and as a feed stock for the production of ammonia through Haber process.

4.0   CONCLUSION

The periodic table has significant role in behaviour of elements. Elements in the periodic table can generally be classified into metals and non metals. Classification of metals into actinide, lanthanide and transition metals are also obtainable. Yet still class of elements called metalloids displayed properties that are in between metals and non metals.

5.0   SUMMARY

The periodic table present information on periodicity of properties such as ionization energy, electron affinity, electronegativity, metallic properties, ionic character and others. Through the variation of these properties across the period and down the group, periodicity provides important link towards the prediction of properties of metals and non metals.

6.0   TUTOR MARK ASSIGNMENTS

1.   Explain the controversial position of hydrogen in the periodic Table
2.   State the expected variation of the following properties down the group and across the period in the periodic Table

(i)   Ionization potential
(ii)   Electronegativity
(iii)   Polarization
(iv)   Electron affinity
(v)   Metallic character

3.   What is the significant of inert pair effect on properties of metals in the periodic table
4.   What is the significant of diagonal line in the periodic table.

7.0   REFERENCES/FURTHER READINGS

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UNIT 2   SECOND AND HIGHER ROW MAIN GROUP ELEMENTS

1.0   Introduction
2.0   Objectives
3.0   Main Contents
        3.1   Group 13
        3.2   Group 14
        3.3   Group 15
        3.4   Group 16
        3.5   Group 17
        3.6   Group 18
4.0   Conclusion
5.0   Summary
6.0   Tutor Mark Assignments
7.0   References/Further Readings

1.0   INTRODUCTION

The second-period element of each group (n = 2: Li, Be, B, C, N, O, and F) differs in many important respects from that of the heavier members. Therefore, the elements of the third period (n = 3: Na, Mg, Al, Si, P, S, and Cl) are generally more representative of the group to which they belong. The anomalous chemistry of second-period elements results from three important characteristics namely,
(i)   Small radii,
(ii)   Possession of energetically unavailable d orbitals,
(iii)   The tendency to form pi ( ) bonds with other atoms.

The second period elements have electron affinities that are less negative than would be predicted from general periodic trends because of their small radii. When an electron is added to such a small atom, increased electron–electron repulsions tend to destabilize the anion. Also, the small sizes of these elements prevent them from forming compounds in which they have more than four nearest neighbours. For example, BF_3 forms only the four-coordinate, tetrahedral BF_4^- ion, whereas under the same conditions AlF_3 forms the six-coordinate, octahedral AlF_6^{3-} ion. Because of the smaller atomic size, simple binary ionic compounds of second-period elements also have more covalent character than the corresponding compounds formed from their heavier congeners. The very small cations derived from second-period elements have a high charge-to-radius ratio and can therefore polarize the filled valence shell of an anion. Consequently, the bonding in such

compounds has a significant covalent component, giving the compounds properties that can differ significantly from those expected for simple ionic compounds. For example, LiCl is is partially covalent in character and is more soluble than NaCl in solvents with a relatively low dielectric constant, such as ethanol (= 25.3 versus 80.1 for H_2O).

It is significant to state that d-orbitals are never occupied for principal quantum numbers less than 3, therefore, the valence electrons of second-period elements occupy only 2s and 2p orbitals. Since the energy of the 3d orbitals far exceeds the energy of the 2s and 2p orbitals, it is not possible to use 3d orbital for bonding. Consequently, electron configurations with more than four electron pairs around a central, second-period element are not observed. Generally, the role of d-orbitals in bonding in main group compounds with coordination numbers of 5 or higher is somewhat controversial. Theoretical descriptions of the bonding in molecules such as SF_6 have been reported without mentioning the participation of d orbitals on sulphur. Arguments based on d-orbital availability and on the small size of the central atom, however, predict that coordination numbers greater than 4 are unusual for the elements of the second period, which is in agreement with experimental results.

One of the most significant differences between the lightest main group elements and their heavier congeners is the tendency of the second-period elements to form species that contain multiple bonds. For example, N is one step above P in group 15: N_2 contains an N N bond, but each phosphorus atom in tetrahedral P_4 forms three P–P bonds. This difference in behavior reflects the fact that within the same group of the periodic table, the relative energies of the pi-bond and the sigma ( ) bond differ. A C=C bond, for example, is approximately 80% stronger than a C–C bond. In contrast, an Si=Si bond is observed with less p-orbital overlap between the valence orbitals of the bonded atoms (because of the larger atomic size) is only about 40% stronger than an Si–Si bond. Consequently, compounds that contain both multiple and single C to C bonds are common for carbon, but compounds that contain only sigma Si–Si bonds are more energetically favorable for silicon and the other third-period elements.

Another important trend to note in main group chemistry is the chemical similarity between the lightest element of one group and the element immediately below and to the right of it in the next group, a phenomenon known as the diagonal effect. There are, for example, significant similarities between the chemistry of Li and Mg, Be and Al, and B and Si. Both $BeCl_2$ and $AlCl_3$ have substantial covalent character, so they are somewhat soluble in nonpolar organic solvents. In contrast, although Mg and Be are in

the same group, $MgCl_2$ behaves like a typical ionic halide due to the lower electronegativity and larger size of magnesium.

The inert-pair effect
Inert pair effect is the empirical observation that the heavier elements of groups 13–17 often have oxidation states that are lower by 2 than the maximum predicted for their group. For example, although an oxidation state of +3 is common for group 13 elements, the heaviest element in group 13, thallium (Tl), is more likely to form compounds in which it has a +1 oxidation state. The observed character has been attributed to increasing ionization energies and decreasing bond strengths.

The ionization energies increase because filled (n − 1)d or (n − 2)f subshells are relatively poor at shielding electrons in ns orbitals. Therefore, the two electrons in the ns subshell experience an unusually high effective nuclear charge, so they are strongly attracted to the nucleus, reducing their participation in bonding. This creates difficulty in removing the two ns electrons by the difference between the first ionization energies of thallium and aluminum. Because Tl is less likely than Al to lose its two ns^2 electrons, its most common oxidation state is +1 rather than +3.

Table.1: Ionization and M-Cl bond energy for group 13 elements

Element	Electronic configuration	I_1 (kJ/mol)	$I_1 + I_2 + I_3$ (kJ/mol)	Average M-Cl bond energy (kJ/mol)
B	$[He]2s^2 2p^1$	801	6828	536
Al	$[Ne]3s^2 3p^1$	578	5139	494
Ga	$[Ar]3d^{10}4s^2 4p^1$	579	5521	481
In	$[Kr]4d^{10}5s^2 5p^1$	558	5083	439
Tl	$[Xe]4d^{10}5d^{10}6s^2 6p^1$	589	5439	373

Source of data: John A. Dean, Lange's Handbook of Chemistry, 15th ed. (New York: McGraw-Hill, 1999)

Going down a group, the atoms generally became larger, and the overlap between the valence orbitals of the bonded atoms decreases. Consequently, bond strengths tend to decrease down a column. As shown by the M–Cl bond energies listed in the above table, which reveals that the strength of the bond between a group 13 atom and a chlorine atom decreases by more than 30% from B to Tl. Similar decreases have been reported for atoms in groups 14 and 15.

The net effect of these two factors—increasing ionization energies and decreasing bond strengths—is that in going down a group in the p-block, the

additional energy released by forming two additional bonds eventually is not great enough to compensate for the additional energy required to remove the two ns^2 electrons.

2.0   OBJECTIVES

* know and classify the elements included in groups 13 to 18
* Understand electronic configuration of groups 13 to 18 elements
* Know the concept of inert pair effect
* Know reactions involving groups 13 to 18 elemenents
* Know the application of some of the elements in groups 13 to 18

3.0   MAIN CONTENT

3.1   Group 13 elements

Group 13 elements are the set of elements that boarder the diagonal line in the periodic table. Most group 13 elements are reductants and are less powerful than the alkali and alkaline earth metals. However, their oxides are thermodynamically stable, such that large amounts of energy are needed for their isolation. The most abundant element in this group is boron and aluminum.

3.1.1 Preparation

Although boron is relatively rare (it is about 10,000 times less abundant than aluminium). Boron is produced on a large scale by reacting borax ($[Na_2B_4O_5(OH)_4 \cdot 8H_2O]$) with acid to produce boric acid $[B(OH)_3]$, which is dehydrated to the oxide (B_2O_3). Reduction of the oxide with magnesium or sodium gives amorphous boron that is about 95% pure:

$$Na_2B_4O_5(OH)_4 \cdot 8H_2O_{(s)} \xrightarrow{acid} B(OH)_{3(s)} \xrightarrow{\Delta} B_2O_{3(s)}$$

$$B_2O_{3(s)} \xrightarrow{\Delta} 2B_{(s)} + 3M$$
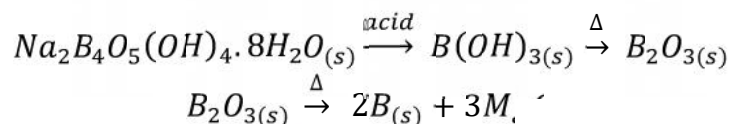
Although it maybe difficult to obtain pure, crystalline boron because of its high melting point (2300 °C) and the high corrosive nature of liquid boron, it can be prepared by reducing pure BCl_3 with hydrogen gas at high temperatures or by the thermal decomposition of boron hydrides such as diborane (B_2H_6):

$$BCl_{3(g)} + \frac{3}{2}H_{2(g)} \xrightarrow{\Delta} B_{(s)} + 3HCl_{(g)}$$

$$B_2H_{6(g)} \xrightarrow{\Delta} 2B_{(s)} + 3H_{2(g)}$$
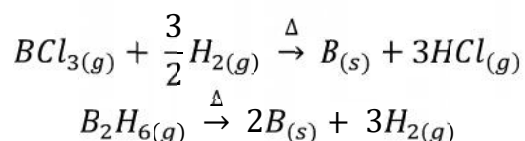
The reaction involving the reduction of BCl_3 by H_2 is significant because it is used to prepare boron fibers, which are stiff and light. Hence, they are used as structural reinforcing materials in objects as diverse as the US space shuttle and the frames of lightweight bicycles that are used in races. Boron is also an important component of some ceramics and heat-resistant borosilicate glasses, such as Pyrex, which is used for ovenware and laboratory glassware.

On the other hand, deposits of aluminum ores such as bauxite, a hydrated form of Al_2O_3, are abundant. With an electrical conductivity about twice that of copper on a weight for weight basis, aluminum is used in more than 90% of the overhead electric power lines in most countries. However, because aluminum–oxygen compounds are stable, obtaining aluminum metal from bauxite is an expensive process. However, aluminum is extracted from oxide ores by treatment with a strong base, which produces the soluble hydroxide complex $[Al(OH)_4]^-$. Neutralization of the resulting solution with gaseous CO_2 results in the precipitation of $Al(OH)_3$:

$$2[Al(OH)_4]^-_{(aq)} + CO_{2(g)} \rightarrow 2Al(OH)_{3(s)} + CO^-_{3(aq)} + H_2O_{(l)}$$
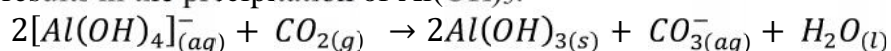
Thermal dehydration of $Al(OH)_3$ produces Al_2O_3, while metallic aluminum is obtained by the electrolytic reduction of Al_2O_3 using the **Hall–Heroult process**. Aluminum is the most useful group 13 elements (also useful in aircraft).

The other members of group 13 are relatively rare. Gallium is approximately 5000 times less abundant than aluminum, and indium and thallium are much scarcer. Consequently, these metals are usually obtained as by-products in the processing of other metals. The extremely low melting point of gallium (29.6°C), however, makes it easy to separate it from aluminum. Due to its low melting point and high boiling point, gallium is used as a liquid in thermometers that have a temperature range of almost 2200 °C.

Indium and thallium are the heavier group 13 elements and are found as trace impurities in sulfide ores of zinc and lead. Indium is used as a crushable seal for high-vacuum cryogenic devices, and its alloys are used as low-melting solders in electronic circuit boards. Thallium, on the other hand, is so toxic that the metal and its compounds have few uses. Both indium and thallium oxides are released in flue dust when sulfide ores are converted to metal oxides and SO_2.

3.1.2 Reactions

Elemental boron is a semimetal that is remarkably unreactive while the other group 13 elements exhibit metallic properties and reactivity. All group 13 elements have fewer valence electrons than valence orbitals, which generally results in delocalized, metallic bonding. With its high ionization energy, low electron affinity, low electronegativity, and small size, however, boron does not form a metallic lattice with delocalized valence electrons. Instead, boron forms unique and intricate structures that contain multicenter bonds, in which a pair of electrons holds together three or more atoms.

The basic building block of elemental boron is not the individual boron atom but the B_{12} icosahedron. These icosahedra do not pack together very well, the structure of solid boron contains voids, resulting in its low density.

Elemental boron can be induced to react with many nonmetallic elements to give binary compounds that have a variety of applications. For example, plates of boron carbide (B_4C) can stop a 30-caliber, armor-piercing bullet, yet they weigh 10%–30% less than conventional armor. Other important compounds of boron with nonmetals include

(i)   boron nitride (BN), which is produced by heating boron with excess nitrogen

$$2B_{(s)} + N_{2(g)} \xrightarrow{\Delta} 2BN_{(s)}$$
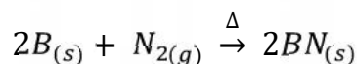
(ii)   boron oxide (B_2O_3), which is formed when boron is heated with excess oxygen

$$4B_{(s)} + O3_{2(g)} \xrightarrow{\Delta} 2B_2O_3$$
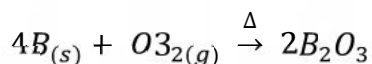
(iii)   boron trihalides (BX_3), which are formed by heating boron with excess halogen

$$2B_{(s)} + 3X_{2(g)} \xrightarrow{\Delta} 2BX_{3(g)}$$
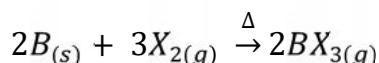
As is typical of elements lying near the dividing line between metals and nonmetals, many compounds of boron are amphoteric, dissolving in either acid or base.

Boron nitride has some similarities with elemental carbon. With eight electrons, the B–N unit is isoelectronic with the C–C unit, and B and N have the same average size and electronegativity as C. The most stable form of n compound (i.e   BN) is similar to graphite, containing six-membered B_3N_3 rings arranged in layers. At high temperature and pressure, hexagonal BN is converted to a cubic structure similar to diamond, which is one of the hardest known substances. Boron oxide (B_2O_3) contains layers of trigonal planar BO_3 groups (analogous to BX_3) in which the oxygen atoms bridge two

boron atoms. It dissolves many metal and nonmetal oxides, including SiO_2, to give a wide range of commercially important borosilicate glasses. A small amount of CoO gives the deep blue color characteristic of cobalt blue glass. At high temperatures, boron also reacts with virtually all metals to give metal borides that contain regular three-dimensional networks, or clusters, of boron atoms. Boron can also form compounds (which contain multicentre bonds), that cannot be explained with simple bonding theories. An example is diborane (B_2H_6) whoch contains two bridging hydrogen atoms (shown in the figure below).

(a) B_2H_6 (b) Al_2Cl_6
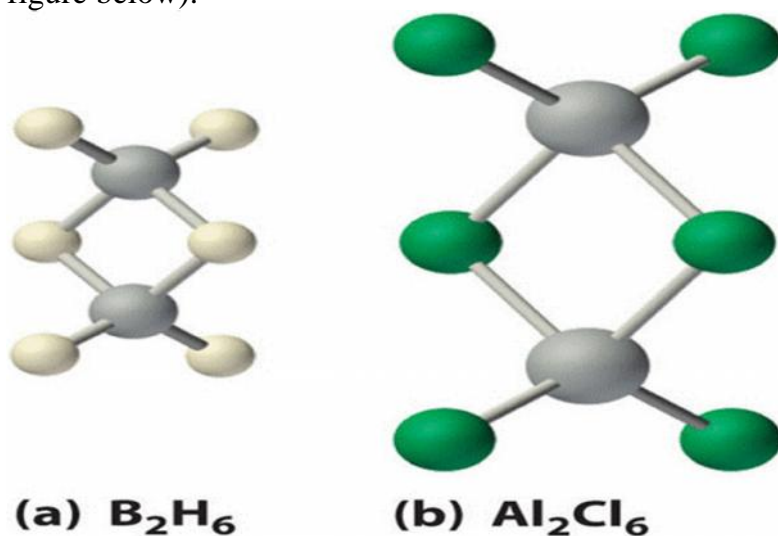
Fig. 1: The Structures of diborane (B_2H_6) and aluminum chloride (Al_2Cl_6). (a) The hydrogen-bridged dimer B_2H_6 contains two three-center, two-electron bonds as described for the $B_2H_7^-$ ion in **Fig. 1** (b) In contrast, the bonding in the halogen-bridged dimer Al_2Cl_6 can be described in terms of electron-pair bonds, in which a chlorine atom bonded to one aluminum atom acts as a Lewis base by donating a lone pair of electrons to another aluminum atom, which acts as a Lewis acid.

An extraordinary variety of polyhedral boron–hydrogen clusters is not uncommon. For example the $B_{12}H_{12}^{2-}$ ion, which has a polyhedral structure similar to the icosahedral B_{12} unit of elemental boron, with a single hydrogen atom bonded to each boron atom. A related class of polyhedral clusters, the carboranes, contain both CH and BH units (see Fig. 2). Replacing the hydrogen atoms bonded to carbon with organic groups have been found to produces substances with novel properties, some of which are currently being investigated for their use as liquid crystals and in cancer chemotherapy.
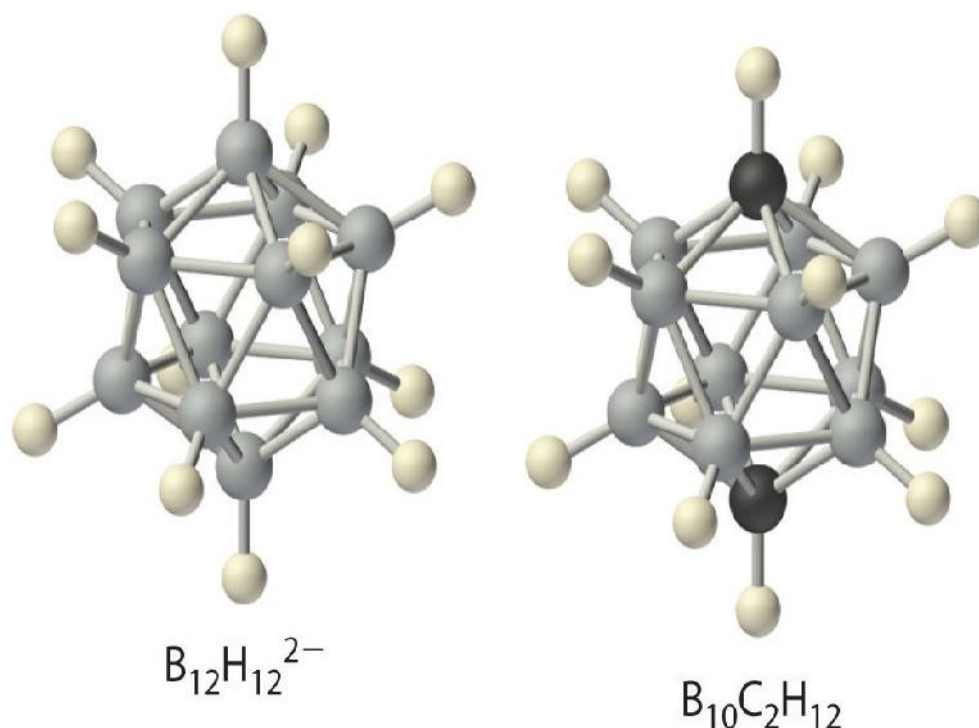
$$B_{12}H_{12}{}^{2-} \qquad\qquad B_{10}C_2H_{12}$$

Fig. 2: Structure of B₁₂H₁₂²⁻ and B₁₀C₂H₁₂

The enthalpy of combustion of diborane (B_2H_6) is -2165 kJ/mol, which is one of the highest known values.

$$B_2H_{6(g)} + 3O_{2(g)} \rightarrow B_2O_{3(g)} + 3H_2O_{(l)} \quad \Delta H^0_{Comb} = -2165 \ kJ/mol$$
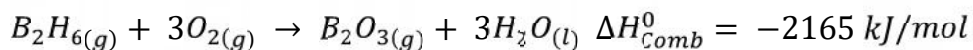
The above reaction can be compared with the combustion of ethane, which also yield oxide of carbon and water but with lower enthalpy value

$$C_2H_{6(g)} + \frac{7}{2}O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)} \quad \Delta H^0_{Comb} = -1560.70 kJ/mol$$
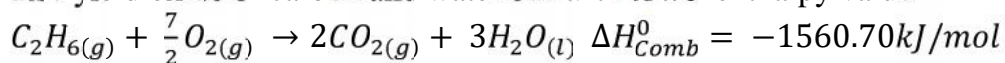
Boron hydrides were used as rocket fuels upto 1960s but was discontinued because boron hydrides are unstable, costly, and toxic. Also, B_2O_3 is highly highly abrasive to rocket nozzles. Reactions carried out during this investigation, however, showed that boron hydrides exhibit unusual reactivity.

Also, boron and hydrogen have closely similar electronegativities, the reactions of boron hydrides are dictated by minor differences in the distribution of electron density in a given compound. In general, two distinct types of reaction are observed. The first is electron-rich species (such as the BH_4^- ion) which are reductants, whereas electron-deficient species (such as B_2H_6) act as oxidants.

Al, Ga, In, and Tl can react readily with the halogens to form compounds with a 1:3 stoichiometry:
$2M(s) + 3X_{2(s,l,g)} \quad 2MX_{3(s)}$ or $M_2X_{6(s)}$

The reaction of Tl with iodine is an exception. However, the product has the stoichiometry TlI_3, it is not thallium(III) iodide, but rather a thallium(I) compound, the Tl^+ salt of the triiodide ion (I_3^-). This compound is formed because iodine is not a a very strong oxidant to oxidize thallium to the +3 oxidation state.

Among all the halides formed by higher group 13 elements, only the fluorides exhibit behaviors that are typical to ionic compound: they have high melting points (>950°C) and low solubility in nonpolar solvents. However, the trichorides, tribromides, and triiodides of aluminium, gallium, and indium, as well as $TlCl_3$ and $TlBr_3$, are more covalent in character and form halogen-bridged dimers. Although the structure of these dimers is similar to that of diborane (B_2H_6), the bonding can be described in terms of electron-pair bonds rather than the delocalized electron-deficient bonding found in diborane.

In water, the halides of the group 13 metals hydrolyze to produce the metal hydroxide $MX_{3(s)} + 3H_2O_{(l)} \quad M(OH)_{3(s)} + 3HX_{(aq)}$
Also, $Al_2(SO_4)_3$ is used to clarify drinking water by the precipitation of hydrated $Al(OH)_3$, which traps particulates. The halides of the heavier metals (In and Tl) are less reactive with water because of their lower charge-to-radius ratio. Instead of forming hydroxides, they dissolve to form the hydrated metal complex ions: $[M(H_2O)_6]^{3+}$.

Aluminum, gallium, and indium also react with the other group 16 elements (chalcogens) to form chalcogenides with the stoichiometry M_2Y_3. However, because Tl(III) is a very strong oxidant, it forms a stable compound with electron-rich anions such as S^{2-}, Se^{2-}, and Te^{2-}. Thallium forms only the thallium(I) chalcogenides with the stoichiometry Tl_2Y. Only aluminium, (like boron) reacts directly with N_2 (at very high temperatures) to give AlN, which is used in transistors and microwave devices as a nontoxic heat sink because of its thermal stability; GaN and InN can be prepared using other methods.

All the metals, except Tl, also react with the heavier group 15 elements (pnicogens) to form the so-called III–V compounds, such as GaAs. These are semiconductors, whose electronic properties, such as their band gaps, differ from those that can be achieved using either pure or doped group 14

elements. For example, nitrogen- and phosphorus-doped gallium arsenide ($GaAs_{1-x-y}P_xN_y$) is used in the displays of calculators and digital watches.
All group 13 oxides dissolve in dilute acid, but Al_2O_3 and Ga_2O_3 are amphoteric. Unlike boron, the heavier group 13 elements do not react directly with hydrogen. Only the aluminum and gallium hydrides are known, but they must be prepared indirectly; AlH_3 is an insoluble, polymeric solid that is rapidly decomposed by water, whereas GaH_3 is unstable at room temperature.

3.1.3 Complex formation

Boron has a relatively limited tendency to form complexes, but aluminum, gallium, indium, and, to some extent, thallium form many complexes. Some of the simplest are the hydrated metal ions [$M(H_2O)_6^{3+}$], which are relatively strong Brønsted–Lowry acids that can lose a proton to form the $M(H_2O)_5(OH)^{2+}$ ion:

$$[M(H_2O)_6]^{3+}_{(aq)} \rightarrow M(H_2O)_5(H( )^{3+}_{(aq)} + H^+_{(aq)}$$
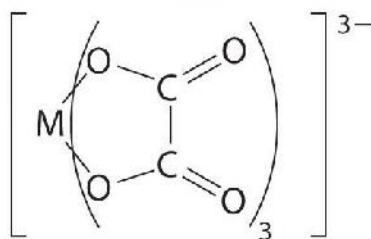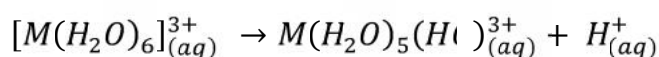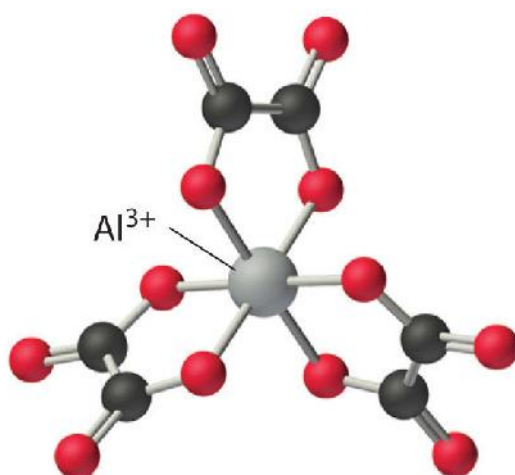
Oxalate ion

Al³⁺–oxalate complex

Group 13 metal ions also form stable complexes with species that contain two or more negatively charged groups, such as the oxalate ion. The stability of such complexes increases as the number of coordinating groups provided by the ligand increases.

In-Text Question (ITQ)
Based on the positions of the group 14 elements C, Si, Ge, Sn, and Pb in the periodic table and the general trends outlined in this section,
(i)   classify these elements as metals, semimetals, or nonmetals.
(ii)   predict which element forms the most stable compounds in the +2-oxidation state.
(iii)   predict which element differs the most from the others in its chemistry.
(iv)   predict which element of group 14 will be chemically most similar to a group 15 element.

3.2   Group 14 elements

The elements in group 14 display greater range of chemical behavior than any other family in the periodic table. Three of the five elements, (including carbon, tin, and lead) are the commonest elements in this group. Activated carbon is a finely divided form of carbon that is produced from the thermal decomposition of organic materials, such as sawdust. It has strong adsorption capacity for most organic and sulphur containing compounds. Therefore, activated carbon is used to decolorize foods, such as sugar, and to purify gases and wastewater.

3.2.1 Preparation and General Properties of Carbon

Pure graphite can be obtained by reacting coke (an amorphous form of carbon used as a reductant in the production of steel) with silica to give silicon carbide (SiC). The SiC is decomposed at very high temperatures (2700 °C) to give graphite according to the following equations

$$SiO_{2(s)} + 3C_{(s)} \xrightarrow{\Delta} SiC_{(s)} + 2CO_{(g)}$$
$$SiC_{(s)} \xrightarrow{\Delta} Si_{(s)} + C_{(graphite)}$$
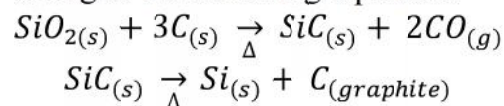
Diamond is an allotrope of carbon that is metastable under normal conditions, with a $G°_f$ of 2.9 kJ/mol against graphite. However, at any pressures greater than 50,000 atm, the diamond structure is favored and is the most stable form of carbon. Since the structure of diamond is more compact than that of graphite, its density is significantly higher (3.51

g/cm^3 versus 2.2 g/cm^3). Because of its high thermal conductivity, diamond powder is used to transfer heat in electronic devices.

The most common sources of diamonds on Earth are ancient volcanic pipes that contain a rock called kimberlite, a lava that solidified rapidly from deep inside the Earth. Most kimberlite formations, however, are much newer than the diamonds they contain

3.2.2 Reactions and Compounds of Carbon

Carbon is the building block of all organic compounds, including biomolecules, fuels, pharmaceuticals, and plastics, whereas inorganic compounds of carbon include metal carbonates, which are found in substances as diverse as fertilizers and antacid tablets, halides, oxides, carbides, and carboranes. Like boron in group 13, the chemistry of carbon differs sufficiently from that of its heavier congeners to merit a separate discussion.

The structures of the allotropes of carbon—diamond, graphite, fullerenes, and nanotubes—are distinct, but they all contain simple electron-pair bonds. Although it was originally believed that fullerenes were a new form of carbon that could be prepared only in the laboratory, fullerenes have been found in certain types of meteorites. Another possible allotrope of carbon has also been detected in impact fragments of a carbon-rich meteorite; it appears to consist of long chains of carbon atoms linked by alternating single and triple bonds, $(–C\ \ C–C\ \ C–)_n$. Carbon nanotubes ("buckytubes") are being studied as potential building blocks for ultramicroscale detectors and molecular computers and as tethers for space stations. They are currently used in electronic devices, such as the electrically conducting tips of miniature electron guns for flat-panel displays in portable computers.

Carbon tetrahalides (CX_4) are known compound, however, they can not be obtained by the direct reaction of carbon with the elemental halogens (X_2) but by indirect methods such as the reaction of methane ith halide (X = Cl or Br) as shown in the following equation

$$CH_{4(g)} + 4X_{2(g)}\ \rightarrow\ CX_{4(g)} + 4H_{(g)}$$

CF₄   CI₄
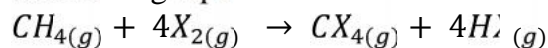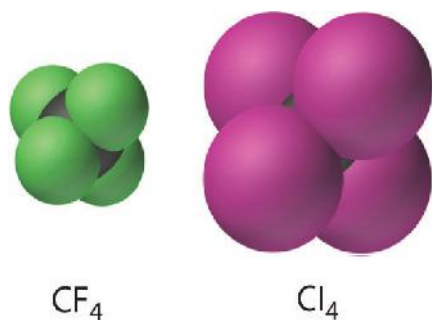
All carbon tetrahalides all have tetrahedral geometry predicted by the valence-shell electron-pair repulsion (VSEPR) model, as shown for CCl₄ and CI₄. Their stability decreases rapidly with the size of the halogen because of poor orbital overlap and increased crowding. Because the C–F bond is about 25% stronger than a C–H bond, fluorocarbons are thermally and chemically more stable than the corresponding hydrocarbons, while having a similar hydrophobic character. A polymer of tetrafluoroethylene ($F_2C=CF_2$), analogous to polyethylene, is the nonstick Teflon lining found on many cooking pans, and similar compounds are used to make fabrics stain resistant (such as Scotch-Gard) or waterproof but breathable (such as Gore-Tex).

$$HCO_2H_{(l)} \xrightarrow{H_2SO_{4(aq)}} CO_{(g)} + H_3O^+_{(aq)} + HS^-_{4(g)}$$
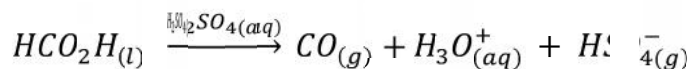
Carbon monoxide also reacts with the halogens to form the oxohalides (COX₂). The commonest oxohalides is phosgene (Cl₂C=O), which is highly poisonous and was used as a chemical weapon during World War I:

$$CO_{(g)} + Cl_{2(g)} \rightarrow Cl_2C = O_{(g)}$$
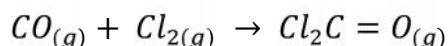
Despite its toxicity, phosgene is an important industrial chemical that is prepared on a large scale, primarily in the manufacture of polyurethanes.
Carbon dioxide can be prepared on a small scale by reacting almost any metal carbonate or bicarbonate salt with a strong acid. As is typical of a nonmetal oxide, CO₂ reacts with water to form acidic solutions containing carbonic acid (H₂CO₃). In contrast to its reactions with oxygen, reacting carbon with sulphur at high temperatures produces carbon disulfide as the only product

$$C_{(s)} + 2S_{(g)} \rightarrow CS_{2(g)}$$
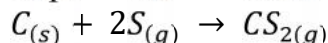
The selenium analog CSe₂ is also known. Both have the linear structure predicted by the VSEPR model, and both are vile smelling (and in the case of CSe₂, highly toxic), volatile liquids. The sulphur and selenium analogues of carbon monoxide, CS and CSe, are unstable because the C Y bonds (Y is S or Se) are much weaker than the C O bond due to poorer pi-orbital overlap.

Binary compounds of carbon with less electronegative elements are called carbides. The chemical and physical properties of carbides depend strongly on the identity of the second element, resulting in three general classes: ionic carbides, interstitial carbides, and covalent carbides. The reaction of carbon at high temperatures with electropositive metals such as those of groups 1 and 2 and aluminum produces ionic carbides, which contain discrete metal cations and carbon anions. The identity of the anions depends on the size of the second element. For example, smaller elements such as beryllium and aluminum give methides such as Be_2C and Al_4C_3, which formally contain the C^{4-} ion derived from methane (CH_4) by losing all four H atoms as protons. In contrast, larger metals such as sodium and calcium give carbides with stoichiometries of Na_2C_2 and CaC_2. Because these carbides contain the C^{4-} ion, which is derived from acetylene (HC CH) by losing both H atoms as protons, they are more properly called acetylides. Reacting ionic carbides with dilute aqueous acid results in protonation of the anions to give the parent hydrocarbons: CH_4 or C_2H_2. For many years, miners' lamps used the reaction of calcium carbide with water to produce a steady supply of acetylene, which was ignited to provide a portable lantern.

The reaction of carbon with most transition metals at high temperatures produces interstitial carbides. Due to the less electropositive nature of the transition metals, these carbides contain covalent metal–carbon interactions, which result in different properties. Most interstitial carbides are good conductors of electricity, have high melting points, and are among the hardest substances known. Interstitial carbides exhibit a variety of nominal compositions, and they are often nonstoichiometric compounds whose carbon content can vary over a wide range. Among the most important are tungsten carbide (WC), which is used industrially in high-speed cutting tools, and cementite (Fe_3C), which is a major component of steel.

Elements with an electronegativity similar to that of carbon form covalent carbides, such as silicon and boron carbides. These substances are extremely hard, have high melting points, and are chemically inert. For example, silicon carbide is highly resistant to chemical attack at temperatures as high as 1600 °C. Because it also maintains its strength at high temperatures, silicon carbide is used in heating elements for electric furnaces and in variable-temperature resistors.

In-Text Question (ITQ)
Explain (using suitable equations) how you can obtain pure graphite from coke

In-Text Question (ITQ)
What is the general geometry of carbon tetrahalides compare to CCl_4?

In-Text Question (ITQ)
Write equation for the production of carbon tetrahalides and explain how it can be produced

In-Text Question (ITQ)
With the aid of suitable equations, state how BN, B_2O_3 and BX_3 can be produced

In-Text Question (ITQ)
Explain the advantage of aluminum sulphate over halides of heavier metals (In and Tl) for the purification of water

In-Text Question (ITQ)
Explain how semiconductors are formed between metals and group 15 elements. Hence state the advantage of semiconductor formed in this way over others

In-Text Question (ITQ)
Consider the reaction between carbon monoxide and chlorine. What is the industrial application of the reaction and also the environmental impact?

In-Text Question (ITQ)
Why is the bond between carbon and the heavier chalcogenides weak?

In-Text Question (ITQ)
What is carbide, what are the factors that affect its chemical and physical properties? Hence list the three types of carbide that you know

In-Text Question (ITQ)
Write short note on interstitial carbides

In-Text Question (ITQ)
Explain how covalent carbides are formed and what their general characteristics are. Give suitable example to justify your answer

In-Text Question (ITQ)
What are the types of carbides formed by groups 1 and 2 and by transition metal elements?

In-Text Question (ITQ)
For each reaction, explain why the given product forms.

(i) $CO_{(g)} + Cl_{2(g)}$ $Cl_2C{=}O_{(g)}$
(ii) $CO_{(g)} + BF_{3(g)}$ $F_3B{:}C\ O_{(g)}$
(iii) $Sr_{(s)} + 2C_{(s)} -$ $SrC_{2(s)}$

3.3   Group 15 elements

The lightest member of group 15 element is nitrogen. Nitrogen is a free element which constitute about 78% by volume of air. However, among all the pnicogens elements, nitrogen was the last to be discovered through the work of Daniel Rutherford/Joseph Black (1772) and Antoine Lavioiser.

About 90% of the nitrogen produced today is used to provide an inert atmosphere for processes or reactions that are oxygen sensitive, such as the production of steel, petroleum refining, and the packaging of foods and pharmaceuticals.

3.3.1 Preparation and General Properties of Nitrogen

The major source of nitrogen gas is the atmosphere. Distillation of liquefied air produces nitrogen gas of purity greater than 99.99%. Laboratory production of pure nitrogen gas can be obtained from the thermal decomposition of sodium azide according to the following equation
$$2NaN_{3(s)} \rightarrow 2Na_{(l)} + 3N_{2(g)}$$

The Earth's crust is relatively poor in nitrogen. The only important nitrogen ores are large deposits of KNO_3 and $NaNO_3$ in the deserts of Chile and Russia, which are believed to have been formed when ancient alkaline lakes evaporated. Therefore, most nitrogen compounds produced on an industrial scale use atmospheric nitrogen as the starting material. Phosphorus, which constitutes only about 0.1% of Earth's crust, is much more abundant in ores than nitrogen. Like aluminum and silicon, phosphorus is always found in combination with oxygen, and large inputs of energy are required to isolate it.
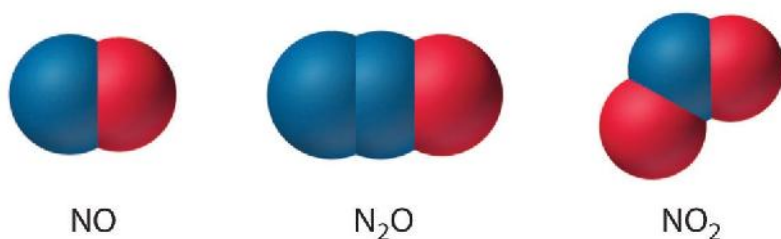
3.3.2 Reactions and Compounds of Nitrogen

Like carbon, nitrogen has four valence orbitals (one 2s and three 2p), so it can participate in with four electron-pair bonds by using sp^3 hybrid orbitals. Unlike carbon, however, nitrogen does not form long chains because of

repulsive interactions between lone pairs of electrons on adjacent atoms. These interactions become important at the shorter internuclear distances encountered with the smaller, second-period elements of groups 15, 16, and 17. Stable compounds with N–N bonds are limited to chains of no more than three N atoms, such as the azide ion (N_3^-).

Nitrogen is the only pnicogen that normally forms multiple bonds with itself and other second-period elements, using   overlap of adjacent np orbitals. Thus the stable form of elemental nitrogen is N_2, whose N N bond is so strong ($D_{N\ N} = 942$ kJ/mol) compared with the N–N and N=N bonds ($D_{N-N} = 167$ kJ/mol; $D_{N=N} = 418$ kJ/mol) that all compounds containing N–N and N=N bonds are thermodynamically unstable with respect to the formation of N_2. In fact, the formation of the N N bond is so thermodynamically favored that virtually all compounds containing N–N bonds are potentially explosive.

In contrast to carbon, nitrogen undergoes only two important chemical reactions at room temperature: The first is the reaction with metallic lithium to form lithium nitride, which is reduced to ammonia by certain microorganisms. At higher temperatures, however, N_2 reacts with more electropositive elements, such as those in group 13, to give binary nitrides, which range from covalent to ionic in character. Like the corresponding compounds of carbon, binary compounds of nitrogen with oxygen, hydrogen, or other nonmetals are usually covalent molecular substances.

NO N_2O NO_2

Few binary molecular compounds of nitrogen are formed by direct reaction of the elements. At elevated temperatures, N_2 reacts with H_2 to form ammonia, with O_2 to form a mixture of NO and NO_2, and with carbon to form cyanogen (N C–C N); elemental nitrogen does not react with the halogens or the other chalcogens. However, all the binary nitrogen halides (NX_3) are known (excepr NF_3) and are toxic, thermodynamically unstable, and potentially explosive. They are prepared by reacting the halogen with NH_3 rather than N_2. Both nitrogen monoxide (NO) and nitrogen dioxide (NO_2) are thermodynamically unstable, with positive free energies of formation. Unlike NO, NO_2 reacts readily with excess water, to form a 1:1 mixture of nitrous acid (HNO_2) and nitric acid (HNO_3) according to the following equation

$$2NO_{2(g)} + H_2O_{(l)} \rightarrow HNO_{3(aq)} + HNO_{2(aq)}$$
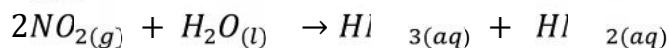
Nitrogen also forms N_2O (dinitrogen monoxide, or nitrous oxide), a linear molecule that is isoelectronic with CO_2 and can be represented as $^-N{=}N^+{=}O$. Like the other two oxides of nitrogen, nitrous oxide is thermodynamically unstable. The structures of the three common oxides of nitrogen are as follows:

At elevated temperatures, nitrogen reacts with highly electropositive metals to form ionic nitrides, such as Li_3N and Ca_3N_2. These compounds consist of ionic lattices formed by M^{n+} and N^{3-} ions. Just as boron forms interstitial borides and carbon forms interstitial carbides, with less electropositive metals nitrogen forms a range of interstitial nitrides, in which nitrogen occupies holes in a close-packed metallic structure. Like the interstitial carbides and borides, these substances are typically very hard, high-melting materials that have metallic luster and conductivity.

Nitrogen also reacts with semimetals at very high temperatures to produce covalent nitrides, such as Si_3N_4 and BN, which are solids with extended covalent network structures similar to those of graphite or diamond. Consequently, they are usually high melting and chemically inert materials. Ammonia (NH_3) is one of the few thermodynamically stable binary compounds of nitrogen with a nonmetal. It is not flammable in air, but it burns in an O_2 atmosphere

$$4NH_{3(g)} + 3O_{2(g)} \rightarrow N_{2(g)} + 6H_2O_{(g)}$$
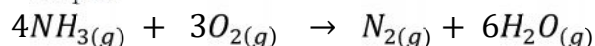
About 10% of the ammonia produced annually is used to make fibers and plastics that contain amide bonds, such as nylons and polyurethanes, while 5% is used in explosives, such as ammonium nitrate, TNT (trinitrotoluene), and nitroglycerine. Large amounts of anhydrous liquid ammonia are used as fertilizer.

Nitrogen forms two other important binary compounds with hydrogen. Hydrazoic acid (HN_3), also called hydrogen azide. Hydrogen axide is a colorless, highly toxic, and explosive substance. Hydrazine (N_2H_4) is also potentially explosive; it is used as a rocket propellant and to inhibit corrosion in boilers.

In-Text Question (ITQ)
Why is it difficult for nitrogen to form long chain molecules unclike carbon?

In-Text Question (ITQ)
How can you prepare nitrogen in the laboratory?

In-Text Question (ITQ)
What is the product of reaction of nitrogen with semi-metals, highly and less electropositive metals at high temperature? Compare the products with those of by carbide and borides.

In-Text Question (ITQ)
What is the reaction that is simple between the transition metals and N, B and C?

In-Text Question (ITQ)
For each reaction, explain why the given products form when the reactants are heated.

(i) $Sr_{(s)} + N_2O_{(g)} \rightarrow SrO_{(s)} + N_{2(g)}$
(ii) $NH_4NO_{2(s)} \rightarrow N_{2(g)} + 2H_2O_{(g)}$
(iii) $Pb(NO_3)_{2(s)} \rightarrow PbO_{2(s)} + 2NO_{2(g)}$

In-Text Question (ITQ)
Predict the product(s) of each reaction and write a balanced chemical equation for each reaction.
$NO_{(g)} + H_2O_{(l)} \rightarrow$
$NH_4NO_{3(s)} \rightarrow$
$Sr_{(s)} + N_{2(g)}$
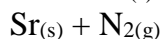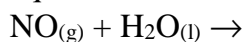
3.4   Group 16 elements

The major element in group 16 is oxygen. The family is called the chalcogens and consists oxygen, sulphur, selenium, tellurium and polonium. These elements are found in nature in both free and combined states. The chalcogens have significant role in life for example, oxygen is needed at time throughout our lives, sulphur is also one of the essential elements responsible for some of the protein structures in all living organisms. Many industries utilize sulphur, but emission of sulphur compounds is often seen more as a problem than the natural phenomenon. The metallic properties of this increase as the atomic number increases. The element polonium has no stable isotopes, and the isotope with mass number 209 has the longest half life of 103 years.

3.4.1 Properties and Periodic Trends

Properties of oxygen are very different from other elements of the group, but they all have 2 elections in the outer s orbital, and 4 electrons in the p orbitals, usually written as s^2p^4

The electron configurations for each element are given below:

- **Oxygen**: $1s^2\ 2s^2\ 2p^4$
- **Sulphur**: $1s^2\ 2s^2p^6\ 3s^2p^4$
- **Selenium**: $1s^2\ 2s^2p^6\ 3s^2p^6d^{10}\ 4s^2p^4$
- **Tellurium**: $1s^2\ 2s^2p^6\ 3s^2p^6d^{10}\ 4s^2p^6d^{10}\ 5s^2p^4$
- **Polonium**: $1s^2\ 2s^2p^6\ 3s^2p^6d^{10}\ 4s^2p^6d^{10}f^{14}\ 5s^2p^6d^{10}\ 6s^2p^4$

Periodic trend of the chalcogens can be summarized as follows,
(i)   The metallic properties increase in the order oxygen, sulphur, selenium, tellurium, or polonium. Polonium is essentially a metal. It was discovered by M. Curie, who named it after her native country Poland.
(ii)   Electronegativity, ionization energy (or ionization potential IP), and electron affinity decrease for the group as atomic weight increases.
(iii)   The atomic radii and melting point increase.
(iv)   Oxygen differs from sulphur in chemical properties due to its small size. The differences between OO and SS are more than the differences between other members.

Metallic character increases down the group, with tellurium classified as a metalloid and polonium as a metal. Melting point, boiling point, density, atomic radius, and ionic radius all increase down **Table 2 : Some properties of group 16 elements**

	Oxygen	Sulphur	Selenium	Tellurium	Polonium
Boiling Pt (°C)	-182.962	444.674	685	989.9	962
Ionization Energy (kJ/mol)	1314	1000	941	869	812
Ionic Radius (pm)	140	184	198	221	

the group. Ionization energy decreases down the group. The most common oxidation state is -2; however, sulphur can also exist at a +4 and +6 state, and +2, +4, and +6 oxidation states are possible for Se, Te, and Po.
Oxygen is a gas at room temperature and 1 atm, and is colourless, odourless, and tasteless. It is the most abundant element by mass in both the Earth's crust and in the human system. It is second to nitrogen as the most abundant element in the atmosphere. There are many commercial uses for oxygen gas,

which is typically obtained through fractional distillation. It is used in the manufacture of iron, steel, and other chemicals. It is also used in water treatment, as an oxidizer in rocket fuel, for medicinal purposes, and in petroleum refining.

Oxygen has two allotropes which are O_2 and O_3. Dioxygen is the most common form of the element. The O_2 bond is very strong, and oxygen can also form strong bonds with other elements. However, compounds that contain oxygen are considered to be more thermodynamically stable than O_2. On the other hand, ozone is a pale-blue poisonous gas with a strong odour. It is a very good oxidizing agent than dioxygen and can be used as a substitute for chlorine in purifying drinking water without giving the water abnormal taste. However, because of its unstable nature, it can disappears and leaves the water unprotected from bacteria. Ozone at very high altitudes in the atmosphere is responsible for protecting the Earth's surface from ultraviolet radiation; however, at lower altitudes it becomes a major component of smog.

Oxygen's primary oxidation states are -2, -1, 0, and -1/2 (in O_2^-), but **-2** is the most common. Typically, compounds with oxygen in +2 oxidation state are called oxides. When oxygen reacts with metals, it forms basic oxides that are mostly ionic in nature because they can dissolve in water and react to form hydroxides. Nonmetal oxides, which form covalent bonds, are simple molecules with low melting and boiling points and are capable of forming acid if dissolve in water.

Compounds with oxygen in an oxidation state of -1 are referred to as *peroxides*. For example, H_2O_2, Na_2O_2 and BaO_2. When oxygen has an oxidation state of -1/2, as in O_2^-, the compound is called a *superoxide*.
Oxygen is rarely the central atom in a structure and can never bond with more than 4 elements due to its small size and its inability to create an expanded valence shell. Oxygen reacts with hydrogen to form water, which is extensively hydrogen-bonded, has a large dipole moment, and is considered an universal solvent.

There are a wide variety of oxygen-containing compounds, both organic and inorganic: oxides, peroxides and superoxides, alcohols, phenols, ethers, and carbonyl-containing compounds such as aldehydes, ketones, esters, amides, carbonates, carbamates, carboxylic acids and anhydrides.
Sulphur

Sulphur is a solid at room temperature and at 1 atm pressure. It is usually yellow, tasteless, and nearly odourless. It is the sixteenth most abundant

element in Earth's crust. It exists naturally in a variety of forms, including elemental sulphur, sulfides, sulfates, and organosulphur compounds. Sulphur is usually mined using the Frasch process, which is useful for recovering sulphur from deposits that are under water or quicksand. Sulphur produced from this process is used in a variety of ways including in vulcanizing rubber and as fungicide to protect grapes and strawberries.

Sulphur is unique in its ability to form a wide range of allotropes, more than any other element in the periodic table. The most common state is the solid S_8 ring because it is the most thermodynamically stable form at room temperature. Sulphur exists in the gaseous form in five different forms (S, S_2, S_4, S_6, and S_8). In order for sulphur to convert between these compounds, sufficient heat must be supplied.

Two common oxides of sulphur are sulphur dioxide (SO_2) and sulphur trioxide (SO_3). Sulphur dioxide is formed when sulphur is combusted in air, producing a toxic gas with a strong odour. These two compounds are used in the production of sulphuric acid, which is used in a variety of laboratory and industrial reactions. Sulphuric acid is one of the top manufactured chemicals in most industrialised countries and are primarily used in the manufacture of fertilizers.

Sulphur also exhibits various oxidation states ranging from -2 to +6. It often serves as the central ion in a compound and can easily form bond with up to 6 atoms. In the presence of hydrogen, it forms hydrogen sulfide, H_2S, a poisonous gas incapable of forming hydrogen bonds and with a very small dipole moment. Hydrogen sulfide can easily be recognized by its strong odour that is similar to that of rotten eggs, but this smell can only be detected at low, nontoxic concentrations. This reaction with hydrogen differentiate between oxygen and sulphur despite their common valence electron configuration and common nonmetallic properties.

A variety of sulphur-containing compounds exist but most of them are organic. The prefix *thio-* in from of the name of an oxygen-containing compound means that the oxygen atom has been substituted with a sulphur atom. General categories of sulphur-containing compounds include thiols (mercaptans), thiophenols, organic sulfides (thioethers), disulfides, thiocarbonyls, thioesters, sulfoxides, sulfonyls, sulfamides, sulfonic acids, sulfonates, and sulfates.

Selenium
Selenium often occurs as a red or black amorphous solid, or a red or grey crystalline structure. The grey crystalline structure is the most stable form.

Selenium has properties that are closely similar to those of sulphur. However, it is more metallic though it is still classified as a nonmetal. It acts as a semiconductor and therefore is often used in the manufacture of rectifiers to convert alternating currents to direct currents. Selenium is also photoconductive, which means that in the presence of light the electrical conductivity of selenium increases. It is also used in the drums of laser printers and copiers. In addition, it has found increased usage as a replacement for lead in plumbing brasses.

It is rare to find selenium in its elemental form in nature; it must typically be removed through a refining process, usually involving copper. It is often found in soils and in plant tissues that have bioaccumulated the element. In large doses, the element is toxic; however, many animals require it as an essential micronutrient. Selenium atoms are found in the enzyme glutathione peroxidase, which destroys lipid-damaging peroxides. In the human body it is an essential cofactor in maintaining the function of the thyroid gland. In addition, some research has shown a correlation between selenium-deficient and an increased risk of contracting the HIV/AIDS virus.

Tellurium
Tellurium is the metalloid of the oxygen family, with a silvery white color and a metallic luster similar to that of tin at room temperature. Like selenium, it is also displays photoconductivity. Tellurium is an extremely rare element, and is commonly found as a telluride of gold. It is often used in metallurgy in combination with copper, lead, and iron. In addition, it is used in solar panels and memory chips for computers. It is not toxic or carcinogenic; however, when humans are exposed to too much of it they develop a garlic-like smell on their breaths.

Polonium
Polonium is a very rare, radioactive metal. There are 33 different isotopes of the element and all of them are radioactive. It exists in a variety of states, and has two metallic allotropes. It dissolves easily into dilute acids. Polonium does not exist in nature in compounds, but it can form synthetic compounds in the laboratory. It is used as an alloy with beryllium to act as a neutron source for nuclear weapons.

Polonium is a highly toxic element. The radiation it emits makes it very dangerous to handle. It can be immediately lethal when applied at the correct dosage, or cause cancer if chronic exposure to the radiation occurs. The best options for treating humans who have come in contact with polonium involves the use of chelating agents.

3.5   Group 17

Chlorine (Cl_2) was the first halogen to be discovered in 1774, followed by iodine (I_2), bromine (Br_2), fluorine (F_2), and astatine (discovered last in 1940). The name "halogen" is derived from the Greek roots hal- ("salt") and -gen ("to form"). Together these words combine to mean "salt former", referencing the fact that halogens form salts when they react with metals. *Halite* is the mineral name for rock salt, a natural mineral consisting essentially of sodium chloride (NaCl). They are also in our daily life, whether it be the fluoride that goes in toothpaste, the chlorine that disinfects drinking water, or the iodine that facilitates the production of thyroid hormones in one's body.

The halogens include fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). They are toxic non metals and are located on the left of the noble gases on the periodic table. Inclusion of astatine (a radioactive element with has short-lived isotopes) in group 17 is based on the similarity of its behaviour to iodine. Because the halogen elements have seven valence electrons, they only require one additional electron to form a full octet. This characteristic makes them more reactive than other non-metal groups.

Halogens form diatomic molecules (of the form X_2, where X denotes a halogen atom) in their elemental states. The bonds in these diatomic molecules are non-polar covalent single bonds. However, halogens readily combine with most elements and are never seen uncombined in nature. As a general rule, fluorine is the most reactive halogen and astatine is the least reactive. All halogens form Group 1 salts with similar properties. In these compounds, halogens are present as halide anions with charge of -1 (e.g. Cl^-, Br^-, etc.). Most of the chemical reactions that involve halogens are redox reactions in aqueous solution. The halogens often form single bonds in -1 oxidation state, with carbon or nitrogen in organic compounds.

3.5.1 Elements in Group 17

Fluorine exists as a diatomic molecule in its free state (F_2) and is the most abundant halogen found in the Earth's crust. Fluorine is the most electronegative element in the periodic table. It appears as a pale-yellow gas at room temperature. Fluorine also has a relatively small atomic radius. Its oxidation state is always -1 except in its elemental, diatomic state (in which its oxidation state is zero). Fluorine is extremely reactive and reacts directly with all elements except helium (He), neon (Ne) and argon (Ar). In H_2O solution, hydrofluoric acid (HF) is a weak acid. Although fluorine is highly electronegative, its electronegativity does not determine its acidity; HF is a

weak acid due to the fact that the fluoride ion is basic (pH>7). In addition, fluorine produces very powerful oxidants. For example, fluorine can react with the noble gas xenon and form the strong oxidizing agent Xenon Difluoride (XeF_2).

Chlorine has the atomic number 17 and the chemical symbol Cl. Chlorine was discovered in 1774 by extracting it from hydrochloric acid. In its elemental state, it forms the diatomic molecule Cl_2. Chlorine exhibits multiple oxidation states, including -1, +1, 3, 5, and 7. At room temperature it appears as a light green gas. Since the bond that forms between the two chlorine atoms is weak, the Cl_2 molecule is very reactive. Chlorine reacts with metals to produce salts called chlorides. Chloride ions are the most abundant ions that dissolve in the ocean. Chlorine also has two isotopes: ^{35}Cl and ^{37}Cl. Sodium chloride is the most prevalent compound of the chlorides. Bromine is a diatomic molecule Br_2 in its elemental form. At room temperature, bromine is a reddish- brown liquid. Its oxidation states vary from -1, +1, 3, 4 and 5. Bromine is more reactive than iodine, but not as reactive as chlorine. Also, bromine has two isotopes: ^{79}Br and ^{81}Br. Bromine consists of bromide salts, which have been found in the sea. The world production of bromide has increased significantly over the years, due to its access and longer existence. Like all of the other halogens, bromine is an oxidizing agent, and is very toxic.

Iodine has oxidation states -1, +1, 5 and 7. Iodine exists as a diatomic molecule, I_2, in its elemental state. At room temperature, it appears as a violet solid. Iodine has one stable isotope: ^{127}I and can be isolated in seawater. Although iodine is not very soluble in water, the solubility may increase if particular iodides are mixed in the solution. Iodine has many important roles in life, including thyroid hormone production.

Astatine is a radioactive element with an atomic number of 85 and symbol At. Its possible oxidation states include: -1, +1, 3, 5 and 7. It is the only halogen that is not a diatomic molecule and it appears as a black, metallic solid at room temperature. Astatine is a very rare element, therefore, little information is available on its activity. Astatine has a very short radioactive half-life, no longer than a couple of hours.
The electronic configuration of the halogens are shown in the Table below. It is evidence for the table that all the halogen requires one electron to attain the stable configuration of the respective noble gas

Table 3: Electronic configuration of the halogen

Halogen	Electronic configuration
F	$1s^2\, 2s^2\, 2p^5$
Cl	$[Ne]3s^2\, 3p^5$
Br	$[Ar]3d^{10}\, 4s^2\, 4p^5$
I	$[Kr]4d^{10}\, 5s^2\, 5p^5$
At	$[Xe]4f^{14}\, 5d^{10}\, 6s^2\, 6p^5$

5.5.2 Period trends for the halogen

3.5.2 Melting and Boiling Points (increases down the group)

The melting and boiling points increase down the group because of the corresponding increase in the strength of the van der Waals forces. The increase in size of the molecule down the group indicates increase in van der Waals interaction giving rise for the observe increase in melting and boiling points (Table 4)

Table 4: Melting and boiling point of the halogens

Halogen	Melting point (°C)	Boiling point (°C)
F	-220	-188
Cl	-101	-35
Br	-7.2	58.8
I	114	184
At	302	337

3.5.3 Atomic Radius (increases down the group)

The size of e nucleus increases down the group $(F < Cl < Br < I < At)$ because the numbers of protons and neutrons increase. In addition, more energy levels are added with each period. This results in a larger orbital, and therefore a longer atomic radius.

Table 5: Covalent and ionic radius of halogens

Halogen	Covalent Radius (pm)	Ionic (X-) radius (pm)
Fluorine	71	133
Chlorine	99	181
Bromine	114	196
Iodine	133	220
Astatine	150	

3.5.4 Ionization Energy (decreases down the group)

If the outer valence electrons are not near the nucleus, it does not take as much energy to remove them. Therefore, the energy required to pull off the outermost electron is not as high for the elements at the bottom of the group since there are more energy levels. Also, the high ionization energy makes the element appear non-metallic. Iodine and astatine display metallic properties, hence ionization energy of the halogen decreases down the group (At < I < Br < Cl < F).

Table 6: First ionization energy of the halogen

Halogen	First Ionization Energy (kJ/mol)
Fluorine	1681
Chlorine	1251
Bromine	1140
Iodine	1008
Astatine	890±40

3.5.5 Electronegativity (decreases down the group)

Electronegativity, symbol , measures the tendency of an atom to attract a shared pair of electrons (or electron density). The number of valence electrons in an atom increases down the group due to the increase in energy levels at progressively lower levels. The electrons are progressively further from the nucleus; therefore, the nucleus and the electrons are not as attracted to each other. An increase in shielding is observed, leading to decrease in electronegativity down the group (At < I < Br < Cl < F).

Table 7: Electronegativity of halogen

Halogen	Electronegativity
Fluorine	4.0
Chlorine	3.0
Bromine	2.8
Iodine	2.5
Astatine	2.2

3.5.6 Electron Affinity (decreases down the group)

Electron affinity is the change in energy (in kJ/mole) of a neutral atom (in the gaseous phase) when an electron is added to the atom to form a negative ion. Since the atomic size increases down the group, electron affinity of the

halogen decreases down the group (At < I < Br < **F** < Cl). An electron will not be as attracted to the nucleus, resulting in a low electron affinity. However, fluorine has a lower electron affinity than chlorine. This can be explained by the small size of fluorine, compared to chlorine.

Table 8: Electron Affinity of Halogens	
Halogen	**Electron Affinity (kJ/mol)**
Fluorine	-328.0
Chlorine	-349.0
Bromine	-324.6
Iodine	-295.2
Astatine	-270.1

3.5.7 Reactivity of Elements (decreases down the group)

The reactivities of the halogens decrease down the group (At < I < Br < Cl < F). This is due to the fact that atomic radius increases in size with an increase of electronic energy levels. This reduces the attraction for valence electrons of other atoms leading to decreasing reactivity. This decrease also occurs because electronegativity decreases down a group indicating that there is less electron pulling, in addition to decrease in oxidizing ability down the group.

3.5.8 Hydrogen Halides and Halogen Oxoacids

Hydrogen Halides
A halide is formed when a halogen reacts with another, less electronegative element to form a binary compound. Hydrogen, for example, reacts with halogens to form halides of the form HX:

- Hydrogen Fluoride: $H_{2(g)} + F_{2(g)} \rightarrow 2HF_{(g)}$
- Hydrogen Chloride: $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$
- Hydrogen Bromide: $H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)}$
- Hydrogen Iodide: $H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$

Hydrogen halides readily dissolve in water to form hydrohalic (*hydrofluoric*, *hydrochloric*, *hydrobromic*, *hydroiodic*) acids. The properties of these acids are
(i)   The acids are formed by the following reaction: $HX_{(aq)} + H_2O_{(l)}$ $X^-_{(aq)} + H_3O^+_{(aq)}$

(i)   All hydrogen halides form strong acids, except HF
(ii)   The acidity of the hydrohalic acids increases in the following order, HF < HCl < HBr < HI

Hydrofluoric acid can etch glass and certain inorganic fluorides over a long period of time.

It may seem counterintuitive to say that HF is the weakest hydrohalic acid because fluorine has the highest electronegativity. However, the H-F bond is very strong; if the H-X bond is strong, the resulting acid is weak. A strong bond is determined by a short bond length and a large bond dissociation energy. Of all the hydrogen halides, HF has the shortest bond length and largest bond dissociation energy.

Halogen Oxoacids
A halogen oxoacid is an acid with hydrogen, oxygen, and halogen atoms. The acidity of an oxoacid can be determined through analysis of the compound's structure. The halogen oxoacids are given below:

- Hypochlorous Acid: $HOCl$
- Chlorous Acid: $HClO_2$
- Chloric Acid: $HClO_3$
- Perchloric Acid: $HClO_4$
- Hypobromous Acid: $HOBr$
- Bromic Acid: $HBrO_3$
- Perbromic Acid: $HBrO_4$
- Hypoiodous Acid: HOI
- Iodic Acid: HIO_3
- Metaperiodic Acid: HIO_4; H_5IO_6

In each of these acids, the proton is bonded to an oxygen atom; therefore, comparing proton bond lengths is not useful in this case. Instead, electronegativity is the dominant factor in the oxoacid's acidity. Acidic strength increases with more oxygen atoms bound to the central atom.

3.5.9 States of Matter at Room Temperature

Table 9 : States of Matter and Appearance of Halogens		
States of Matter (at Room Temperature)	Halogen	Appearance
Solid	Iodine	Violet
	Astatine	Black/Metallic [Assumed]
Liquid	Bromine	Reddish-Brown
Gas	Fluorine	Pale Yellow-Brown
	Chlorine	Pale Green

The colour of the halogen is a consequence of the absorption of visible light by the molecules, which causes electronic excitation. Fluorine absorbs violet light, and therefore appears light yellow. Iodine absorbs yellow light and appears violet (yellow and violet are complementary colors). Generally, the colour of the halogens grow darker down the group:

- Fluorine   pale yellow/brown
- Chlorine   pale green
- Bromine   red-brown
- Iodine   violet
- Astatine*   black/metallic

In closed containers, liquid bromine and solid iodine are in equilibrium with their vapors, which can often be seen as colored gases. Although the color for astatine is unknown, it is assumed that astatine must be darker than iodine's violet (i.e. black) based on the preceding trend.

3.5.10 Oxidation States of Halogens in Compounds

As a general rule, halogens usually have an oxidation state of -1. However, if the halogen is bonded to oxygen or to another halogen, it can adopt different states: the -2 rule for oxygen takes precedence over this rule; in the case of two different halogens bonded together, the more electronegative atom takes precedence and adopts the -1 oxidation state.

For example, chlorine has an oxidation state of -1, and iodine will have an oxidation of +1. Chlorine is more electronegative than iodine, therefore giving it the -1 oxidation state.

Oxygen has a total oxidation state of -8 (-2 charge x 4 atoms= -8 total charge). Hydrogen has a total oxidation state of +1. Adding both of these values together, the total oxidation state of the compound so far is -7. Since the final oxidation state of the compound must be 0, bromine's oxidation state is +7.

One third exception to the rule is this: if a halogen exists in its elemental form (X2), its oxidation state is zero.

Table 10: Oxidation States of Halogens	
Halogen	**Oxidation States in Compounds**
Fluorine	(always) -1*
Chlorine	-1, +1, +3, +5, +7
Bromine	-1, +1, +3, +4, +5
Iodine	-1, +1,+5, +7
Astatine	-1, +1, +3, +5, +7

In-Text Question (ITQ)
Why does fluorine always have an oxidation state of-1 in its compounds?

3.5.11 Applications of Halogens

Fluorine: Although fluorine is very reactive, it serves many industrial purposes. For example, it is a key component of the plastic *polytetrafluoroethylene* (called *Teflon-TFE* by the DuPont company) and certain other polymers, often referred to as fluoropolymers.

Chlorofluorocarbons (CFCs) are organic chemicals that were used as refrigerants and propellants in aerosols before growing concerns about their possible environmental impact led to their discontinued use.

Hydrochlorofluorocarbons (HFCs) are now used instead. Fluoride is also added to toothpaste and drinking water to help reduce tooth decay. Fluorine also exists in the clay used in some ceramics. Fluorine is associated with generating nuclear power as well. In addition, it is used to produce fluoroquinolones, which are antibiotics. Below is a list of some of fluorine's important inorganic compounds.

Table 10: Important Inorganic Compounds of Fluorine	
Compound	**Uses**
Na_3AlF_6	Manufacture of aluminum
BF_3	Catalyst
CaF_2	Optical components, manufacture of HF, metallurgical flux
ClF_3	Fluorinating agent, reprocessing nuclear fuels
HF	Manufacture of F_2, AlF_3, Na_3AlF_6, and fluorocarbons
LiF	Ceramics manufacture, welding, and soldering
NaF	Fluoridating water, dental prophylaxis, insecticide
SF_6	Insulating gas for high-voltage electrical equipment
SnF_2	Manufacture of toothpaste
UF_6	Manufacture of uranium fuel for nuclear reactors

Chlorine: Chlorine has many industrial uses. It is used to disinfect drinking water and swimming pools. Sodium hypochlorite (NaClO) is the main component of bleach. Hydrochloric acid, sometimes called muriatic acid, is a commonly used acid in industry and laboratories. Chlorine is also present in polyvinyl chloride (PVC), and several other polymers. PVC is used in wire insulation, pipes, and electronics. In addition, chlorine is very useful in the pharmaceutical industry. Medicinal products containing chlorine are used to treat infections, allergies, and diabetes. The neutralized form of hydrochloride is a component of many medications. Chlorine is also used to sterilize hospital machinery and limit infection growth. In agriculture, chlorine is a component of many commercial pesticides: DDT (dichlorodiphenyltrichloroethane) was used as an agricultural insecticide, but its use was discontinued.

Bromine: Bromine is used in flame retardants because of its fire-resistant properties. It also found in the pesticide methyl bromide, which facilitates the storage of crops and eliminates the spread of bacteria. However, the excessive use of methyl bromide has been discontinued due to its impact on the ozone layer. Bromine is involved in gasoline production as well. Other uses of bromine include the production of photography film, the content in fire extinguishers, and drugs treating pneumonia and Alzheimer's disease.

Iodine: Iodine is important in the proper functioning of the thyroid gland of the body. If the body does not receive adequate iodine, a goiter (enlarged thyroid gland) will form. Table salt now contains iodine to help promote proper functioning of the thyroid hormones. Iodine is also used as an antiseptic. Solutions used to clean open wounds likely contain iodine, and it is commonly found in disinfectant sprays. In addition, silver iodide is important for photography development.

Astatine: Because astatine is radioactive and rare, there are no proven uses for this halogen element. However, there is speculation that this element could aid iodine in regulating the thyroid hormones. Also, ^{211}At has been used in mice to aid the study of cancer.

3.6   Group 18

he noble gases (Group 18) are located in the far right of the periodic table and were previously referred to as the "inert gases" due to the fact that their filled valence shells (octets) make them extremely nonreactive.

3.6.1 The Chemical Properties

Noble gases are odorless, colorless, nonflammable, and monotonic gases that have low chemical reactivity.

| Atomic Number	Element	Number of Electrons/Shell
2	Helium	2
10	Neon	2,8
18	Argon	2,8,8
36	Krypton	2,8,18,8
54	Xenon	2,8,18,18,8
86	Radon	2,8,18,32,18,8

The full valence electron shells of these atoms make noble gases extremely stable and unlikely to form chemical bonds because they have little tendency to gain or lose electrons. Although noble gases do not normally react with other elements to form compounds, there are some exceptions. Xe may form compounds with fluoride and oxide.

Examples
Xenon Difluoride (XeF_2XeF_2)
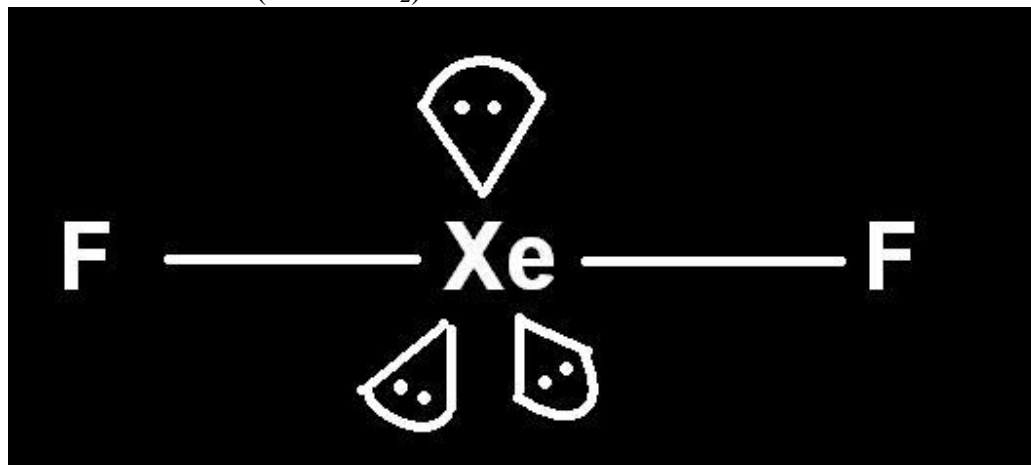
Dense white crystallized solid
Powerful fluorinating agent
Covalent inorganic fluorides
Stable xenon compound
Decomposes on contact with light or water vapor
Linear geometry
Moisture sensitive
Low vapor pressure
Xenon Tetrafluoride (XeF_4XeF_4)
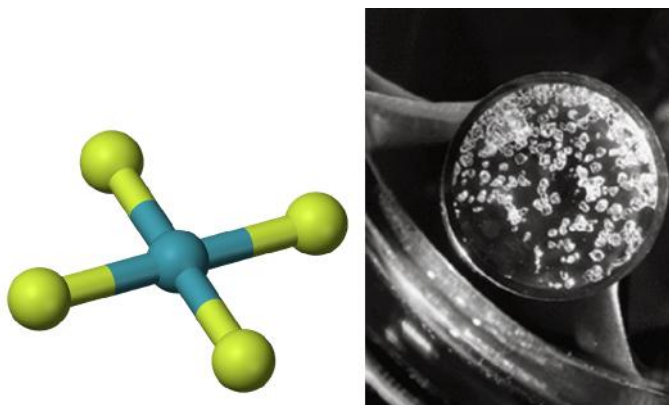
Argonne announced the creation of xenon tetrafluoride, the first simple compound of xenon, a noble gas widely thought to be chemically inert.
Colorless Crystals
Square planar geometry
Discovered in 1963
Xenon Hexafluoride (XeF_6XeF_6)
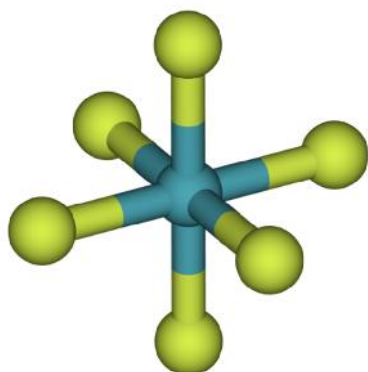
Strongest fluorinating agent

Colorless solid

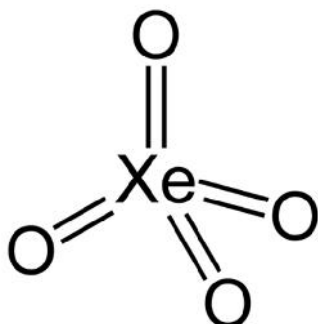Highest coordination of the three binary fluorides of xenon (XeF2XeF2 and XeF4XeF4)

Formation is exergonic, and the compound is stable at normal temperatures

Readily sublimes into intense yellow vapors

Structure lacks perfect octahedral symmetry

Example 2: Xenon Oxide

Xenon Tetroxide (XeO4)

Yellow crystalline solid

Relatively stable

Oxygen is the only element that can bring xenon up to its highest oxidation state of +8

Two other short-lived xenon compounds with an oxidation state of +8, XeO_3F_2 and XeO_2F_4, are produced in the reaction of xenon tetroxide with xenon hexafluoride.

Example 3: Radon Compounds

Radon difluoride (RnF2) is one of the few reported compounds of radon. Radon reacts readily with fluorine to form a solid compound, but this decomposes on attempted vaporization and its exact composition is uncertain. The usefulness of radon compounds is limited because of the noble

gas's radioactivity. The longest-lived isotope, 222Ra, has a half-life of only 3.82 days.

In-Text Question (ITQ)
What is the major differences between diamond and graphite and of what application are is one of them better than the other

SELF ASSESSMENT EXERCISE

i. Why is it difficult for group 13 elements to form compound in with four nearest neighbouring atoms? (Use aluminum and boron as examples)

ii. Give reasons why the ionic compounds of second period elements of group 13 have more covalent character compare to the heavier congeners

iii Explain why it is difficult for group 13 elements to use d-block orbital for bonding and what is the consequence?

iv What are the major differences between the lightest main group elements and their heavier congeners? (Use nitrogen and phosphorus to explain your answer)

v Use Li/Mg, Be/Al and B/Si to explain the concept of diagonal and their effect on the behaviour of main group elements

vi Explain the concept of inert pair effect with respect to group 13 to 17 elements

vii Briefly describe the steps involves in the preparation and purification of boron (provide all relevant equations)

viii. Compare and contrast the chemistry of boron and other group 13 elements

ix What is the basic building block of elemental boron?

x Explain why boron is no longer use as fuel in aircrafts?

xi Explain why the following reactions led to the products that are indicated in the equations
     a. $B_2H_{6(g)} + 3O2(g)$ $B_2O_{3(s)} + 3H_2O_{(l)}$
     b. $BCl_{3(l)} + 3H_2O_{(l)}$ $B(OH)_{3(aq)} + 3HCl_{(aq)}$
     c. $2BI_3(s)+3H_{2(g)-}$ $16B12(s)+6HI(g)2BI3(s)+3H2(g)$ $16B12(s)+6HI(g)$

xii Complete and balance the following chemical equations
$B_2H_{6(g)} + H_2O_{(l)} \rightarrow$
$BBr_{3(l)}+O_{2(g)} \rightarrow$
$B_2O_{3(s)}+Ca_{(s)} \rightarrow$

4.0   CONCLUSION

Groups 13 to 18 constitute the group in the periodic table. Elements in these groups have closely similar properties but as the period increases some variation such as metallic, nonmetallic and semi-metallic properties are observed. These set of elements have significant industrial and life applications indicating their compounds (hence bonding and geometry), behaviour and other properties provide relevant information to their usefulness. Elements in period 17 are uniquely toxic.

5.0   SUMMARY

Compounds of the group 13 elements with oxygen are thermodynamically stable. Many of the anomalous properties of the group 13 elements can be explained by the increase in Z_{eff} moving down the group. Isolation of the group 13 elements requires a large amount of energy because compounds of the group 13 elements with oxygen are thermodynamically stable. Boron behaves chemically like a nonmetal, whereas its heavier congeners exhibit metallic behavior. Many of the inconsistencies observed in the properties of the group 13 elements can be explained by the increase in Z_{eff} that arises from poor shielding of the nuclear charge by the filled $(n - 1)d^{10}$ and $(n - 2)f^{14}$ subshells. Instead of forming a metallic lattice with delocalized valence electrons, boron forms unique aggregates that contain multicenter bonds, including metal borides, in which boron is bonded to other boron atoms to form three-dimensional networks or clusters with regular geometric structures. All neutral compounds of the group 13 elements are electron deficient and behave like Lewis acids. The trivalent halides of the heavier elements form halogen-bridged dimers that contain electron-pair bonds, rather than the delocalized electron-deficient bonds characteristic of diborane. Their oxides dissolve in dilute acid, although the oxides of aluminum and gallium are amphoteric. None of the group 13 elements reacts directly with hydrogen, and the stability of the hydrides prepared by other routes decreases as we go down the group. In contrast to boron, the heavier group 13 elements form a large number of complexes in the +3 oxidation state.

The chemistry of the third-period element in a group is most representative of the chemistry of the group because the chemistry of the second-period elements is dominated by their small radii, energetically unavailable d orbitals, and tendency to form bonds with other atoms. The most important unifying principle in describing the chemistry of the elements is that the systematic increase in atomic number and the orderly filling of atomic orbitals lead to periodic trends in atomic properties. The most fundamental

property leading to periodic variations is the effective nuclear charge (Z_{eff}). Because of the position of the diagonal line separating metals and nonmetals in the periodic table, the chemistry of groups 13, 14, and 15 is relatively complex. The second-period elements (n = 2) in each group exhibit unique chemistry compared with their heavier congeners because of their smaller radii, energetically unavailable d orbitals, and greater ability to form bonds with other atoms. Increasing ionization energies and decreasing bond strengths lead to the inert-pair effect, which causes the heaviest elements of groups 13–17 to have a stable oxidation state that is lower by 2 than the maximum predicted for their respective groups.

The stability of the carbon tetrahalides decreases as the halogen increases in size because of poor orbital overlap and steric crowding. Carbon forms three kinds of carbides with less electronegative elements: ionic carbides, which contain metal cations and C^{4-} (methide) or C_2^{2-} (acetylide) anions; interstitial carbides, which are characterized by covalent metal–carbon interactions and are among the hardest substances known; and covalent carbides, which have three-dimensional covalent network structures that make them extremely hard, high melting, and chemically inert.

Nitrogen behaves chemically like nonmetals, Nitrogen forms compounds in nine different oxidation states. Nitrogen does not form stable catenated compounds because of repulsions between lone pairs of electrons on adjacent atoms, but it does form multiple bonds with other second-period atoms. Nitrogen reacts with electropositive elements to produce solids that range from covalent to ionic in character. Reaction with electropositive metals produces ionic nitrides, reaction with less electropositive metals produces interstitial nitrides, and reaction with semimetals produces covalent nitrides

6.0   TUTOR MARK ASSIGNMENTS

1.   State the various allotropes and oxidation states of sulphur
2.   What is the unique differences between the chemistry of oxygen and sulphur
3.   What is photoconductivity
4.   What is the role of germanium, selenium and polonium in conductivity over other members of the same group
5.   State the name of the compound that has oxygen in the oxidation state of -1
6.   State the various oxidation of chlorine and give one example for each of the oxidation state

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