NATIONAL OPEN UNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLOGY

COURSE CODE: CHM 204

COURSE TITLE: STRUCTURE AND BONDING

COURSE GUIDE

CHM 204
STRUCTURE AND BONDING

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INTRODUCTION

A chemical structure composes molecular geometry, electronic structure and crystal structure of molecules. Molecular geometry refers to the spatial arrangement of atoms in a molecule and the chemical bonds that hold the atoms together. Molecular geometry can range from the very simple molecules, such as diatomic oxygen or nitrogen molecules, to the very complex, such as protein or DNA molecules. Molecular geometry can be roughly represented using a structural formula. Electronic structure describes the occupation of a molecule's molecular orbitals.

Atoms of almost every element have the ability to combine with other atoms to form more complex structures. The forces of attraction that bind them together are chemical bonds. To understand chemistry, the nature and origin of chemical bonds is important, since the basis of chemical reactions is the forming and the breaking of bonds and the changes in bonding forces.

There are two main classes of bonding forces: covalent bonds and ionic bonds. Covalent bonding deals with the sharing of electrons between atoms. Ionic bonding deals with the transfer of electrons between atoms. The theory of chemical structure was first developed by Aleksandra Butlerov, stated that the chemical compounds are not a random cluster of atoms and functional groups but structures with definite order formed according to the valency of the composing atoms.

COURSE DESCRIPTION

Structure and Bonding (CHM 204) is a course which explores and expands upon many of the ideas covered in CHM 101 (Introductory Inorganic Chemistry). This course sets a foundation for scientific inquiry, motivates and emphasises scientific thinking, and exposes students to the origin of structure and bonding in chemistry.

You may think you do not need some of the contents now, but you will learn something along the way. And, hopefully at some point during the course of the semester something will spark your curiosity or you will make a valuable connection between chemistry and your chosen field of study.

WHAT YOU WILL LEARN IN THIS COURSE

In this course, you will learn the contribution of some notable scientists to the structure of an atom, the structure and properties of the atom as well as the trends in the variation of atomic properties in the periodic table.

You will learn a more detailed picture of molecules - including some which do not obey the *octet* rule. You will learn how both the shapes and bonding of molecules may be described in terms of orbitals. In addition, it will become apparent that the distinction between covalent and ionic bonding is not as sharp as it may have seemed. You will find that many covalent molecules are electrically unbalanced, causing their properties to tend toward those of ion pairs. Rules will be developed so that you can predict which combinations of atoms will exhibit this kind of behaviour.

COURSE AIMS

The course aims to introduce aspects of the structure and bonding of main group elements and compounds. You will learn the classical and modern ideas about the development of atomic structure. They will also learn the atomic properties and their variation in the periodic table. The course is also intended to make learners understand the concept of bonding and the theories that explain the concept.

COURSE OBJECTIVES

At the end of the course, you should be able to:

- describe the nature and structure of atom as well as its electronic structure
- relate the electron configuration of an atom to its position in the periodic table
- apply the rules for the filling of electrons in atomic orbitals
- write out the electron configurations of atoms
- describe various types of primary bonds including ionic, covalent and metallic
- describe various types of secondary bonds and differentiate between these and primary bonds
- explain the use of valence shell electron pair repulsion theory (VSEPR) in predicting molecular shapes.

WORKING THROUGH THIS COURSE

The course is in three modules which are subdivided into 11 units. It is required that you study the units in details, attend tutorial classes and participate in group discussion with classmates.

COURSE MATERIALS

You will be provided with the following materials:

1. Course Guide
2. Study Units

STUDY UNITS

The following are the three modules and the eight units contained in this course:

Module 1

Unit 1	Bohr’s Model of the Atom
Unit 2	The Quantum-Mechanical Model of the Atom

Module 2

Unit 1	The Electronic Structure of the Representative Elements
Unit 2	The Periodic Table and Atomic Properties

Module 3

Unit 1	Ionic Bonding
Unit 2	The Covalent Bond
Unit 3	Other Types of Bonding
Unit 4	Bonding Theories and Molecular Geometry

Understanding the structure and bonding of molecules is fundamental to understand their properties and reactions. This is because the properties and reactions are controlled by the interactions between molecules which in turn dictate the types of bonds within those molecules.

In Module 1, the contributions of notable scientists to the structure of the atoms are explored.

The Bohr’s model of the atom is ideal for people who do not understand what an atom is, as of yet. It is very simple, but as things get more complicated, such as multi-electron systems, this model will not be sufficient. This model of the atom has now been replaced with quantum mechanics. A more sophisticated theory of the electronic structure of the atom is described in Unit 2 - wave mechanics. It does not only give results as good as the Bohr theory for the case of the hydrogen atom, but also can be used to explain both the energies and the intensities of the spectral lines of hydrogen. Moreover, approximate descriptions of atoms which have more than one electron may be given in terms of this theory.

In Module 2, the rules for writing the electronic configurations of the representative elements as well as those of their monatomic ions are described. The elements have also been classified into groups in the Periodic Table, and the characteristic properties of elements in each group were explored. Also, the atomic properties – atomic (and ionic) radius, ionisation energy, electron affinity and electronegativity are discussed. The trends in the variation of these properties among the elements in the periodic table are examined.

Module 3 explained the basic principles behind chemical bonding, and how this principle explains the observed structure of chemical compounds. This module focused on the interactions that lead to the formation of chemical bonds. We classify these bonds into two broad groups: ionic bonds which are the electrostatic forces that exist between ions of opposite charge, and covalent bonds, which result from the sharing of electrons by two atoms. Other types of bonding include metallic bonds, which bind together the atoms in metals, the hydrogen bond, which only forms between hydrogen and the elements oxygen (O), nitrogen (N), or (less commonly) fluorine (F).

The formation of bonds involves interactions of the outermost electrons of atoms which is their valence electrons. The valence electrons of an atom can be represented by electron-dot symbols, called Lewis symbols. The tendencies of atoms to gain, lose, or share their valence electrons often follow the octet rule, which can be viewed as an attempt by atoms to achieve a noble-gas electron configuration.

The prediction of molecular shape using the VSEPR model is also discussed in this module.

TEXTBOOKS AND REFERENCES

There are numerous books and other materials that treat Structure and Bonding; some of these are listed at the end of units. In addition, the internet provides a lot of information relating to the course title; the learner is encouraged to use the internet, though with some level of caution. The learner may wish to consult any of the following resources in aid of effective learning:

Author (2011). *General Chemistry: Principles and Modern Applications.* Upper Saddle River: Pearson Education Inc.

Hein, M. & Arena, S. (2000). *Foundations of College Chemistry.* Pacific Grove: Brooks/Cole Publishing Company.

Hollas, M. J. (2002). *Basic Atomic and Molecular Spectroscopy*. Cambridge: Royal Society of Chemistry.

Workman, J. (1998). *Applied Spectroscopy: A Compact Reference for Practitioners*. San Diego: Academic Press.

Martin, S. S. (2000). *Chemistry: The Molecular Nature of Matter and Change*. (2nd ed.). Boston: McGraw-Hill, pp. 277-284, 293-307.

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.

SUMMARY

CHM 204: Structure and Bonding introduces the main features of atoms and accounts for their position in the Periodic Table. We shall discuss how some of the properties of an element are related to its location in the Periodic Table.. The course also explains, in terms of the electronic structures of the atoms, how atoms bond together to form compounds. It shows how to predict the types of compounds an element can form, the number of bonds it can make with other atoms, and how the valence electrons are reorganised when a bond is formed.

MAIN COURSE

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MODULE 1

UNIT 1 BOHR'S MODEL OF THE ATOM

CONTENTS

1.0 INTRODUCTION

In the early 20th century, experiments by Ernest Rutherford established that atoms consisted of a diffuse cloud of negatively charged electrons surrounding a small, dense, positively charged nucleus. Given this experimental data, Rutherford considered a planetary-model atom, the Rutherford model of 1911: "electrons orbiting round a solar nucleus" – however, said planetary-model atom has a technical difficulty. The laws of classical mechanics (i.e. the Larmor formula), predict that the electron will release electromagnetic radiation while orbiting a nucleus. Because the electron would lose energy, it would gradually spiral inwards, collapsing into the nucleus. This atom model is disastrous, because it predicts that all atoms are unstable. Also, as the electron spirals inward, the emission would gradually increase in frequency as the orbit gets smaller and faster. This would produce a continuous smear, in frequency, of electromagnetic radiation. However, late 19th century experiments with electric discharges have shown that atoms will only emit light (that is, electromagnetic radiation) at certain discrete frequencies.

To overcome this difficulty, Niels Bohr proposed in 1913, what is now called the **Bohr model of the atom.**

2.0 OBJECTIVES

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

- describe the components of the atom
- describe the principles of atomic excitation and de-excitation
- state the origin of the spectral lines in the hydrogen spectrum
- explain the postulates which altogether make up the Bohr Theory
- identify the various line series in the hydrogen spectrum
- state the shortcomings of the Bohr Theory.

3.0 MAIN CONTENT

3.1 Composition of the Atom

Atoms have a definite structure. This structure determines the chemical and physical properties of matter. This atomic structure was not fully understood until the discovery of the neutron in 1932. The history of the discovery of atomic structure is one of the most interesting and profound stories in science. In 1910 Rutherford was the first to propose what is accepted today as the basic structure of the atom. Today, the Rutherford model is called the "planetary" model of the atom. In the planetary model of the atom, there exists a nucleus at the centre made up of positively charged particles called "protons" and electrically neutral particles called "neutrons". These particles that surround or "orbit" the nucleus are the electrons. In elements, the number of electrons equals the number of protons.

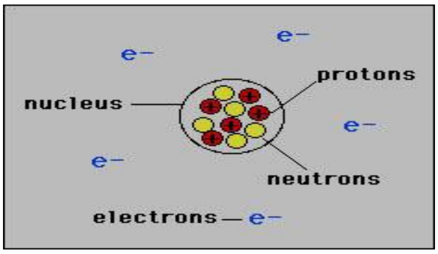


Fig. 1.1: Composition of the Atom

The Figure 1 above greatly exaggerates the size of the nucleus relative to that of the atom. The nucleus is about 100,000 times smaller than the atom. Nevertheless, the nucleus contains essentially all of the mass of the atom. In order to discuss the mass of an atom, we have to define a new unit of mass appropriate to that of an atom. This new unit of mass is called the **atomic mass unit** or amu. The conversion between the amu and gram is:

1 amu = 1.67 x10^{-24} g. The mass, in amu, of the three particles is given in the table below:

Table 1.1: Properties of the Sub-Atomic Particles

Name	Symbol	Electrical Charge	Mass (amu)
Electron	e	-1	0.000549
Proton	P	+1	1.00728
Neutron	n	0	1.00867

Note that the mass of an electron is about 2000 times smaller than that of the proton and neutron. Also note that the mass of the proton and neutron is close to 1 amu. This is a useful fact to remember. If the number of electrons does not equal the number of protons in the nucleus then the atom is an ion:

- **cation:** number of electrons < number of protons
- **anion:** number of electrons > number of protons

3.2 Atomic Excitation and De-Excitation

Atoms can make transitions between the orbits allowed by quantum mechanics by absorbing or emitting exactly the energy difference between the orbits. Figure 1.2 shows an atomic excitation caused by absorption of a photon and an atomic de-excitation caused by emission of a photon.

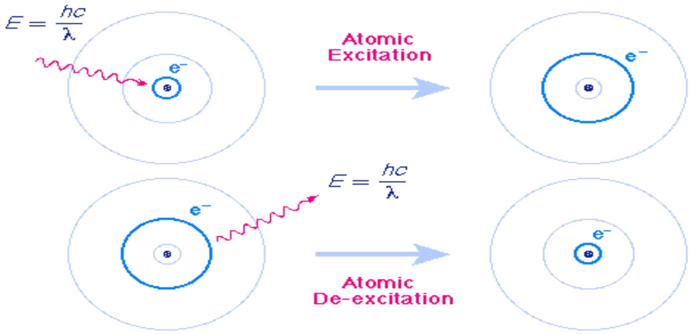


Fig. 1.2: Excitation by Absorption of Light and De-Excitation by Emission of Light

In each case, the wavelength of the emitted or absorbed light is equal such that the photon carries the energy difference between the two orbits. This energy may be calculated by dividing the product of the Planck constant and the speed of light *hc* by the wavelength of the light. Thus, an atom can absorb or emit only certain discrete wavelengths (or equivalent frequencies or energies).

3.3 Atomic Spectra

After an atom absorbs a quantum of energy, it will be transited to an excited state relative to its normal (ground) state. When an excited atom returns to the ground state, it emits light. For example, when glass is heated in a flame; the yellow light observed which is as a result of the excited sodium atoms in the glass being returned to their ground state. Similarly, the familiar red light of neon signs is due to neon atoms which have been excited by an electrical discharge. When light from excited atoms is viewed through a spectroscope, images of the slit appear along the scale of the instrument as a series of coloured lines. The various colours correspond to light of definite wavelengths, and the series of lines is called a **line spectrum**. The line spectrum of each element is the characteristic of that element and its spectrum may be used to identify it. The simplest spectrum is that of hydrogen, the simplest element (Figure 1.3).

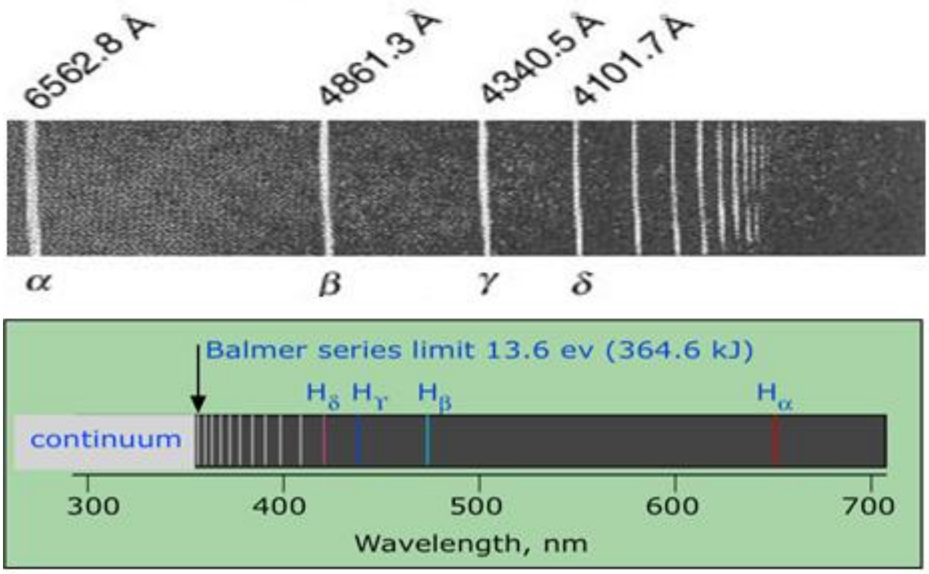


Fig. 1.3: Balmer Series of Hydrogen Atom; Spectral Lines in the Visible

The part of the hydrogen spectrum which appears as **visible** light is shown in Figures 1.3. It should be noted that the lines at shorter wavelengths have progressively lower intensities. The wavelengths of successive lines are closer and closer together until they finally become a continuum, a region of continuous faint light. In 1885, J.J. Balmer suggested that the lines in the visible spectrum of hydrogen could be represented by the equation

$$\bar{\upsilon} = \frac{1}{\lambda} = R\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right)$$

Where $\bar{\upsilon}$ is the wavenumber (inverse of wavelength), n_1 has the value 2, n_2 is an integer having the values 3, 4, 5,....∞. The value of the constant *R* is ~ 109,677.581 cm^{-1}. It is known as the Rydberg constant.

3.4 The Bohr Theory

Although the Balmer equation successfully represented the hydrogen spectrum, there was no theoretical justification for it. In 1914, Niels Bohr proposed a theory of the hydrogen atom which explained the origin of its spectrum. This theory also led to an entirely new concept of atomic structure. The Bohr model of the hydrogen atom was based on four postulates.

1st Postulate: The hydrogen atom consists of a nucleus containing a proton (and therefore having a charge of +*e*), and an electron (with a charge of –*e*) moving about the nucleus in a circular orbit of radius *r* (Figure 1.4).

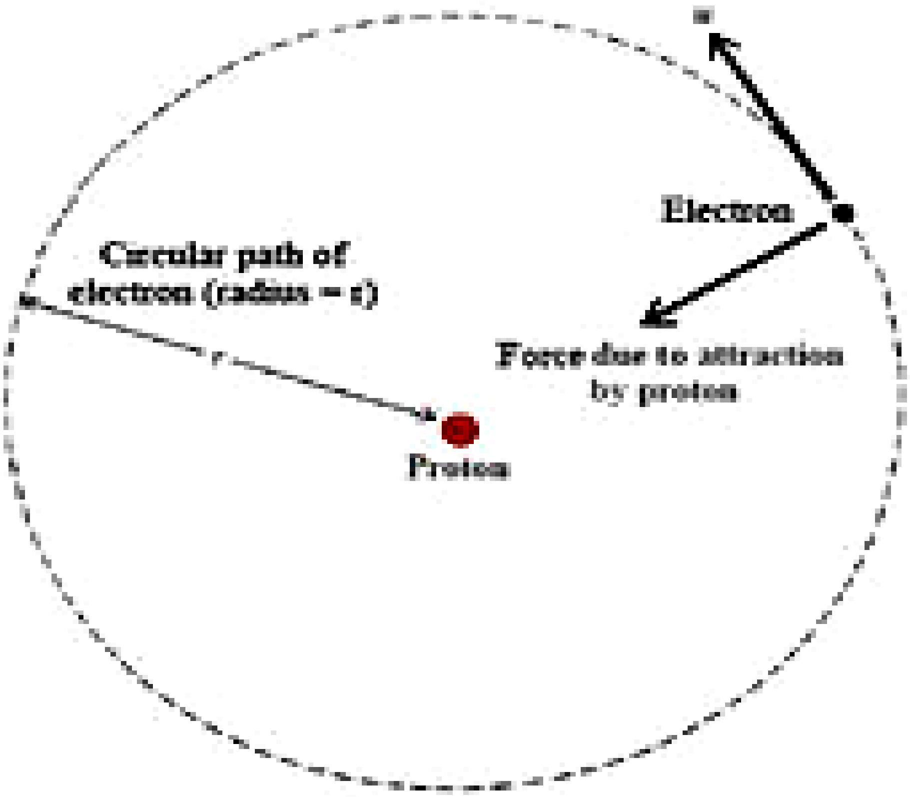


Fig. 1.4: The Force of Attraction keeps bending the Path of the Electron toward the Nucleus and away from the Straight-line Motion

Note: the net result is a circular path.

According to Coulomb's law, the force of attraction between the nucleus and the electron is

$$f = k\,\frac{e^2}{r^2}$$

Where $k = \frac{Z}{4\pi\varepsilon_o}$ (ε_o is the permittivity of the vacuum; Z = 1 for the hydrogen atom)

This force balances the centrifugal force on the electron, mv^2/r, where m is the mass of the electron and υ its velocity:

$$\frac{mv^2}{r} = k\frac{e^2}{r^2} = \frac{e^2}{4\pi\varepsilon_o r^2}$$

$$v^2 = \frac{e^2}{4\pi\varepsilon_o rm}$$

The kinetic energy of the electron may be determined from this equation also:

Kinetic energy = $\frac{1}{2}mv^2 = \frac{1}{8}\frac{e^2}{\pi\varepsilon_o r}$

Note:

m_e = Mass of an electron (9.109 x10^{-31} kg)
e = Quantity of electrical charge (1.602 x10^{-19} C)
h = Planck's constant (6.626 x10^{-34} Js)
ε_o = Vacuum permittivity (8.854 x10^{-12} C^2 N^{-1} m^{-2})
c = Speed of light (3.0 x10^8 m s^{-1})
R = Rydberg's constant (1.097 x10^7 m^{-1})
1 eV = 1.602 x10^{-19} J

2nd Postulate: Not all circular orbits are permitted for the electron. Only the orbits which have angular momentum of the electron, $m\upsilon r$, and equal to integral multiples of $\frac{h}{2\pi}$ are allowed:

$$mvr = \frac{nh}{2\pi} \qquad \text{n = 1, 2, 3, 4, 5, ...}$$

$$v = \frac{nh}{2\pi rm}$$

$$v^2 = \frac{n^2h^2}{4\pi^2r^2m^2}$$

Equating the two expressions for υ^2 yields an expression for r, the radius of an allowed orbit:

$$r = \frac{n^2h^2\varepsilon_o}{\pi me^2}$$

The value $n = 1$ defines the first (smallest) orbit. Larger orbits have higher values for n.

3rd Postulate: As a consequence of the restrictions on the angular momentum of an orbit, the energy of an electron in a given orbit is fixed. As long as the electron stays in that orbit, it neither absorbs nor radiates energy (hence the orbit is called a **stationary state**). The total energy, E, of an electron is the sum of its potential energy, $\frac{-e^2}{4\pi\varepsilon_o r}$ (negative because the electric force between the electron and the nucleus is attractive and its kinetic energy), $\frac{1}{2}mv^2 = \frac{1}{8}\frac{e^2}{\pi\varepsilon_o r}$ (from postulate 1). Therefore

$$E = -\frac{1}{8}\frac{e^2}{\pi\varepsilon_o r}$$

Thus, the total energy is equal to half the potential energy.
Substituting the expression for r from the above yields

$$E = -\frac{me^4}{8{\varepsilon_o}^2 n^2 h^2}$$

All of the quantities on the right-hand side of this equation are known constants except for the arbitrary integer n. Hence, the possible energies of the electron are determined by the values of n. It should be noted that the negative sign in the energy expression means that the larger the value of n, the higher will be the energy of the electron.

4th Postulate: To change from one orbit to another, the electron must absorb or emit a quantity of energy exactly equal to the difference in energy between the two orbits. When light energy is involved, the photon has a frequency given by
$h\upsilon = E_2 - E_1$
Substitution of the corresponding energy expression yields

$$E_2 - E_1 = hv = \frac{hc}{\lambda} = \frac{me^4}{8{\varepsilon_o}^2 h^2}\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right)$$

$$\frac{1}{\lambda} = \bar{v} = \frac{v}{c} = \frac{me^4}{8{\varepsilon_o}^2 ch^3}\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right)$$

$$= R\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right)$$

The last equation is identical to the Balmer equation. The constant R may be evaluated by using the numerical values of π, m, e, c, and h, and the result agrees closely with the experimentally determined value for the Rydberg constant.

It follows from the Bohr theory, since n_1 can have values 1, 2, 3, 4, 5, etc., that several other series of line should exist in the hydrogen spectrum besides the Balmer series. Subsequent to the theory, other series have been discovered in the ultraviolet, infrared, and far infrared regions of the spectrum. All of these series have lines with wavelengths which are given by the Balmer equation when appropriate values of n_1 and n_2 are used.

Each spectral line represents an energy difference between two possible states of the atom. Each of these states corresponds to the electron in the hydrogen atom being in an "orbit" whose radius increases with the quantum number n. The lowest allowed value of n is 1; because the electron is as close to the nucleus as possible, the energy of the system has its minimum (most negative) value. This is the "normal" (most stable) state of the hydrogen atom, and is called the **ground state**.

If a hydrogen atom absorbs radiation whose energy corresponds to the difference between that of n=1 and some higher values of n, then the atom is said to be in an **excited state**. Excited states are unstable and quickly decay to the ground state, but not always in a single step. For example, if the electron is initially promoted to the $n = 3$ state, it can decay either to the ground state or to the $n = 2$ state, which then decays to $n = 1$. Thus, this single $n = 1 \rightarrow 3$ excitation can result in the three emission lines depicted in Figure 1.5, corresponding to $n = 3 \rightarrow 1$, $n = 3 \rightarrow 2$, and $n = 2 \rightarrow 1$.

If, instead, enough energy is supplied to the atom to completely remove the electron, we end up having a hydrogen ion and an electron. When these two particles recombine ($H^+ + e^- \rightarrow H$), the electron can initially find itself in a state corresponding to any value of n, leading to the emission of many lines.

The lines of the hydrogen spectrum can be organised into different series according to the value of n at which the emission terminates (or at which absorption originates.) The first few series are named after their founders. The most well-known (and first-observed) of these is the Balmer series, which lies mostly in the visible region of the spectrum. The Lyman lines are in the ultraviolet, while the other series lie in the infrared. The lines in each series crowd together as they converge toward the *series limit* which corresponds to ionisation of the atom and is observed at the beginning of the *continuum* emission.

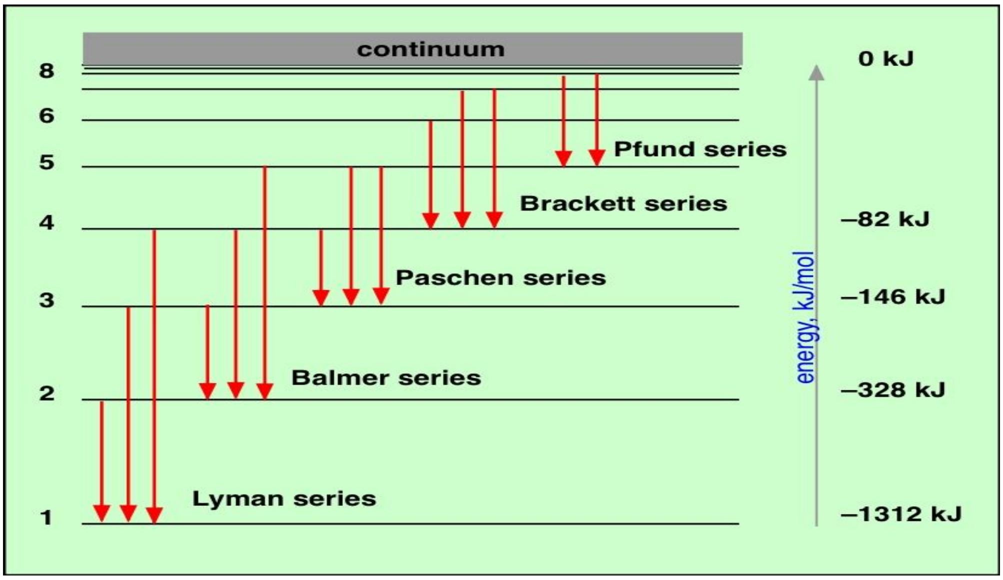


Fig. 1.5: Line Series in the Hydrogen Spectrum

Table 1.2: Description of the Line Series of the Hydrogen Spectrum

Series name	n_1	n_2 **values**	**Spectral region**
Lyman	1	2 to ∞	Ultraviolet
Balmer	2	3 to ∞	Visible
Paschen	3	4 to ∞	Infrared
Brackett	4	5 to ∞	Far infrared
Pfund	5	6 to ∞	Far infrared

The Bohr theory accounts for the hydrogen spectrum in the following ways:

- when hydrogen atoms are excited, their electrons occupy orbitals having higher energies.
- when an electron returns to a more stable orbit, it emits a photon of energy corresponding to the energy difference between the orbits.

The transition back to the ground state can occur directly or stepwise, yielding a single photon or several photons. The various spectral series correspond to transitions between higher orbits and those having a given value of *n*. It is customary to refer to the integer *n* as a **quantum number**.

The Bohr theory can be applied with equal success to "hydrogen-like atoms" that is, ions containing only one electron (He^+, Li^{2+}, etc.). The expression for the energy of the electron in the *n*th orbit for these ions is given as:

$$E = -\frac{mZ^2e^4}{8\varepsilon_0{}^2n^2h^2}$$

Where Z represents the atomic number.

3.5 Shortcomings of the Bohr Theory

1. The Bohr theory cannot explain the spectra of atoms containing more than one electron.
2. 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).
3. The theory ignores the wave nature of the electron.
4. 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.
5. It regards the electron as being stationary, with a specific position and distance from the nucleus.
6. It does not explain molecular bonds.
7. It does not predict the relative intensities of spectral lines.
8. The Bohr model does not explain fine structure and hyperfine structure in spectral lines.

4.0 CONCLUSION

Niels Bohr proposed the Bohr model of the Atom in 1915. Because the Bohr model is a modification of the earlier Rutherford Model, some people call Bohr's model the Rutherford-Bohr model. The modern model of the atom is based on quantum mechanics. The Bohr model has shortcomings, but it is important because it describes most of the accepted features of atomic theory without the entire high-level mathematics of the modern version. Unlike earlier models, the Bohr model explains the Rydberg formula for the spectral emission lines of atomic hydrogen.

5.0 SUMMARY

The Bohr model described the energy in atoms as being quantised. Bohr explained how he perceived elements' spectral-lines; electron jumps - from high energy levels to low energy levels and thus science was able to explain phenomena that until 1913 were not explainable.

When an electron changes to a different orbit, it either gets more energy, or it loses some energy - the larger the orbit is, the more energy. If an electron moves inward towards the core, then it emits or loses energy, while it absorbs energy when moving to an outward orbit.

This model of the atom is ideal for people who do not understand the nature of atom. It is very simple, but as things get more complicated, such as multi-electron systems, this model will not be sufficient. This model of the atom has now been replaced with quantum mechanics.

6.0 TUTOR-MARKED ASSIGNMENT

i. Using the Balmer equation, find the frequency of the radiation corresponding to $n = 3$.
ii. What is the frequency of the spectral line produced when an electron moves from $n = 5$ to $n = 2$ in a hydrogen atom?
iii. What value of n does the line at 656.3nm in the Balmer series correspond to?
iv. A photon with a wavelength of 397nm is emitted from an electron in energy level 7 of a hydrogen atom. What is the new energy level of the electron?
v. Find the frequency in Hertz of radiation with energy of 2.179×10^{-18} J per photon.
vi. What frequency of light would be needed to make an electron in a Hydrogen atom jump from $n = 1$ to $n = 3$?
vii. A spectral line is measured to have a wavelength of 1000 nm. Is this spectral within the Balmer series?
viii. Calculate the radius of the first allowed Bohr orbit for hydrogen.
ix. Calculate the energy of an electron in the first Bohr orbit of hydrogen.
x. Calculate the wavelength of the first line and the series limit for the Lyman series for hydrogen.

7.0 REFERENCES/FURTHER READING

Hein, M. & Arena, S. (2000). *Foundations of College Chemistry*. Pacific Grove: Brooks/Cole Publishing Company.

Hollas, M. J. (2002). *Basic Atomic and Molecular Spectroscopy*. Cambridge: Royal Society of Chemistry.

http://csep10.phys.utk.edu/astr162/lect/light/bohr.html

http://www.chem1.com/acad/webtext/atoms/atpt-3.html

Workman, J. (1998). *Applied Spectroscopy: A Compact Reference for Practitioners*. San Diego: Academic Press.

UNIT 2 THE QUANTUM MECHANICAL MODEL OF THE ATOM

CONTENTS

1.0 INTRODUCTION

The Bohr theory was a milestone; however, it had major defects. It explained the energies of the electron transitions in hydrogen and hydrogen-like atoms, but not in any atom having more than one electron. Even for hydrogen, the theory could not explain the different intensities of the spectral lines.

In this unit, a more sophisticated theory of the electronic structure of the atom will be described. This theory, known as **wave mechanics**, does not only give results as good as the Bohr theory for the case of the hydrogen atom but also can be used to explain both the energies and the intensities of the spectral lines of hydrogen. Moreover, approximate descriptions of atoms which have more than one electron may be given in terms of this theory.

The branch of science that takes into account this dual behaviour of matter is called quantum mechanics. Quantum mechanics is a theoretical science that deals with the study of the motion of the microscopic objects that have both observable wave-like and particle-like properties. This science was developed independently by Louis de Broglie, Werner Heisenberg and Erwin Schrödinger.

The quantum mechanical model is based on quantum theory, which says matter also has properties associated with waves. According to quantum theory, it is impossible to know the exact position and momentum of an electron at the same time. This is known as the **uncertainty principle**. The quantum mechanical model of the atom uses complex shapes of orbitals (sometimes called electron clouds), volumes of space in which there is likely to be an electron. So, this model is based on probability rather than certainty.

The major difference is that in the Bohr model the electrons revolve around the nucleus in fixed orbits similar to the way planets orbit around the sun. The wave mechanical model, influenced by the Heisenberg uncertainty principle, says that electrons do not orbit in fixed orbits. In fact, it is impossible to know both the position and momentum of a particle like an electron. Instead, the wave mechanical model uses the Schrödinger equation to predict the probabilities of where the electron may be positioned at any given time (without any certainty where the electron actually is).

There are other differences (differences in shapes of electron orbits/atomic orbitals; failure of the Bohr model to account for hybrid orbitals, molecular orbitals, resonance, etc.), but the major difference is that Bohr's model gives the electron orbit an exact travel path while the wave mechanical model does not claim to know where the electron is at any given time, only probabilities of where it is likely to be).

2.0 OBJECTIVES

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

- describe the quantisation of energy
- describe the wave-particle nature of an electron
- explain the uncertainty principle
- write the Schrödinger equation and highlight its significance
- identify the quantum numbers which describe the behaviour of electrons in an atom
- draw a table which shows how the energy levels are actually broken down into sub-levels – s, p, d, f
- recognise how many orbitals there are in a sublevel: s = 1; p = 3; d = 5; f = 7 and how many electrons fit in each orbital
- comprehend the order in which the orbitals are filled based on the Periodic Table
- write electron configurations for the elements in the first 4 periods of the Periodic Table.

3.0 MAIN CONTENT

3.1 Energy is Quantised (The Planck-Einstein Relation: $E = h\upsilon$)

After Max Planck determined that energy is released and absorbed by atoms in certain fixed amounts known as quanta, Albert Einstein took his work a step further. He stated that radiant energy is also quantised—he called the discrete energy packets, photons. Einstein's theory states that electromagnetic radiation (light, for example) has characteristics of both a wave and a stream of particles.

The Planck-Einstein relation is the equation relating energy to frequency. It was the first equation of quantum mechanics, implying that energy comes in multiples ("quanta") of a fundamental constant *h*. It is written as:

$E = h\upsilon$

υ is linear frequency and w is angular frequency. The fundamental constant *h* is called Planck's constant and is equal to 6.62608 ×10−34 Js

This relation was first proposed by Planck in 1900 to explain the properties of black body radiation. The interpretation was that matter energy levels are quantised. At that time, this appeared compatible with the notion that matter is composed of particles that oscillate. The discovery that the energy of electrons in atoms is given by discrete levels also fitted well with the Planck's relation.

In 1905, Einstein proposed that the same equation should hold also for photons, in his explanation of the photoelectric effect. The light incident on a metal plate gives rise to a current of electrons only when the frequency of the light is greater than a certain value. This value is associated with the energy required to remove an electron from the metal (the "work function"). The electron is ejected only when the light energy matches the discrete electron binding energy. Einstein's proposal that the light energy is quantised just like the electron energy was more radical at the time: light quantisation was harder for people to accept than quantisation of energy levels of matter particles. (The word "photon" for these quantised packets of light energy came later, given by G. N. Lewis, of Lewis Hall!).

3.2 Wave-Particle Duality

In 1924, a young French scientist, Louis de Broglie, proposed that, like light, a stream of electrons might have wave properties in addition to particle properties. He suggested that a particle such as an electron travelling at a velocity υ possessed a wavelength λ which is given by

$$\lambda = \frac{h}{m\upsilon}$$

Where h is Planck’s constant and m is the mass of the particle. In 1927, two Americas, C.J. Davison and L.H. Germer, measured the wavelength of an electron beam by diffraction through a crystal in a manner similar to the diffraction of X rays. Thus de Broglie’s hypothesis was confirmed.

De Broglie proposed this relationship as a general one. With every particle, there is an associated wave. The wavelength of the particle depends on its mass and how fast it is moving.

A particle occupies a particular location, but a wave has no exact position. A wave extends over some region of space. Because of their wave properties, electrons are always spread out rather than located in one particular space. As a result, the position of an electron cannot be precisely defined. Electrons are said to be delocalised because their waves are spread out rather than pinpointed.

Viewing the electron and other particle-waves as delocalised, however, changes the way we look at things. Instead of things having an exact location and motion, they are distributed over some volume.
An electrons beam is deflected by a magnetic field; this is evidence that electrons have a particle-like nature. Electron diffraction is an evidence for the wave nature of the electron.

3.3 The Uncertainty Principle

This is also known as the Indeterminacy principle. Werner Heisenberg, a German Physicist, found in the 1920s that the position and motion of a particle-wave cannot be “pinned down”. If a particular particle-wave can be pinpointed in a specific location, its motion must be unknown. Conversely, if the motion of a particular particle-wave is known precisely, its location must be unknown. Heisenberg summarised this uncertainty in what has become known as the uncertainty principle: The more accurately position is known, the less accurately can the momentum be determined, and *vice-versa*. Mathematically we describe the uncertainty principle as the following, where `x' is position and `p' is momentum:

$$\Delta x . \Delta p > \frac{h}{2\pi}$$

Where h is Planck’s constant. The principle, which was first stated by Heisenberg, arises from the dual particle-wave nature of matter.

For example, you can measure the location of an electron, but not its momentum (energy) at the same time.

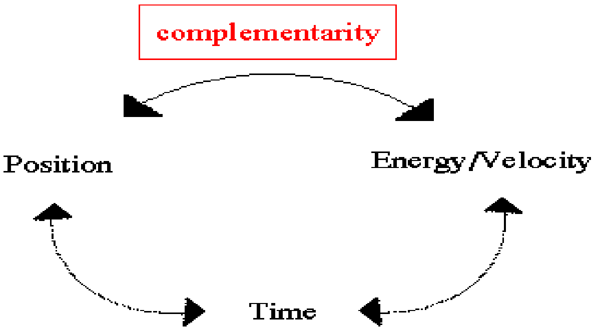


Fig. 2.1: The Uncertainty Principle

This is perhaps the most famous equation next to $E = mc^2$ in physics. It basically says that the combination of the error in position times the error in momentum must always be greater than Planck's constant. So, you can measure the position of an electron to some accuracy, but then its momentum will be inside a very large range of values. Likewise, you can measure the momentum precisely, but then its position is unknown.

3.4 The Schrödinger Equation

In 1926, Erwin Schrödinger postulated an equation similar to those which describe wave motion, the solutions of which describe the properties of the electron in the atom. The solutions to Schrödinger equation are exact for the electron in the hydrogen atom and approximate for the electrons in other atoms. These solutions are related to the probability of finding the electron in a given locality in the atom.

The wave function
Since an electron has wave properties, it is described as a wave function, ψ, or $\psi(x,y,z)$; the latter meaning that ψ is a function of coordinates x, y, and z. The probability of finding an electron in any volume in space is proportional to the square of the absolute value of the wave function, integrated over that volume of space. This is the physical significance of the wave function. The measurements we make of electronic charge density, then, should be related to $|\psi|^2$, and not $|\psi|$.

Expressed as an equation, we have:

Probability $(x,y,z) \propto |\psi(x,y,z)|^2$.
The Schrödinger equation is commonly written in the form:
$H\psi = E\psi$

This looks deceptively simple.

H is called the Hamiltonian operator and contains terms for the kinetic and potential energies of the system.

E is the numerical value of the energy for any particular ψ.

The complete Schrödinger equation is:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}\left[E - V_{(x,y,z)}\right]\psi = 0$$

Before the Schrödinger equation can be solved, the exact form of V must be specified. V contains information about all the Coulumbic attractions and repulsions among the electrons and nuclei of the atom of molecule.

V ≡ Potential energy.

The solutions of the Schrödinger equation involve integers which determine the energies and momenta of the electrons. The integers correspond to the quantum numbers of the Bohr theory, but in this case they are required by the mathematical form of the wave equation, whereas the quantum numbers of the Bohr theory were assumed arbitrarily. At this point, it is not necessary to learn how to solve the Schrödinger equation. It is only necessary to know that the solutions are used to describe the arrangement of electron in atoms and that the quantum numbers are the most characteristic feature of the solutions. The arrangements of the electrons in atoms can be predicted in terms of the quantum numbers alone. The properties of electrons which are determined by this arrangement include their energies, their orientations in space, and their interactions with other electrons within the same atom and with electrons of other atoms. All the chemical and physical properties of an atom depend on the arrangement of its electrons; therefore the quantum numbers are immediately useful in providing chemical information.

Each electron in an atom is assigned four quantum numbers, which define its energy, its orientation in space, and its possible interaction with other electrons.

3.5 Quantum Numbers

By solving the Schrödinger equation (Hψ = Eψ), we obtain a set of mathematical equations, called **wave functions** (ψ), which describe the probability of finding electrons at certain energy levels within an atom.

A wave function for an electron in an atom is called an **atomic orbital**; this atomic orbital describes a region of space in which there is a high probability of finding the electron. Energy changes within an atom are the result of an electron changing from a wave pattern with one energy to a wave pattern with a different energy (usually accompanied by the absorption or emission of a photon of light).

Each electron in an atom is described by four different **quantum numbers**. The first three (n, l, m_l) specify the particular orbital of interest, and the fourth (m_s) specifies how many electrons can occupy that orbital.

i. **Principal Quantum Number (n): n = 1, 2, 3… ∞** Specifies the energy of an electron and the **size** of the orbital (the distance from the nucleus of the peak in a radial probability distribution plot). All orbitals that have the same value of n are said to be in the same shell (level). For a hydrogen atom, the most stable state is when $n = 1$, and levels for $n > 1$ are excited states of the atom. The total number of orbitals for a given n value is n^2.

ii. **Angular Momentum (Azimunthal) Quantum Number (l): l = 0, ..., n-1** As the name implies, it specifies the angular momentum of the electron. In any atom other than the hydrogen atom, n and l together define the energy of the electron. l also specifies the **shape** of an orbital with a particular principal quantum number. The secondary quantum number divides the shells into smaller groups of orbitals called subshells (sublevels). Usually, a letter code is used to identify l to avoid confusion with n:

l	0	1	2	3	4	5	....
Letter	*s*	*p*	*d*	*f*	*g*	*h*	....

The subshell with $n = 2$ and $l = 1$ is the 2*p* subshell; if $n = 3$ and $l = 0$, it is the 3*s* subshell, and so on. The value of l also has a slight effect on the energy of the subshell; the energy of the subshell increases with l ($s < p < d < f$).

iii. **Magnetic Quantum Number (m_l): $m_l = -l, ..., 0, ..., +l$** Specifies the orientation in space of an orbital of a given energy (n) and shape (l). It defines the possible orientations of the angular momentum in space with respect to some arbitrarily defined axis. The magnetic quantum number becomes important in situations in which the electron interacts with external magnetic fields, including the fields generated by the motions of other electrons. This number divides the subshell into individual orbitals which hold the electrons; there are 2*l*+1 orbitals in each subshell. Thus, the s subshell has only one orbital, the p subshell has three orbitals, and so on.

iv. **Spin Quantum Number (m_s): m_s = +½ or -½.** To account for the fine details observed in atomic spectra, it is necessary to introduce the fourth quantum number, m_s, which specifies the **orientation of the spin axis** of an electron. This quantum number takes into account the spinning of the electron about its own axis as it moves about the nucleus. An electron can spin in only one of two directions. Although m_s has the possible non-integral values -½ and +½, the difference between the permitted values is integral.

Table 2.1: Allowed Quantum Numbers

n	***l***	***m_l***	**No. of orbitals**	**Orbital name**	**No. of electrons**	**Maximum no. of electrons**
1	0	0	1	1*s*	2	2
2	0 1	0 -1, 0, +1	1 3	2*s* 2*p*	2 6	8
3	0 1 2	0 -1, 0, +1 -2, -1, 0, +1, +2	1 3 5	3*s* 3*p* 3*d*	2 6 10	18
4	0 1 2 3	0 -1, 0, +1 -2, -1, 0, +1, +2 -3, -2, -1, 0, +1, +2, +3	1 3 5 7	4*s* 4*p* 4*d* 4*f*	2 6 10 14	32

Table 2.2: Sublevels are broken down into orbitals; each orbital holds 2 electrons

sublevel	No. of electrons in each sublevel	No. of orbitals	Names of each orbital
s	2	1	*s*
p	6	3	p_z p_x p_y
d	10	5	d_{z^2} d_{xz} d_{yz} d_{xy} $d_{x^2-y^2}$
f	14	7	f_{z^3} f_{xz^2} f_{yz^2} f_{xyz} $f_{z(x^2-y^2)}$ $f_{x(x^2-3y^2)}$ $f_{y(3x^2-y^2)}$

3.6 Orbitals

Atomic orbital: This is the volume containing all the points within a free atom at which the wave function of an electron has an appreciable magnitude. More simply, orbital is a region around the nucleus of an atom where the probability of finding an electron is high.

A solution of the Schrödinger equation, expressed in terms of a set of permitted values of n, l, and m_l, defines an orbital. The most characteristic property of an orbital is its energy. Since in the absence of external field the value of m_l does not influence the energy, orbitals are grouped into sets called subshells, which are denoted by the values of n and *l* only. The use of two numbers is awkward, hence orbitals with *l* values of 0, 1, 2, and 3, are denoted as s, p, d, and f, respectively.

The energies of atomic orbitals also describe their shapes. The shapes are uncertain, but predictions have been made by experimentation. Another difficult task is describing where an electron is. We can think of it as a wave, and describing its exact location is impossible for us to comprehend. Instead, we can think of it as the statistical probability of the electron being found at a particular place. At any given moment, an electron can be found at any distance from the nucleus and in any direction according to the Heisenberg Uncertainty Principle.

The s-Orbital

The s orbital is a spherically-shaped region describing where an electron can be found, within a certain degree of probability. The shape of the orbital depends on the quantum numbers associated with an energy state. All s orbitals have $l = m = 0$, but the value of n can vary.

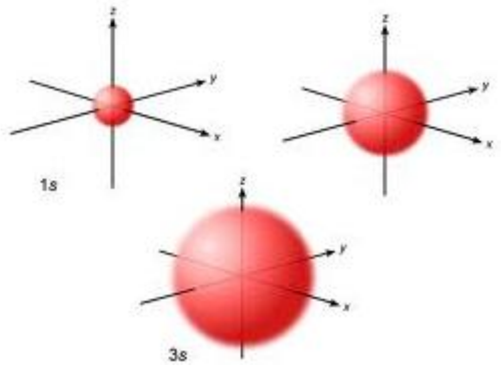
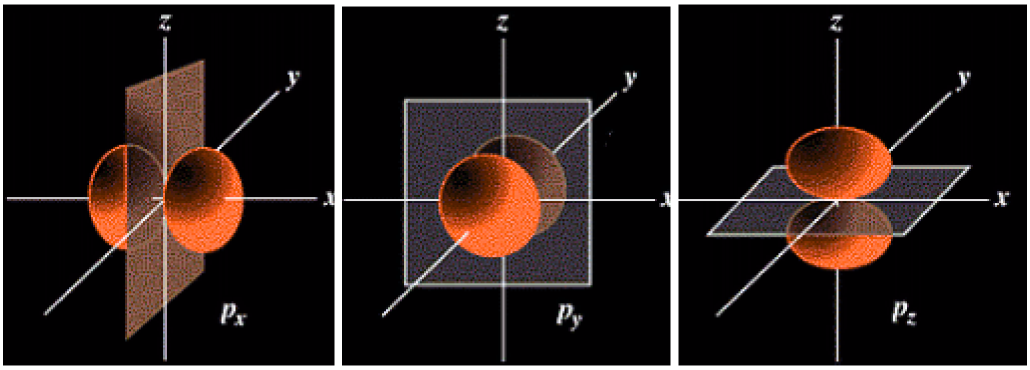


Fig. 2.2: The s-Orbitals

The p-Orbital

The p-orbital is a dumbbell-shaped region describing where an electron can be found, within a certain degree of probability. The shape of the orbital depends on the quantum numbers associated with an energy state. Since there are 3 p-orbitals per energy level, the lobes extend out along the x-axis (p_x orbital), the y-axis (p_y orbital), and the z-axis (p_z orbital).

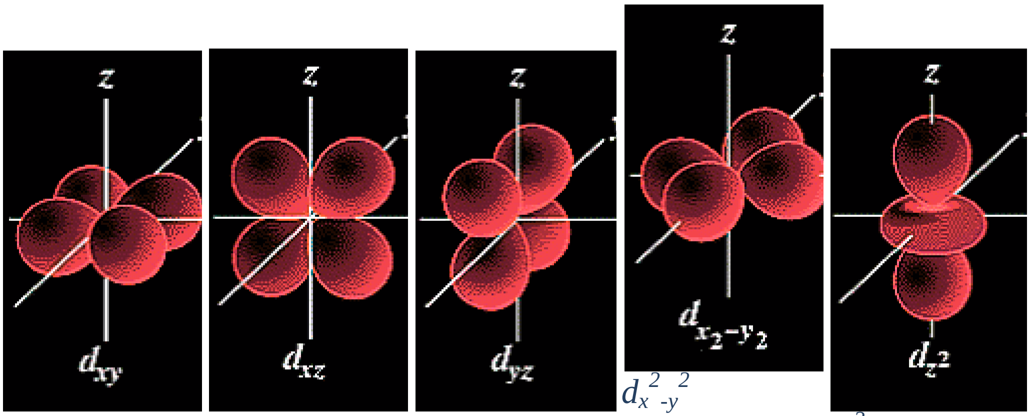


p_x orbital p_y orbital p_z orbital

Fig. 2.3: The p-Orbitals

The d-Orbital

The d orbital's shapes are even more complex because there are 5 orbitals in a d subshell. Four of the five d-orbitals (d_{xy}, d_{xz}, d_{yz}, and $d_{x^2-y^2}$) have four lobes extending out perpendicular to each other. The last one, d_{z^2}, has two lobes extending out along the z-axis with a torus (doughnut-shaped ring) around the centre on the x-y plane.



d_{xy} orbital d_{xz} orbital d_{yz} orbital $d_{x^2-y^2}$ orbital d_{z^2} orbital

Fig. 2.4: The d-Orbitals

The energy of an electron in a given orbital can be specified precisely from the values of its quantum numbers. As a consequence, the position of the electron is quite uncertain. Therefore, it turns out that while the solutions to the Schrödinger equation give the energies of the electron, they can give only the probability of finding the electron in any arbitrary volume around the nucleus.

The probability distribution for an electron in a 1s, 2s or 3s orbital of hydrogen is:

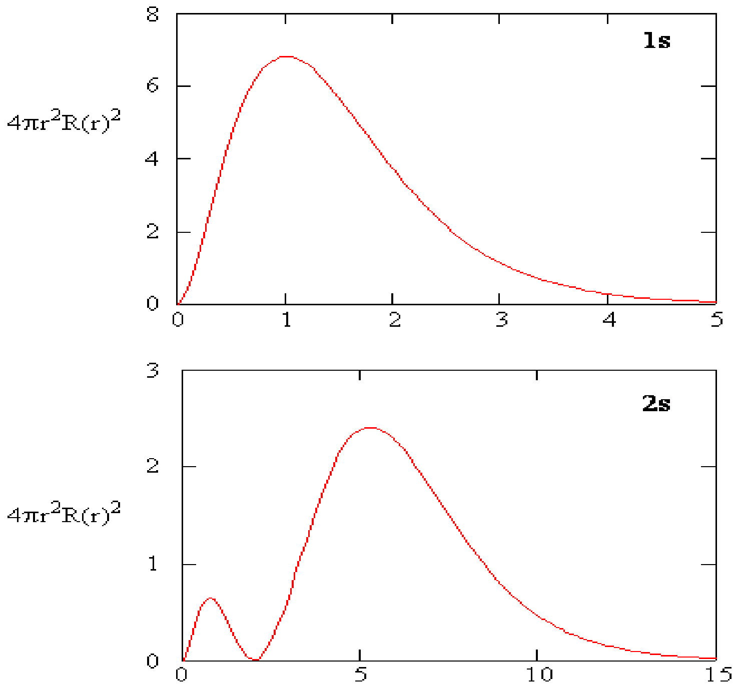


Fig. 2.5: Radial Distribution Functions of the 1s and 2s Orbitals

Note that as the principal quantum number increases, the maximum in the probability density occurs at larger distances for orbitals of the same angular momentum type. For example, the maximum probability for the 1s orbital occurs at 1 bohr (0.529 Å), for the 2s orbital the primary maximum occurs at 5.3 bohr, and for the 3s orbital the primary maximum occurs at about 13 bohr.

For the hydrogen atom, it is seen that there is maximum probability of finding the electron at a distance of 1 bohr (0.529 Å) from the nucleus. This distance is the same as the experimental radius of the hydrogen atom and also agrees with the radius derived by means of the Bohr theory.

Similar representation for the 2s orbital of hydrogen is shown – there is a greater probability of finding the electron further away from the nucleus than in the case of the 1s orbital, but there is still some chance of finding the electron very close to the nucleus. Also significant is the fact that at an intermediate distance, there is a surface at which the probability of finding the electron is zero. Surfaces at which the probability goes to zero are called **nodes**. For any orbital having principal quantum number *n*, there are always *n-1* nodes. This nodal character of the probability distribution is consistent with the assumption that the motion of the electron has the character of a wave.

3.7 Writing Electron Configuration

3.7.1 The Pauli Exclusion Principle

The **Pauli Exclusion Principle** (Wolfgang Pauli, Nobel Prize 1945) states that *no two electrons in the same atom can have identical values for all four of their quantum numbers*. What this means is that no more than **two** electrons can occupy the same orbital, and that two electrons in the same orbital must have opposite spins.

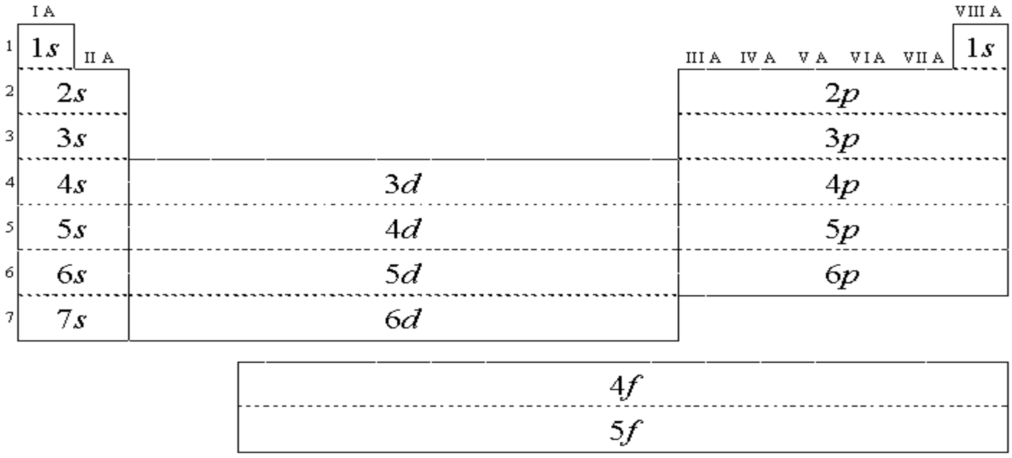
Because an electron spins, it creates a magnetic field, which can be oriented in one of the two directions. For two electrons in the same orbital, the spins must be opposite to each other; the spins are said to be paired. These substances are not attracted to magnets and are said to be diamagnetic. Atoms with more electrons that spin in one direction than another contain unpaired electrons. These substances are weakly attracted to magnets and are said to be paramagnetic.

3.7.2 The Aufbau Principle

The distribution of electrons among the orbitals of an atom is called the **electron configuration**. The electrons are filled in according to a scheme known as the **Aufbau principle** ("building-up"), which corresponds (for the most part) to increasing energy of the subshells:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f

It is not necessary to memorise this listing, because the order in which the electrons are filled in can be read from the periodic table in the following fashion:



Or, summarised:

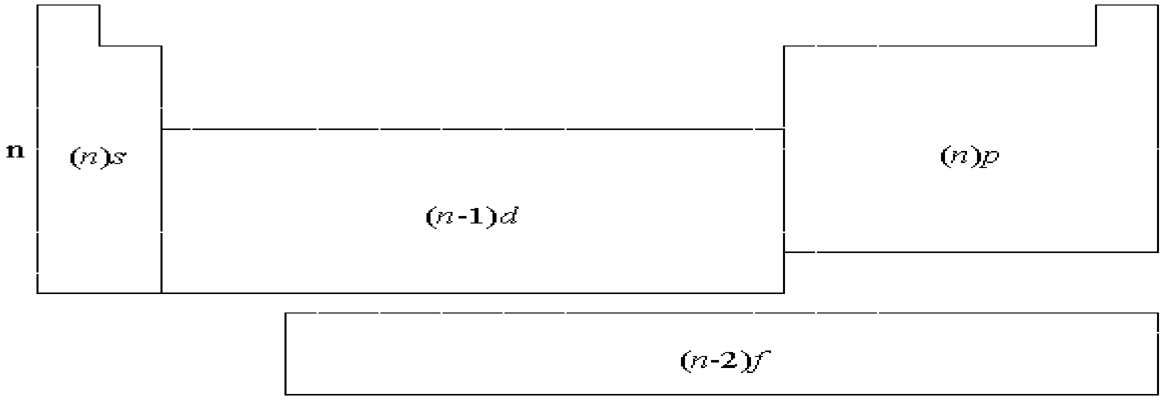


Fig. 2.6: Writing Electronic Configurations

In electron configurations, write the orbitals that are occupied by electrons, followed by a superscript to indicate how many electrons are in the set of orbitals (e.g., H $1s^1$).

Another way to indicate the placement of electrons is an orbital diagram, in which each orbital is represented by a square (or circle), and the electrons as arrows pointing up or down (indicating the electron spin).

3.7.3 The Hund's Rule of Maximum Multiplicity

When electrons are placed in a set of orbitals of equal energy, they are spread out as much as possible to give as few paired electrons as possible (Hund's rule).

According to this rule, electron pairing will not take place in orbitals of same energy (same sub-shell) until each orbital is first singly filled with parallel spin. In other words, in a set of orbitals having same energy (degenerate orbitals), the electrons distribute themselves to occupy separate orbitals with same spin as far as possible. This rule can be illustrated by considering the example of carbon. The atomic number of carbon is 6 and it contains two electrons in 2p subshell and these can be distributed in the following three ways:

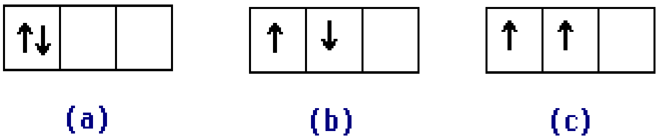


Fig. 2.7: Hund's Rule of Maximum Multiplicity

Since all the three 2p orbitals have same energy, therefore, it does not take any difference as to which of the three orbitals contain electrons. In state (a), both the electrons are in the same orbital. In state (b), the two electrons are present in different orbitals but with opposite spins while in state (c), the electrons are present in different orbitals with same spins. Now, the electrons are charged particles and repel one another. The electron-electron repulsions are minimum when the electrons are as far apart as possible with parallel spins. Thus, state (c) has minimum repulsions and corresponds to lower energy (stable) state. This is in accordance with Hund's rule. This principle is very important in guiding the filling of p, d and f subshells, which have more than one type of orbitals.

In a ground state configuration, all of the electrons are in as low an energy level as it is possible. When an electron absorbs energy, it occupies a higher energy orbital, and is said to be in an excited state.

4.0 CONCLUSION

Most of the physical and chemical properties of atoms, and hence of all matter, are determined by the nature of the electron cloud enclosing the nucleus.

The nucleus of an atom, with its positive electric charge, attracts negatively charged electrons. This attraction is largely responsible for holding the atom together. The revolution of electrons about a nucleus is determined by the force with which they are attracted to the nucleus.

The electrons move very rapidly, and determination of exactly where any particular one is at a given time is theoretically impossible (Uncertainty Principle). If the atom were visible, the electrons might appear as a cloud, or fog, that is dense in some spots, thin in others. The shape of this cloud and the probability of finding an electron at any point in the cloud can be calculated from the equations of wave mechanics (Quantum Theory). The solutions of these equations are called orbitals. Each orbital is associated with a definite energy, and each may be occupied by no more than two electrons. If an orbital contains two electrons, the electrons must have opposite *spins*, a property related to the angular momentum of the electrons. The electrons occupy the orbitals of lowest energy first, then the orbitals next in energy, and so on, building out until the atom is complete.

5.0 SUMMARY

In this unit, we observed that electrons do not quite behave that nicely. Instead, electrons behave like a particle and a wave, so a new model was created. We discussed the differences between the Bohr model and the quantum mechanical model, the similarities and how we can represent/illustrate electron locations via electron configuration and box diagrams. We also learned that solution to the Schrödinger equation gave rise to the quantum numbers, which describe the behaviour of electrons in atoms. The different types of orbitals and rules governing the writing of electronic configurations of atoms were also discussed.

6.0 TUTOR-MARKED ASSIGNMENT

i. What is the de Broglie wavelength of a person with a mass of 50 kg jogging at 5 m/s?
ii. What is the de Broglie wavelength of an electron moving at 2.2 x 10^6 m/s?
iii. Electrons experience a drop in energy of 6.409 x 10^{-15} J, what is the wavelength of the electrons?

7.0 REFERENCES/FURTHER READING

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MODULE 2

UNIT 1 THE ELECTRONIC STRUCTURE OF THE REPRESENTATIVE ELEMENTS

CONTENTS

1.0 INTRODUCTION

This unit explores how to write electronic structures for atoms and ions using s, p, and d notation. It assumes that you know about simple atomic orbitals - at least as far as the way they are named, and their relative energies. If you want to look at the electronic structures of simple monatomic ions (such as Cl^-, Ca^{2+} and Cr^{3+}), you need to know the electronic structure of the atom and the number of electrons gained/lost in forming the ion.

Elements in the periodic table are arranged in periods (rows) and groups (columns). Each of the seven periods is filled sequentially by atomic number. Groups include elements having the same electron configuration in their outer shell, which results in group elements sharing similar chemical properties. The electrons in the outer shell are termed valence electrons. Valence electrons determine the properties and chemical reactivity of the element and participate in chemical bonding. The Roman numerals found above each group specify the usual number of valence electrons. There are two sets of groups. Groups 1 & 2 and 13 - 18 (formerly Group A) elements are the representative elements, which have s or p sublevels as their outer orbitals. Groups 3 – 12 (formerly Group B) elements are the non-representative elements, which have partly filled d sublevels (the transition elements) or partly filled f sublevels (the lanthanide series and the actinide series). The

Roman numeral and letter designations give the electron configuration for the valence electrons (e.g., the valence electron configuration of a Group 15 (formerly group VA) element will be s^2p^3 with 5 valence electrons).

Even in the earliest studies of chemistry, it became evident that certain elemental substances were very much like other substances in their physical and chemical properties. For example, common alkali metals (Na and K) were almost indistinguishable to early chemists. Both metals are similar in appearance and undergo reactions with the same reagents. As more and more elemental substances were identified, more and more similarities between the new elements and previously known elements were detected. Chemists began to wonder why similarities existed. In the modern periodic table, elements are arranged in order in order of increasing atomic number, and the properties of the elements fall into a completely regular order.

An element is defined by its atomic number (the number of protons in the nucleus of its atoms), but its chemical reactivity is determined by the number of electrons in its outer shells, a property fundamental to the organization of the periodic table of the elements. In the periodic table, elements with the same number of outermost electrons fall into the same group.

2.0 OBJECTIVES

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

- write the electronic configurations of the representative elements
- write the electronic configurations of monatomic ions of the representative elements
- classify the elements into different groups of the periodic table
- highlight the characteristic properties of the representative elements.

3.0 MAIN CONTENT

3.1 Structures of Monatomic Ions

The electrons in the outermost shell (the ones with the highest value of n) are the most energetic, and are the ones which are exposed to other atoms. This shell is known as the **valence shell**. The inner, core electrons (inner shell) do not usually play a role in chemical bonding.
Elements with similar properties generally have similar outer shell configurations. For instance, we already know that the alkali metals

(Group I) always form ions with a +1 charge; the "extra" s^1 electron is the one that is lost:

Group 1	Li	$1s^22s^1$	Li^+	$1s^2$
	Na	$1s^22s^22p^63s^1$	Na^+	$1s^22s^22p^6$
	K	$1s^22s^22p^63s^23p^64s^1$	K^+	$1s^22s^22p^63s^23p^6$

The next shell down is now the outermost shell, which is now full — meaning there is very little tendency to gain or lose more electrons. The ion's electron configuration is the same as the nearest noble gas — the ion is said to be **isoelectronic** with the nearest noble gas. Atoms "prefer" to have a filled outermost shell because this makes them more electronically stable.

- The Group IIA (Group 2) and IIIA (Group 13) metals also tend to lose all of their valence electrons to form cations.

Group 2	Be	$1s^22s^2$	Be^{2+}	$1s^2$
	Mg	$1s^22s^22p^63s^2$	Mg^{2+}	$1s^22s^22p^6$
Group 13	Al	$1s^22s^22p^63s^23p^1$	Al^{3+}	$1s^22s^22p^6$

The Group IV and V metals can lose either the electrons from the *p* subshell, or from both the *s* and *p* subshells, thus attaining a **pseudo-noble gas configuration**.

Group 14	Sn	$[Kr]4d^{10}5s^25p^2$	Sn^{2+}	$[Kr]4d^{10}5s^2$
			Sn^{4+}	$[Kr]4d^{10}$
	Pb	$[Xe]4f^{14}5d^{10}6s^26p^2$	Pb^{2+}	$[Xe]4f^{14}5d^{10}6s^2$
			Pb^{4+}	$[Xe]4f^{14}5d^{10}$
Group 15	Bi	$[Xe]4f^{14}5d^{10}6s^26p^3$	Bi^{3+}	$[Xe]4f^{14}5d^{10}6s^2$
			Bi^{5+}	$[Xe]4f^{14}5d^{10}$

The Groups 14 - 17 non-metals gain electrons until their valence shells are full (8 electrons).

Group 14	C	$1s^22s^22p^2$	C^{4-}	$1s^22s^22p^6$
Group 15	N	$1s^22s^22p^3$	N^{3-}	$1s^22s^22p^6$
Group 16	O	$1s^22s^22p^4$	O^{2-}	$1s^22s^22p^6$
Group 17	F	$1s^22s^22p^5$	F^-	$1s^22s^22p^6$

- The Group 18 noble gases already possess a full outer shell, so they have no tendency to form ions.

Group 18 Ne $1s^2 2s^2 2p^6$
Ar $1s^2 2s^2 2p^6 3s^2 3p^6$

3.2 Properties of the Representative Elements

The main group elements of the periodic table are groups 1, 2 and 13 through 18. Elements in these groups are collectively known as main group or representative elements. These groups contain the most naturally abundant elements, comprise 80% of the earth's crust and are the most important for life. Economically, the most produced chemicals are main group elements or their compounds. It is in the main group elements that we most clearly see the trends in physical and chemical properties of the elements that chemists have used to understand the "stuff" things are made of.

Group 1 (Alkali Metals)
The **alkali metals** are the series of elements in Group 1 of the periodic table (excluding hydrogen in all but one rare circumstance). The series consists of the elements lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs), and francium (Fr).

Properties
The alkali metals are silver-coloured (caesium has a golden tinge), soft, low-density metals. These elements all have one valence electron which is easily lost to form an ion with a single positive charge. They have the lowest ionisation energies in their respective periods. This makes them very reactive and they are the most active metals. Due to their activity they occur naturally in ionic compounds not in their elemental state.

The alkali metals react readily with halogens to form ionic salts, such as table salt, sodium chloride (NaCl). They are famous for their vigorous reactions with water to liberate hydrogen gas. These reactions also often liberate sufficient energy to ignite the hydrogen and can be quite dangerous. As we move down the group the reactions become increasingly violent. The reaction with water is as follows:

Alkali metal + water → Alkali metal hydroxide + hydrogen
With potassium as an example: $2K(s) + 2H_2O(l) \rightarrow 2KOH(aq) + H_2(g)$
The oxides, hydrides, and hydroxides of these metals are basic (alkaline). In particular, the hydroxides resulting from the reaction with water are our most common laboratory bases (alkalis). It is from this character that they derive their group name.

Hydrogen also has a single valence electron and is usually placed at the top of Group 1, but it is not a metal (except under extreme circumstances as metallic hydrogen); rather it exists naturally as a diatomic gas. Hydrogen can form ions with a single positive charge, but removal of its single electron requires considerably more energy than removal of the outer electron from the alkali metals. Unlike the alkali metals, hydrogen atoms can also gain an electron to form the negatively charged hydride ion. The hydride ion is an extremely strong base and does not usually occur except when combined with the alkali metals and some transition metals (i.e. the ionic sodium hydride, NaH). In compounds, hydrogen most often forms covalent bonds.

Under extremely high pressure, such as it is found at the core of Jupiter, hydrogen does become metallic and behaves like an alkali metal

Group 2 (Alkaline Earth Metals)

The alkaline earth metals are the series of elements in Group 2 of the periodic table. The series consists of the elements beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra) (though radium is not always considered an alkaline on earth due to its radioactivity).

Properties

The alkaline earth metals are silvery coloured, soft, low-density metals, though are a bit harder than the alkali metals. These elements all have two valence electrons and tend to lose both to form ions with a two plus charge. Beryllium is the least metallic element in the group and tends to form covalent bonds in its compounds.

These metals are less active than the alkali metals, but are still fairly active. They react readily with halogens to form ionic salts, and can react slowly with water. Magnesium reacts only with steam and calcium with hot water. Beryllium is an exception: it does not react with water or steam, and its halides are covalent. The oxides are basic and dissolve in acids and the hydroxides are strong bases, though not as soluble as the alkali metal hydroxides.

The alkaline earth metals are named after their oxides, the alkaline earths, whose old-fashioned names were beryllia, magnesia, lime, strontia and baryta. These were named alkaline earths because of their intermediate nature between the alkalis (oxides of the alkali metals) and the rare earths (oxides of rare earth metals). The classification of some apparently inert substances as 'earths' is millennia old. The earliest known system used by the Greeks consisted of four elements, including earth. Later alchemists applied the term to any solid substance that did not melt and was not changed by fire. The realisation that 'earths' were not elements but compounds is attributed to the chemist Antoine Lavoisier. In his *Traité Élémentaire de Chimie* (“Elements of

Chemistry”) of 1789 he called them *Substances simples salifiables terreuses*, or salt-forming earth elements. Later, he suggested that the alkaline earths might be metal oxides, but admitted that this was mere conjecture. In 1808, acting on Lavoisier's idea, Humphrey Davy became the first to obtain samples of the metals by electrolysis of their molten earths.

Group 13 (Boron Group)

The Boron group is the series of elements in group 13 (formerly group III) in the periodic table. It consists of the elements boron (B), aluminium (Al), gallium (Ga), indium (In), thallium (Tl), and ununtrium (Uut) (unconfirmed).

Properties

In this group, we begin to see the changeover toward non-metallic character. First appearing at the top of the group, boron is a metalloid, it has characteristics intermediate between metals and non-metals, and the rest of the group are metals. These elements are characterised by having three valence electrons. The metals can lose all three electrons to form ions with a three plus charge in ionic compounds, but boron tends to form covalent bonds. The oxides of these metals dissolve in acids so may be considered basic, but aluminum oxide also dissolves in bases. It is amphoteric; that is, it displays both acidic and basic characteristics. This is another indication of the changeover to non-metallic character. Aluminum is the third most abundant element in the earth's crust (7.4%), and is widely used in packaging materials. Aluminum is an active metal, but the stable oxide forms a protective coating over the metal making resistant to corrosion.

Group 14 (Carbon Group)

The carbon group is the series of elements in group 14 ([formerly group IV) in the periodic table. It consists of the elements carbon (C), silicon (Si), germanium (Ge), tin (Sn), lead (Pb), and ununquadium (Uuq).

Properties

This group has mixed types of element; with the non-metal carbon, two metalloids, and two metals. The common characteristic is four valence electrons. The two metals, tin and lead, are fairly unreactive metals and both can form ions with a two plus or a four plus charge in ionic compounds. Carbon forms four covalent bonds in compounds rather than form monatomic ions. In the elemental state, it has several forms, the most known of which are graphite and diamond. Carbon is the basis of organic chemistry and of biological molecules. Life depends on carbon. One oxide of carbon, carbon dioxide (CO_2), dissolves in water to give a weakly acidic solution. Acidic oxides are characteristic of non-metals. Silicon in some respects is similar to carbon in that it forms four covalent bonds, but it does not form the wide range of compounds. Silicon is the second most abundant element in the earth's crust (25.7%) and we are surrounded by silicon containing materials: bricks, pottery, porcelain, lubricants, sealants, computer chips, and solar cells. The simplest oxide, silicon dioxide (SO_2) or silica, is a component of many rocks and minerals.

Group 15 (Nitrogen Group)

The nitrogen group is the series of elements in group 15 (formerly Group V) of the periodic table. It consists of the elements Nitrogen (N), Phosphorus (P), Arsenic (As), Antimony (Sb), Bismuth (Bi) and Ununpentium (UUp) (unconfirmed). The collective name pnicogens (now also spelled pnictogens) is also sometimes used for elements of this group, with binary compounds being called pnictides; neither term is approved by IUPAC. Both spellings are said to derive from the Greek *πνίγειν* (*pnigein*), to choke or stifle, which is a property of nitrogen.

Properties

These elements all have five valence electrons. Nitrogen and phosphorous are non-metals. They can gain three electrons to form fairly unstable ions with a three minus charge, the nitride and phosphide ions. In compounds, they more often form covalent bonds. Though they are not in the top ten most common elements in the earth's crust, they are very important elements. Nitrogen, as a diatomic molecule is the major constituent of air and both elements are essential for life. Nitrogen comprises about 3% of the weight of the human body and phosphorous about 1.2%. Commercially, these elements are important for fertilizers. Arsenic and Antimony are metalloids, and bismuth is the only metal in the group. Bismuth can lose three electrons to form an ion with a three plus charge. Bismuth is also the heaviest completely stable element that does not decay radioactively to other simpler elements.

Group 16 (Chalcogens)

The chalcogens (with the "ch" pronounced with a hard "c" as in "chemistry") are the name for the periodic table Group 16 (formerly Group VIb or VIa) in the periodic table. It is sometimes known as the oxygen family. Elements in this group include oxygen (O), sulfur (S), selenium (Se), tellurium (Te), the radioactive polonium (Po), and the synthetic ununhexium (Uuh). The compounds of the heavier chalcogens (particularly the sulphides, selenides, and tellurides) are collectively known as chalcogenides. Unless grouped with a heavier chalcogen, oxides are not considered chalcogenides.

Properties

This group has six valence electrons. Oxygen and sulphur are non-metals; their elemental form is molecular, and they can gain two electrons to form ions with a two minus charge. Oxygen is by far the most abundant element in the earth's crust (49.5%), and is present in almost everything. It existents elementally in the air as a diatomic molecule, is part of water and many great minerals, and is essential for life. Sulphur has probably the most allotropes of any element, though the most common and stable form is the yellow crystals of S_8 molecules. Though selenium is lumped with the non-metals, and can form selenides similar to oxides and sulphides, its elemental state is that of a metalloid semiconductor as is tellurium and polonium. In their elemental state, they are often referred to as metals. Oxygen can combine with sulphur, selenium and tellurium to form polyatomic ion oxo-anions. Oxygen is more electronegative than these elements (S, Se and Te), so they assume a positive oxidation number in these ions; example is SO_4^{2-}.

The name chalcogen is generally considered to mean "ore former" from the Greek *chalcos* "*ore*" and *-gen* "formation". Chalcogenides are quite common as minerals. For example, FeS_2 (pyrite) is an iron ore and $AuTe_2$ gave its name to the gold rush town of Telluride, Colorado in the United States.

Group 17 (Halogens)

The halogens are the elements in Group 17 (formerly Group VII or VIIa) of the periodic table. They are fluorine (F), chlorine (Cl), bromine (Br), iodine (I), astatine (At) and the as yet undiscovered ununseptium (Uus).

Properties

These elements all have seven valence electrons. This group is the first one to consist of entirely non-metals. They exist as diatomic molecules in their natural state and have a progressive variation of physical properties (see Table 1.1 below). Fluorine and chlorine exist as gases at room temperature, bromine as a liquid, and iodine as a solid. They require one more electron to fill their outer electron shells, and so have a tendency to gain one electron to form singly-charged negative ions. These negative ions are referred to as halide ions, and salts containing these ions are known as halides.

Halogens are highly reactive, and as such can be harmful or lethal to biological organisms in sufficient quantities. Fluorine is the most reactive and the reactivity declines as we go down the group. Chlorine and iodine are both used as disinfectants. In their elemental state, the halogens are oxidising agents and are used in bleaches. Chlorine is the active ingredient of most fabric bleaches and is being used in the production of most paper products. The oxides and hydrides, like those of most non-metals, of the halogens are acidic. Halide ions combined with single hydrogen atoms to form the hydrohalic acids (i.e., HF, HCl, HBr, HI), a series of particularly strong acids. (HAt, or "hydrastatic acid", should also qualify, but it is not typically included in discussions of hydrohalic acid due to astatine's extreme instability toward radioactive alpha decay.) They can react with each other to form inter-halogen compounds, and can combine with oxygen in polyatomic oxoanions (e.g., SO_4^{2-}) Diatomic inter-halogen compounds (BrF, ICl, ClF, etc.) bear strong superficial resemblance to the pure halogens.

Many synthetic organic compounds, and a few natural ones, contain halogen atoms; these are known as halogenated compounds or organic halides. Chlorine is by far the most abundant of the halogens, and the only one needed in relatively large amounts (as chloride ions) by human beings. For example, chloride ions play a key role in brain function by mediating the action of the inhibitory transmitter Gamma-aminobutyric acid (GABA). Chloride ions are also used by the body to produce stomach acid. Iodine is needed in trace amounts for the production of thyroid hormones such as thyroxine. On the other hand, neither fluorine nor bromine is believed to be really essential for humans, although small amounts of fluoride can make tooth enamel resistant to decay.

The term halogen was coined to mean elements which produce salt in union with a metal. It comes from 18th century scientific French nomenclature based on erring adaptations of Greek roots.

Table 2.1: Trends in Melting Point, Boiling Point, and Electronegativity of Halogens

Halogen	**Atomic Mass (amu)**	**Melting Point (°C)**	**Boiling Point (°C)**	**Electronegativity (Pauling)**
Fluorine	18.998	−219.62	−188/12	3.98
Chlorine	35.453	−101.15	−34.04	3.16
Bromine	79.904	−7.35	58.86	2.96
Iodine	126.904	113.70	202.25	2.66
Astatine	(210)	302	337	2.2

Group 18 (Noble Gases)

The noble gases are the chemical elements in group 18 (formerly group VIII) of the periodic table. They are helium, neon, argon, krypton, xenon, and radon. They are sometimes called inert gases or rare gases. The name 'noble gases' is an allusion to the similarly unreactive noble metals, so called due to their preciousness, resistance to corrosion and long association with the aristocracy.

Properties

The noble gasses are all non-metals and are characterised by having completely filled shells of electrons. In general this makes them very unreactive chemically since it is difficult to add or remove electrons. Physically they exist as monatomic gases at room temperature; even those with larger atomic masses (see Table 2.2). This is because they have very weak inter-atomic forces of attraction, and consequently very low melting points and boiling points. Krypton and Xenon are the only noble gasses that does not form any compounds at all. These elements can do this because they have the potential to form an expanded octet by accepting electrons in an empty d subshell.

Because of their unreactivity, the noble gases were not discovered until 1868, when helium was detected spectrographically in the Sun. The isolation of helium on Earth had to wait until 1895. The noble gasses are commonly encountered in helium balloons (safer than flammable hydrogen) and lighting. Some of the noble gases glow distinctive colours when used inside discharge tubes (neon lights), and Argon is often used inside filament light bulbs.

Table 2.2: Trends in Melting Point, Boiling Point and Density of Noble Gases

Noble Gas	Atomic Mass (amu)	Melting Point (ºC)	Boiling Point (ºC)	Density (g/L)
Helium	4.003	−272	−268.83	0.1786
Neon	20.18	−248.52	−245.92	0.9002
Argon	39.95	−189.6	−185.81	1.7818
Krypton	83.80	−157	−151.7	3.708
Xenon	131.3	−111.5	−106.6	5.851
Radon	(222)	−71	−62	9.97

4.0 CONCLUSION

Each chemical element has a characteristic number of electrons. For example, a carbon atom has six electrons and a neon atom has ten electrons. The first, or innermost, shell of each of these atoms can contain two electrons, and it is full for both of them. The second shell—which is the outermost shell for both of these elements—can contain eight electrons. Carbon has only four electrons in its outer shell, so it needs four more electrons to fill this layer. Neon has eight electrons in its outer shell, so its outer shell is full. Atoms are very stable when their outermost electron shell is full. Neon and the other so-called noble gases all have full outer electron shells. They are extremely stable and rarely react with other elements. Atoms of other elements bond with each other to fill their outermost shell of electrons and thus attain the stable configuration of the noble gases

5.0 SUMMARY

In this unit, you have learnt how to write the electronic configurations of the representative elements as well as those of their monatomic ions. The elements have also been classified into groups in the periodic table, and the characteristic properties of elements in each group were explored.

6.0 TUTOR-MARKED ASSIGNMENT

i. Write the electronic configurations of the following ions: Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}.
ii. Classify the first 20 elements into different groups of the periodic table
iii. Write equations for the reaction of Na, Mg and Ca with water.
iv. List three physical properties and three chemical properties which are typical of metals.

7.0 REFERENCES/FURTHER READING

http://www.newworldencyclopedia.org/entry/Periodic_table,_main_group_elements

Huheey, J.E.*et al*.. (1993). *Inorganic Chemistry: Principles of Structure and Reactivity*. (4th ed.). New York: HarperCollins.

Martin, S. S. (2000). *Chemistry: The Molecular Nature of Matter and Change*. (2nd ed.). Boston: McGraw-Hill.

UNIT 2 THE PERIODIC TABLE AND ATOMIC PROPERTIES

CONTENTS

1.0 INTRODUCTION

The chemistry of the elements is immensely varied. But amidst that variety there are patterns, and the best known and most useful is chemical periodicity: if the elements are laid out in order of atomic number, similar elements occur at regular intervals.

The properties of the elements exhibit trends. These trends can be predicted using the periodic table and can be explained and understood by analysing the electron configurations of the elements. Elements tend to gain or lose valence electrons to achieve stable octet formation. Stable octets are seen in the inert gases, or noble gases, of Group VIII of the periodic table. In addition to this activity, there are two other important trends:

- First, electrons are added one at a time moving from left to right across a period. As this happens, the electrons of the outermost shell experience increasingly strong nuclear attraction, so the electrons become closer to the nucleus and more tightly bound to it.
- Second, moving down a column in the periodic table, the outermost electrons become less tightly bound to the nucleus. This happens because the number of filled principal energy levels

(which shield the outermost electrons from attraction to the nucleus) increases downward within each group. These trends explain the periodicity observed in the elemental properties of atomic radius, ionisation energy, electron affinity, and electronegativity.

2.0 OBJECTIVES

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

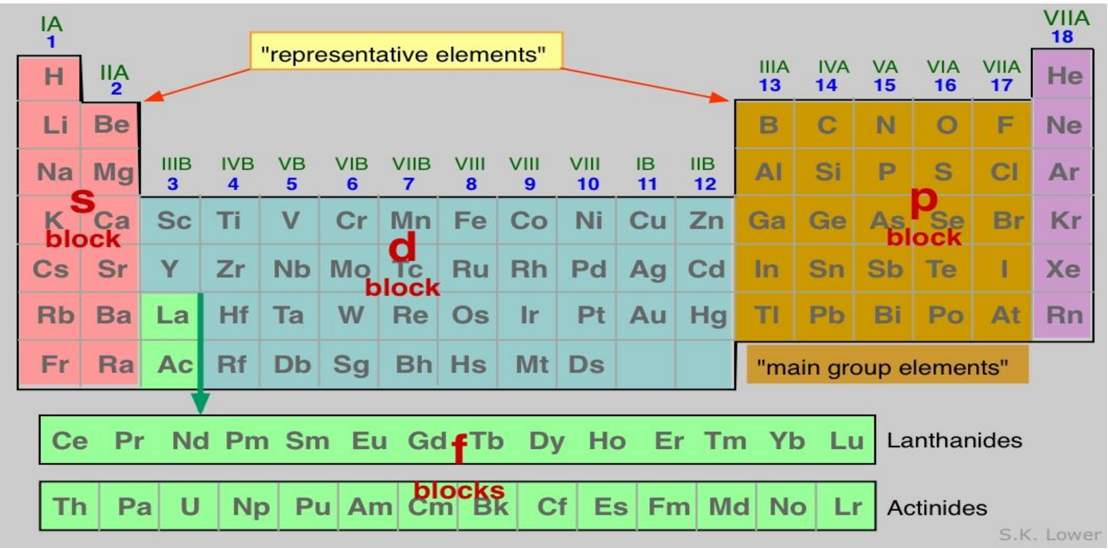
- sketch the general form of the periodic table and identify the various blocks and identify the groups corresponding to the alkali metals, the transition elements, the halogens, and the noble gases
- predict the formulas of typical binary compounds they can be expected to form with hydrogen and with oxygen (for the first eighteen elements)
- comment on the concept of the "size" of an atom
- give examples of how radii are defined in at least two classes of substances
- define ionisation energy and electron affinity, and explain their periodic general trends
- state the meaning and significance of electronegativity.

3.0 MAIN CONTENT

3.1 Organisation of the Periodic Table

From the table highlighted in Module 1 that shows the long form of table with the "block" structure emphasized. You will recall that the two f blocks are written at the bottom merely to keep the table from becoming inconveniently wide; these two blocks actually go in between La-Hf and Ac-Db, respectively, in the *d* block.

Table 2.3: The Periodic Table of Elements



IA 1	IIA 2	IIIB 3	IVB 4	VB 5	VIB 6	VIIB 7	VIII 8	VIII 9	VIII 10	IB 11	IIB 12	IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	VIIA 18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Cs	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Rb	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds								

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Lanthanides
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Actinides

Adapted from: http://www.chem1.com/acad/webtext/atoms/atpt-6.html
To understand how the periodic table is organised, imagine that we write down a long horizontal list of the elements in order of their increasing atomic number. It would begin this way:

H He Li Be B C N O F Ne Na Mg Al Si P S Cl Ar K Ca...

Now if we look at the various physical and chemical properties of these elements, we would find that their values tend to increase or decrease with *Z* in a manner that reveals a repeating pattern— that is, a periodicity. For the elements listed above, these breaks can be indicated by the vertical bars shown in colour:

H **He** | Li Be B C N O F **Ne** | Na Mg Al Si P S Cl **Ar** | Ca ...

Periods

To construct the table, we place each sequence in a separate row, which is known as a *period*. The rows are aligned in such a way that the elements in each vertical column possess certain similarities. Thus the first short-period elements H and He are chemically similar to the elements Li and Ne at the beginning and end of the second period. The first period is split in order to place H above Li and He above Ne.

The "block" nomenclature shown above refers to the sub-orbital type (quantum number l, or s-p-d-f classification) of the highest-energy orbitals that are occupied in a given element. For *n* = 1 there is no *p* block, and the *s* block is split so that helium is placed in the same group as the other inert gases, which it resembles chemically. For the second period (*n* = 2), there is a *p* block but no *d* block; in the usual "long form" of the periodic table it is customary to leave a gap between these two blocks in order to accommodate the *d* blocks that occur at *n* = 3 and above. At *n* = 6 we introduce an *f* block, but in order to hold the table to reasonable dimensions the *f* blocks are placed below the main body of the table.

Groups

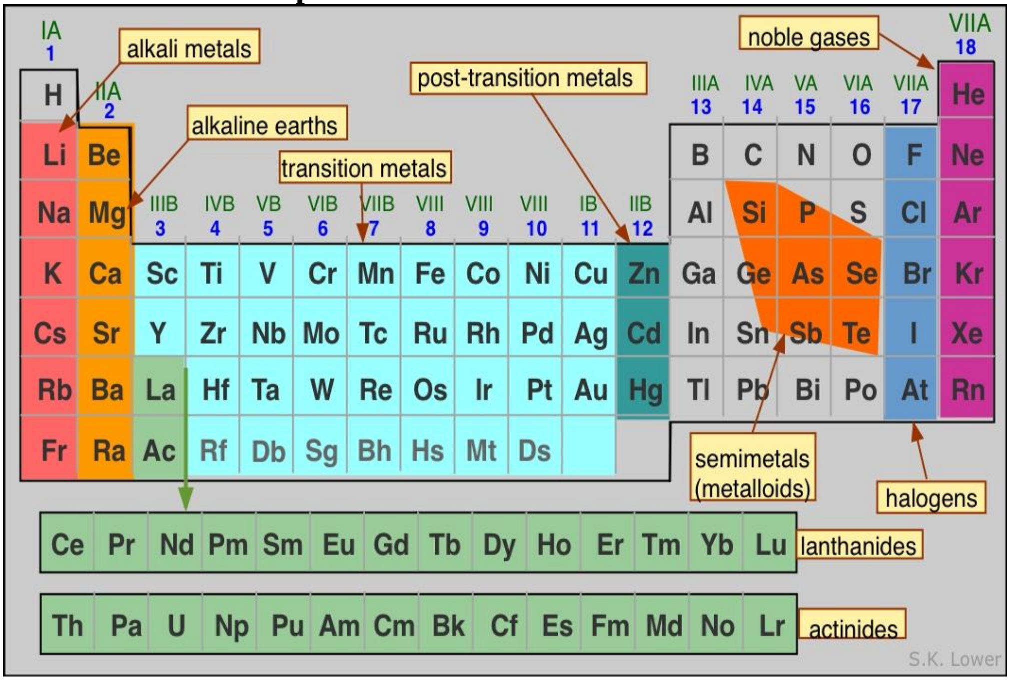
Each column of the periodic table is known as a *group*. The elements belonging to a given group bear a strong similarity in their chemical behaviours.

In the past, two different systems of Roman numerals and letters were used to denote the various groups. North Americans added the letter *B* to denote the *d*-block groups and *A* for the others; this is the system shown in the table above. The rest of the world used *A* for the *d*-block elements and *B* for the others. In 1985, a new international system was adopted in which the columns were simply labelled 1-18. Although this system has met sufficient resistance in North America to slow its incorporation into textbooks, it seems likely that the "one to eighteen" system will gradually take over as older professors (the main hold-outs!) retire.

Families

Chemists have long found it convenient to refer to the elements of different groups, and in some cases of spans of groups by the names indicated in Table 2.4. The two of these that are most important for you to know are the *noble gases* and the *transition metals*.

Table 2.4: Groups of Elements in the Periodic Table



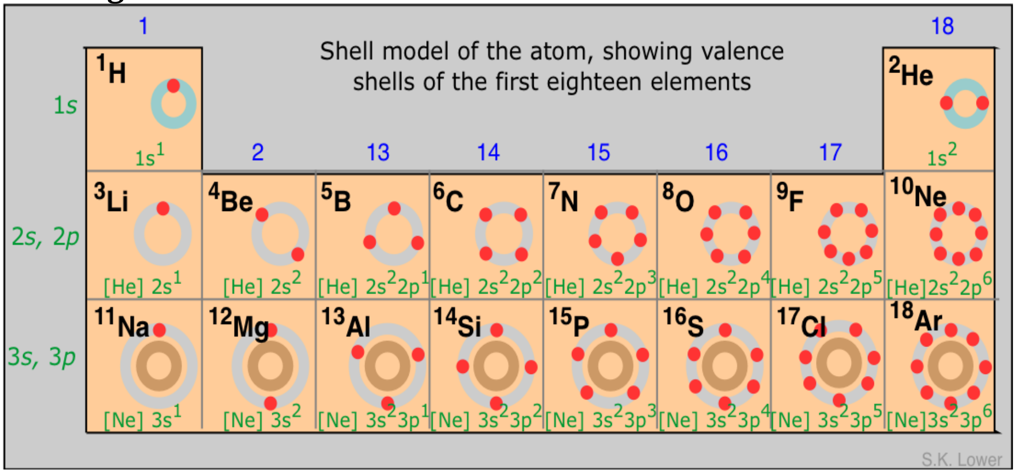
IA 1	IIA 2	IIIB 3	IVB 4	VB 5	VIB 6	VIIB 7	VIII 8	VIII 9	VIII 10	IB 11	IIB 12	IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	VIIA 18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Cs	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Rb	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds								
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Adapted from: http://www.chem1.com/acad/webtext/atoms/atpt-6.html

3.2 The Shell Model of the Atom

The properties of an atom depend ultimately on the number of electrons in the various orbitals, and on the nuclear charge which determines the compactness of the orbitals. In order to relate the properties of the elements to their locations in the periodic table, it is often convenient to make use of a simplified view of the atom in which the nucleus is surrounded by one or more concentric spherical "shells", each of which consists of the highest-principal quantum number orbitals (always *s*- and *p*-orbitals) that contain at least one electron. The shell model (as with any scientific model) is less a description of the world than a simplified way of looking at it that helps us to understand and correlate diverse phenomena. The principal simplification here is that it deals only with the *main group elements* of the *s*- and *p*-blocks, omitting the *d*- and *f*-block elements whose properties tend to be less closely tied to their group numbers.

Table 2.5: Shell Model of the Atom showing Valence Shells of the First Eighteen Elements



Shell model of the atom, showing valence shells of the first eighteen elements

	1	2	13	14	15	16	17	18
1s	^{1}H $1s^1$							^{2}He $1s^2$
2s, 2p	^{3}Li [He] $2s^1$	^{4}Be [He] $2s^2$	^{5}B [He] $2s^2 2p^1$	^{6}C [He] $2s^2 2p^2$	^{7}N [He] $2s^2 2p^3$	^{8}O [He] $2s^2 2p^4$	^{9}F [He] $2s^2 2p^5$	^{10}Ne [He]$2s^2 2p^6$
3s, 3p	^{11}Na [Ne] $3s^1$	^{12}Mg [Ne] $3s^2$	^{13}Al [Ne] $3s^2 3p^1$	^{14}Si [Ne] $3s^2 3p^2$	^{15}P [Ne] $3s^2 3p^3$	^{16}S [Ne] $3s^2 3p^4$	^{17}Cl [Ne] $3s^2 3p^5$	^{18}Ar [Ne]$3s^2 3p^6$

S.K. Lower

Adapted from: http://www.chem1.com/acad/webtext/atoms/atpt-6.html

The electrons (denoted by the dots) in the outer-most shell of an atom are the ones that interact most readily with other atoms, and thus play a major role in governing the chemistry of an element. Notice the use of noble-gas symbols to simplify the electron-configuration notation.

In particular, the number of outer-shell electrons (which is given by the rightmost digit in the *group number*) is a major determinant of an element's "combining power", or *valence*. The general trend is for an atom to gain or lose electrons, either directly (leading to formation of *ions*) or by sharing electrons with other atoms so as to achieve an outer-shell configuration of s^2p^6. This configuration, known as an *octet*, corresponds to that of one of the noble-gas elements of Group 18.

- The elements in Groups 1, 2 and 13 tend to give up their valence electrons to form positive ions such as Na^+, Mg^{2+} and Al^{3+}, as well as compounds NaH, MgH_2 and AlH_3. The outer-shell configurations of the metal atoms in these species correspond to that of neon.
- Elements in Groups 15-17 tend to acquire electrons, forming ions such as P^{3-}, S^{2-} and Cl^- or compounds such as PH_3, H_2S and HCl. The outer-shell configurations of these elements correspond to that of argon.
- The Group 14 elements do not normally form ions at all, but share electrons with other elements in tetravalent compounds such as CH_4.

The above diagram shows the first three rows of what are known as the *representative elements*— that is, the *s*- and *p*-block elements only. As we move farther down (into the fourth row and below), the presence of *d*-electrons exerts a complicating influence which allows elements to exhibit multiple valances. This effect is especially noticeable in the transition-metal elements; this is the reason for not including the d-block with the representative elements at all.

3.3 Effective Nuclear Charge

Those electrons in the outmost or valence shell are especially important because they are the ones that can engage in the sharing and exchange that is responsible for chemical reactions; how tightly they are bound to the atom determines much of the chemistry of the element. The degree of binding is the result of two opposing forces:

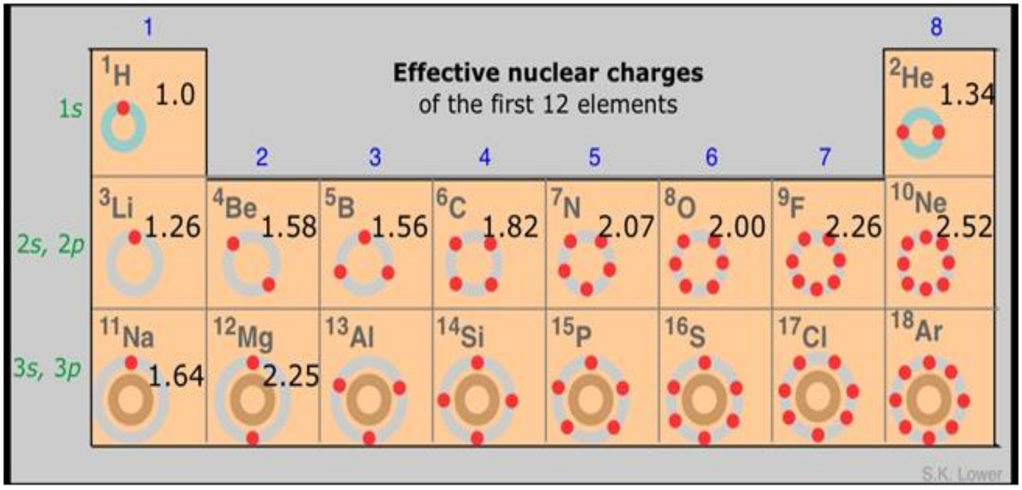
- the attraction between the electron and the nucleus
- the repulsions between the electron in question and all the other electrons in the atom.

All that matters is the net force, the difference between the nuclear attraction and the totality of the electron-electron repulsions.

We can simplify the shell model even further by imagine that the valence shell electrons are the *only* electrons in the atom, and that the nuclear charge has whatever value that would be required to bind these electrons as tightly as it is observed experimentally. Because the number of electrons in this model is less than the atomic number *Z,* the required nuclear charge will also be smaller; this is known as the *effective nuclear charge*. Effective nuclear charge is essentially the positive charge that a valence electron "sees".

Part of the difference between Z and $Z_{effective}$ is due to other electrons in the valence shell, but this is usually only a minor contributor because these electrons tend to act as if they are spread out in a diffuse spherical shell of larger radius. The main actors here are the electrons in the much more compact inner shells which surround the nucleus and exert what is often called a shielding or "*screening*" effect on the valence electrons.

Table 2.6: Effective Nuclear Charges of the first 12 Elements



Effective nuclear charges
of the first 12 elements

	1	2	3	4	5	6	7	8
1s	^{1}H 1.0							^{2}He 1.34
2s, 2p	^{3}Li 1.26	^{4}Be 1.58	^{5}B 1.56	^{6}C 1.82	^{7}N 2.07	^{8}O 2.00	^{9}F 2.26	^{10}Ne 2.52
3s, 3p	^{11}Na 1.64	^{12}Mg 2.25	^{13}Al	^{14}Si	^{15}P	^{16}S	^{17}Cl	^{18}Ar

S.K. Lower

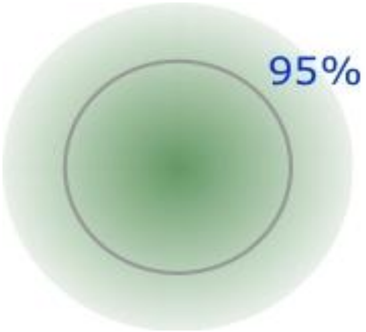
Adapted from: http://www.chem1.com/acad/webtext/atoms/atpt-6.html
The formula for calculating effective nuclear charge is not very complicated, but we will skip a discussion of it here. An even simpler although rather crude procedure is to just subtract the number of inner-shell electrons from the nuclear charge; the result is a form of effective nuclear charge which is called the *core charge* of the atom.

Fig. 2.1: Calculation of Effective Nuclear Charge

3.4 Sizes of Atoms and Ions

What do we mean by the "size" of an atom?

The concept of "size" is somewhat ambiguous when applied to the scale of atoms and molecules. The reason for this is apparent when you recall that an atom has no definite boundary; there is a finite (but very small) probability of finding the electron of a hydrogen atom, for example, 1 cm, or even 1 km from the nucleus. It is not possible to specify a definite value for the radius of an isolated atom; the best we can do is to define a spherical shell within whose radius some arbitrary percentage of the electron density can be found.



When an atom is combined with other atoms in a solid element or compound, an effective radius can be determined by observing the distances between adjacent rows of atoms in these solids. This is most commonly carried out by X-ray scattering experiments. Because of the different ways in which atoms can aggregate together, several different kinds of atomic radii can be defined.

Distances on the atomic scale have traditionally been expressed in Ångstrom (Å) units (1 Å = 10^{-8} cm = 10^{-10} m); but nowadays the picometer is preferred:

1 pm = 10^{-12} m = 10^{-10} cm = 10^{-2} Å, or 1Å = 100 pm. The radii of atoms and ions are typically in the range of 70 - 400 pm.

A rough idea of the size of a metallic atom can be obtained simply by measuring the density of a sample of the metal. This gives us the number of atoms per unit volume of the solid. The atoms are assumed to be spheres of radius r in contact with each other, each of which sits in a cubic box of edge length $2r$. The volume of each box is just the total volume of the solid divided by the number of atoms in that mass of the solid; the atomic radius is the cube root of r.

Although the radius of an atom or ion cannot be measured directly, in most cases it can be inferred from measurements of the distance between adjacent nuclei in a crystalline solid. This is most commonly carried out by X-ray scattering experiments. Because such solids fall into several different classes, several kinds of atomic radius are defined. Many atoms have several different radii; for example, sodium forms a metallic solid and thus has a metallic radius, it forms a gaseous molecule Na_2 in the vapour phase (covalent radius), and of course, it forms ionic solids such as NaCl.

Metallic radius is half the distance between nuclei in a metallic crystal.

Covalent radius is half the distance between like atoms that are bonded together in a molecule.

Van der Waals radius is the effective radius of adjacent atoms which are not chemically bonded in a solid, but are presumably in "contact".

An example would be the distance between the iodine atoms of adjacent I_2 molecules in crystalline iodine.

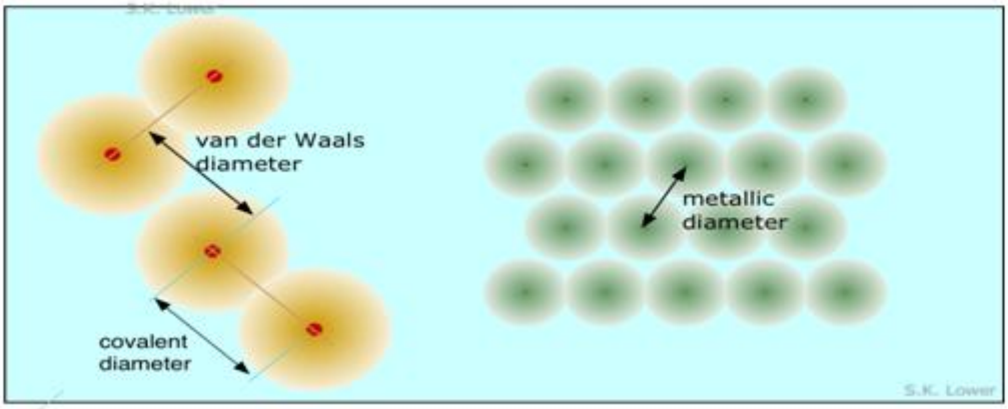


Fig. 2.2: Sizes of Atoms (Adapted from: http://www.chem1.com/acad/webtext/atoms/atpt-6.html).

Ionic radius is the effective radius of ions in solids such as NaCl. It is easy enough to measure the distance between adjacent rows of Na^+ and Cl^- ions in such a crystal, but there is no unambiguous way to decide what portions of this distance are attributable to each ion. The best one can do is make estimates based on studies of several different ionic solids (LiI, KI, NaI, for example) that contain one ion in common. Many such estimates have been made, and they turn out to be remarkably consistent.

The lithium ion is sufficiently small that in LI, the iodide ions are in contact, so I-I distances are twice the ionic radius of I^-. This is not true for KI, but in this solid, adjacent potassium and iodide ions are in contact, allowing estimation of the K^+ ionic radius.

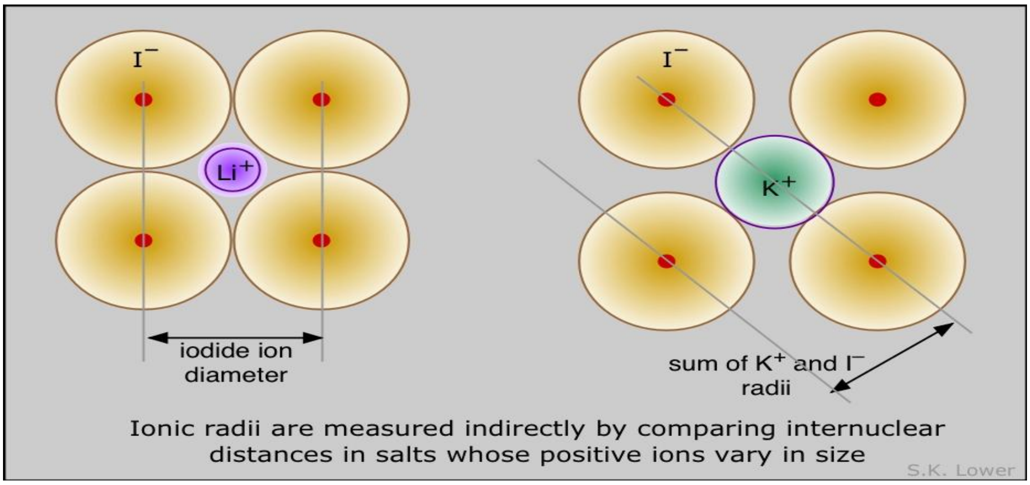


Fig. 2.3: Ionic Radius of I⁻

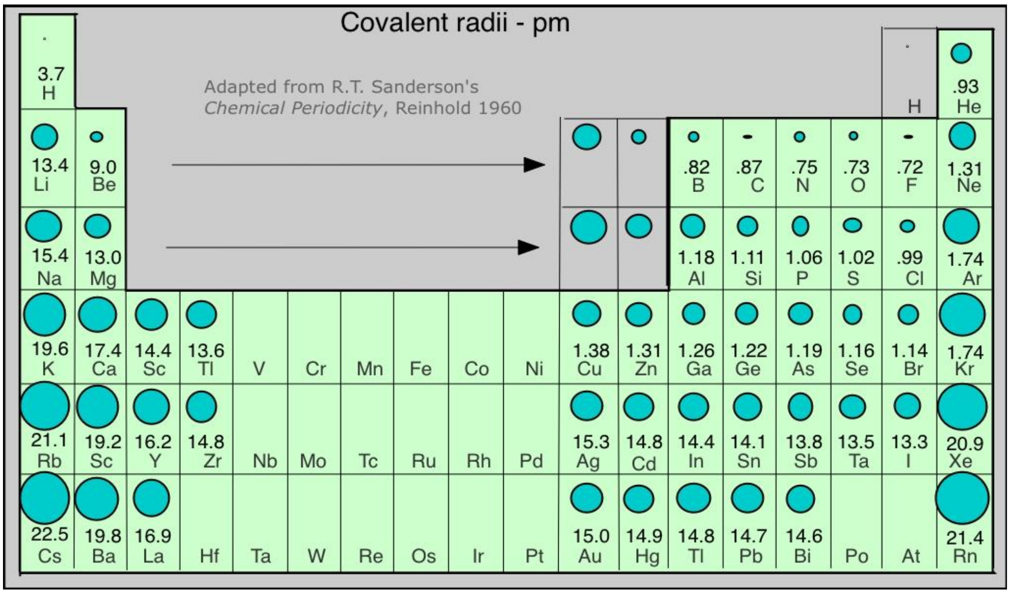
Adapted from: http://www.chem1.com/acad/webtext/atoms/atpt-6.html)
Many atoms have several different radii; for example, sodium forms a metallic solid and thus has a metallic radius. It also forms a gaseous molecule Na_2 in the vapour phase (covalent radius), and of course it forms ionic solids as mentioned above.

3.5 Periodic Trends in Atomic Properties

3.5.1 Atomic Size

We would expect the size of an atom to depend mainly on the principal quantum number of the highest occupied orbital; in other words, on the "number of occupied electron shells". Since each row in the periodic table corresponds to an increment in n, atomic radius increases as we move down a column. The other important factor is the nuclear charge; the higher the atomic number, the more strongly will the electrons be drawn toward the nucleus, and the smaller the atom. This effect is responsible for the contraction we observe as we move across the periodic table from left to right.

Table 2.7: Covalent Radii of Elements



Adapted from: http://www.chem1.com/acad/webtext/atoms/atpt-6.html
Table 2.7 shows a periodic table in which the sizes of the atoms are represented graphically. The apparent discontinuities in this diagram reflect the difficulty of comparing the radii of atoms of metallic and non-metallic bonding types. Radii of the noble gas elements are estimates from those of nearby elements.

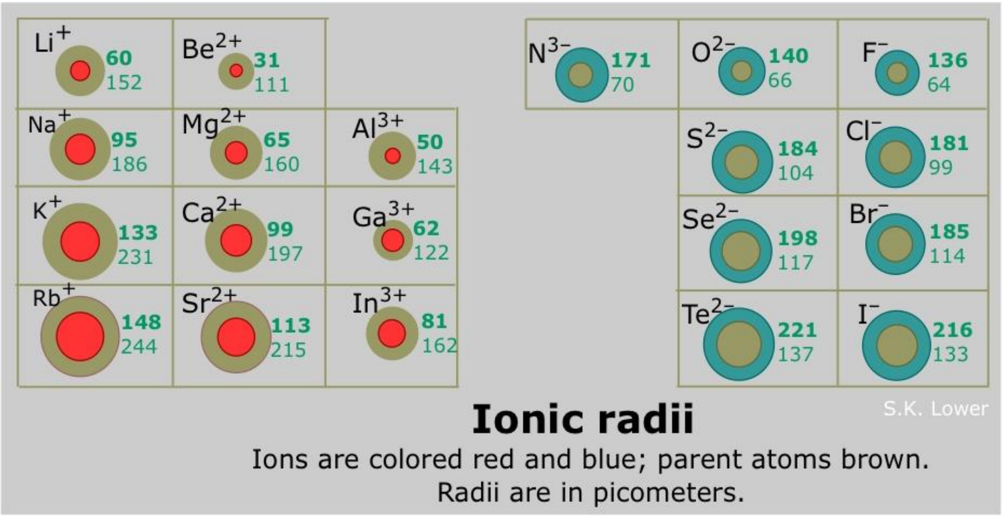
3.5.2 Ionic Radii

A positive ion is always smaller than the neutral atom. This is due to the diminished electron-electron repulsion. If a second electron is lost, the ion gets even smaller; for example, the ionic radius of Fe^{2+} is 76 pm, while that of Fe^{3+} is 65 pm. If formation of the ion involves complete emptying of the outer shell, then the decrease in radius is especially great.

The hydrogen ion H^+ is in a class by itself; having no electron cloud at all, its radius is that of the bare proton, or about 0.1 pm— a contraction of 99.999%. Because the unit positive charge is concentrated into such a small volume of space, the *charge density* of the hydrogen ion is extremely high; it interacts very strongly with other matter, including water molecules, and in aqueous solution, it exists only as the *hydronium ion* H_3O^+.

Negative ions are always larger than the parent ion; the addition of one or more electrons to an existing shell increases *electron-electron repulsion* which results in a general expansion of the atom.

Table 2.8: Ionic Radii of Elements



An *isoelectronic series* is a sequence of species all having the same number of electrons (and thus, the same amount of electron-electron repulsion) but differing in nuclear charge. Of course, only one member of such a sequence can be a neutral atom (for instance, neon in the series shown below.) The effect of increasing nuclear charge on the radius is clearly seen.

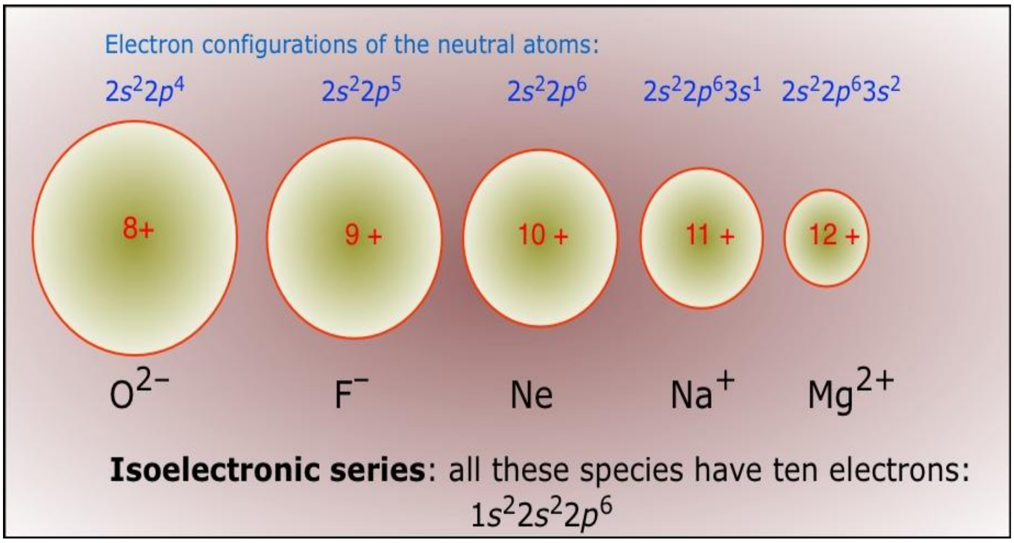


Fig. 2.4: Isoelectronic Series

Periodic trends in ion formation

Chemical reactions are based largely on the interactions between the most loosely bound electrons in atoms, so it is not surprising that the tendency of an atom to gain, lose or share electrons is one of its fundamental chemical properties.

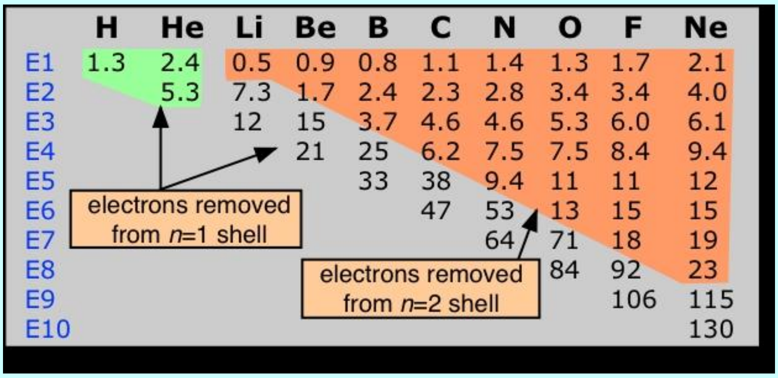
3.5.3 Ionisation Energy

This term refers to the formation of *positive* ions. In order to remove an electron from an atom, work must be done to overcome the electrostatic attraction between the electron and the nucleus; this work is called the *ionisation energy* of the atom and corresponds to the exothermic process in which M(*g*) stands for any isolated (gaseous) atom.

$M(g) \rightarrow M^{+}(g) + e^{-}$

An atom has as many ionisation energies as it has electrons. Electrons are always removed from the highest-energy occupied orbital. An examination of the successive ionisation energies of the first ten elements (below) provides experimental confirmation that the binding of the two innermost electrons (1*s* orbital) is significantly different from that of the *n* = 2 electrons. Successive ionisation energies of an atom increase rapidly as the reduction in the electron-electron repulsion causes the electron shells to contract; thus binding the electrons even more tightly to the nucleus.

Table 2.9: Successive Ionisations of the first Ten Elements



	H	He	Li	Be	B	C	N	O	F	Ne
E1	1.3	2.4	0.5	0.9	0.8	1.1	1.4	1.3	1.7	2.1
E2		5.3	7.3	1.7	2.4	2.3	2.8	3.4	3.4	4.0
E3			12	15	3.7	4.6	4.6	5.3	6.0	6.1
E4				21	25	6.2	7.5	7.5	8.4	9.4
E5					33	38	9.4	11	11	12
E6						47	53	13	15	15
E7							64	71	18	19
E8								84	92	23
E9									106	115
E10										130

Note the very large jumps in the energies required to remove electrons from the 1s orbitals of atoms of the second-row elements Li-Ne.

Ionisation energies increase with the nuclear charge Z as we move across the periodic table. They decrease as we move down the table because in each period, the electron is being removed from a shell one step farther from the nucleus than in the atom immediately above it. This results in the familiar zigzag lines when the first ionisation energies are plotted as a function of Z.

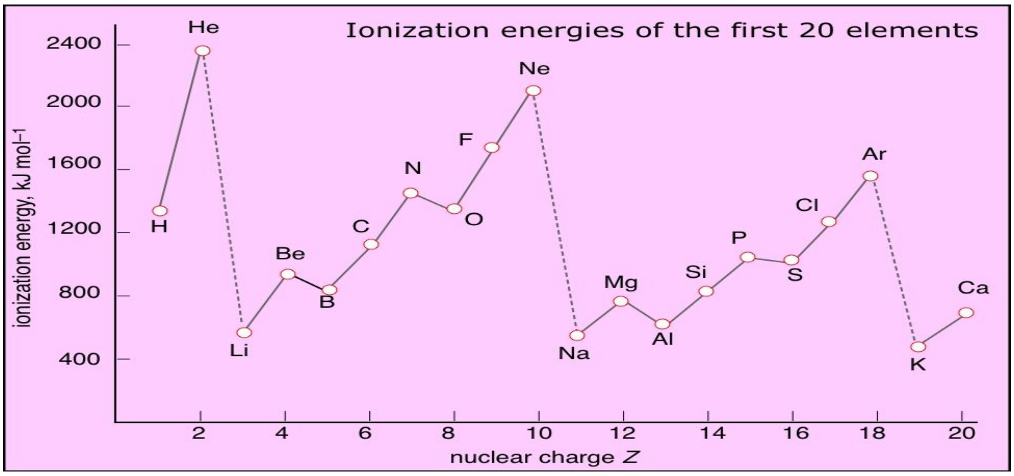


Fig. 2.5: Ionisation Energies of the first Twenty Elements

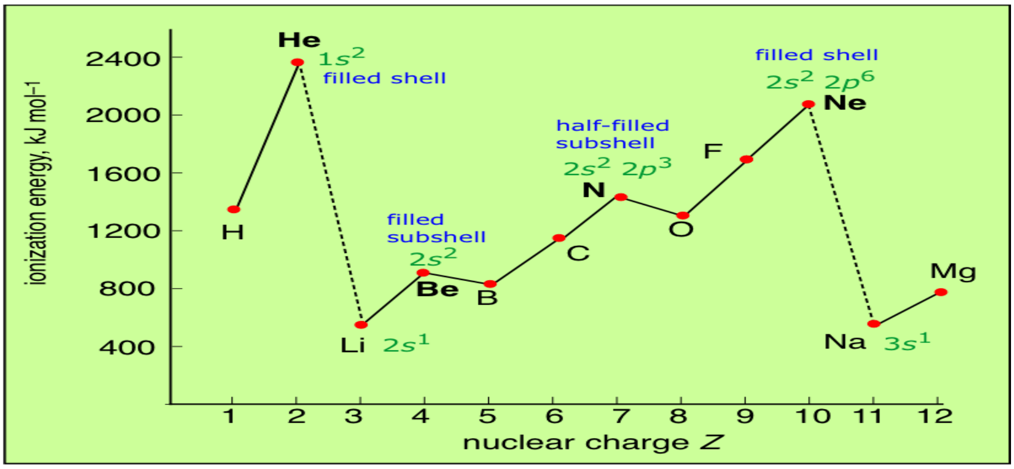
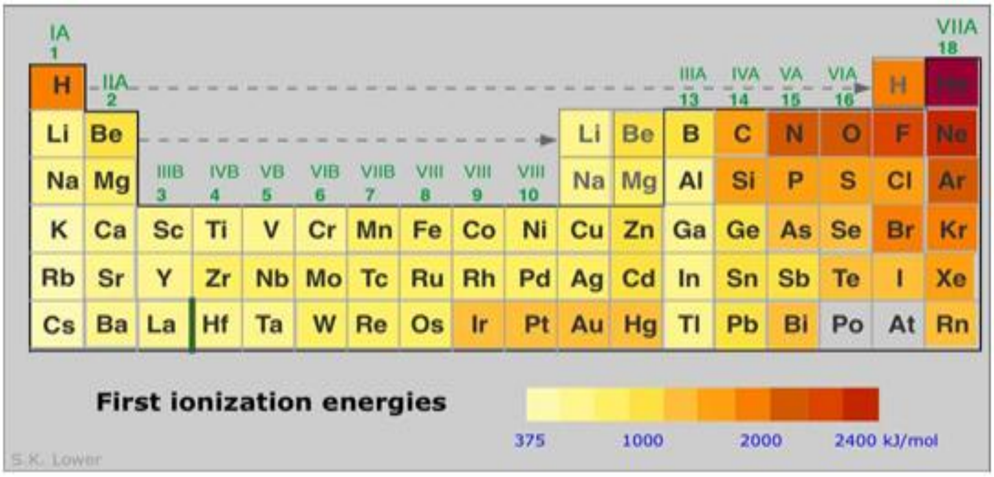


Fig. 2.6: Plot of Ionisation Energies against Nuclear Charges of Elements - This more detailed plot of the ionisation energies of the atoms of the first ten elements reveals some interesting irregularities that can be related to the slightly lower energies (greater stabilities) of electrons in half-filled (spin-unpaired) relative to completely-filled sub-shells.

Finally, a more comprehensive survey of the ionisation energies of the main group elements is shown below:

Table 2.8: First Ionisation Energies of Elements



IA 1	IIA 2	IIIB 3	IVB 4	VB 5	VIB 6	VIIB 7	VIII 8	VIII 9	VIII 10			IIIA 13	IVA 14	VA 15	VIA 16		VIIA 18
H																H	He
Li	Be									Li	Be	B	C	N	O	F	Ne
Na	Mg									Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

Some points to note:

- The noble gases have the highest ionisation energies of any element in the period. This has nothing to do with any mysterious "special stability" of the s^2p^6 electron configuration; it is simply a matter of the high nuclear charge acting on more contracted orbitals.
- Ionisation energies (as well as many other properties) tend not to vary greatly amongst the *d*-block elements. This reflects the fact that as the more-compact *d* orbitals are being filled, they exert a screening effect that partly offsets the increasing nuclear charge on the outermost *s* orbitals of higher principal quantum number.
- Each of the Group 13 elements has a lower first- ionisation energies than that of the element preceding it. The reversal of the ionisation energies trend in this group is often attributed to the more easy removal of the single outer-shell p electron compared to that of electrons contained in filled (and thus spin-paired) *s*- and *d*-orbitals in the preceding elements.

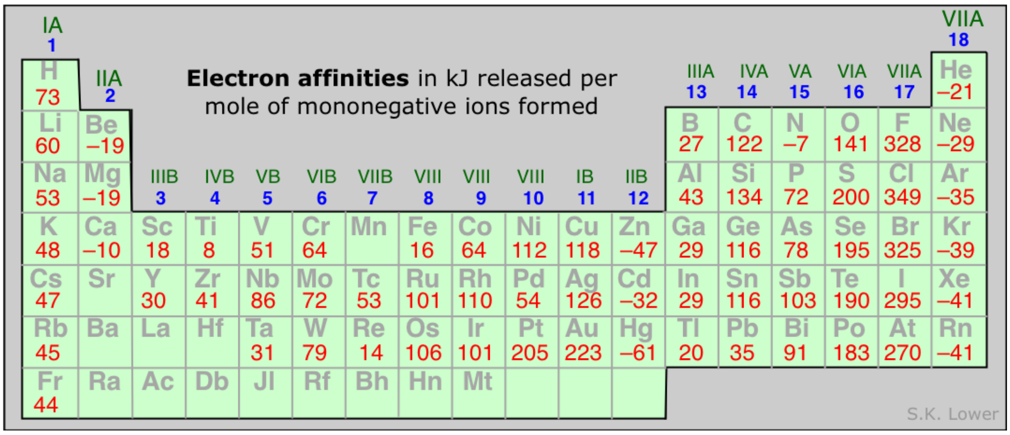
3.5.4 Electron Affinity

Formation of a negative ion occurs when an electron from some external sources enters the atom and become incorporated into the lowest energy orbital that possesses a vacancy. Because the entering electron is attracted to the positive nucleus, the formation of negative ions is usually exothermic. The energy given off is the electron affinity of the atom. For some atoms, the electron affinity appears to be slightly negative, suggesting that electron-electron repulsion is the dominant factor in these instances.

In general, electron affinities tend to be much smaller than ionisation energies, suggesting that they are controlled by opposing factors having similar magnitudes. These two factors are, as stated before, the nuclear charge and electron-electron repulsion. But the latter which is only a minor actor in positive ion formation, is now much more significant. One reason for this is that the electrons contained in the inner shells of the atom exert a collective negative charge that partially cancels the charge of the nucleus, thus exerting a so-called shielding effect which diminishes the tendency for negative ions to form.

Because of these opposing effects, the periodic trends in electron affinities are not as clear as are those of ionisation energies. This is particularly evident in the first few rows of the periodic table, in which small effects tend to be magnified anyway because an added electron produces a large percentage increase in the number of electrons in the atom.

Table 2.9: Electron Affinities for Elements



Electron affinities in kJ released per mole of mononegative ions formed

IA 1	IIA 2	IIIB 3	IVB 4	VB 5	VIB 6	VIIB 7	VIII 8	VIII 9	VIII 10	IB 11	IIB 12	IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	VIIA 18
H 73																	He –21
Li 60	Be –19											B 27	C 122	N –7	O 141	F 328	Ne –29
Na 53	Mg –19											Al 43	Si 134	P 72	S 200	Cl 349	Ar –35
K 48	Ca –10	Sc 18	Ti 8	V 51	Cr 64	Mn	Fe 16	Co 64	Ni 112	Cu 118	Zn –47	Ga 29	Ge 116	As 78	Se 195	Br 325	Kr –39
Cs 47	Sr	Y 30	Zr 41	Nb 86	Mo 72	Tc 53	Ru 101	Rh 110	Pd 54	Ag 126	Cd –32	In 29	Sn 116	Sb 103	Te 190	I 295	Xe –41
Rb 45	Ba	La	Hf	Ta 31	W 79	Re 14	Os 106	Ir 101	Pt 205	Au 223	Hg –61	Tl 20	Pb 35	Bi 91	Po 183	At 270	Rn –41
Fr 44	Ra	Ac	Db	Jl	Rf	Bh	Hn	Mt									

S.K. Lower

In general, we can say that electron affinities become more exothermic as we move from left to right across a period (owing to increased nuclear charge and smaller atom size). There are some interesting irregularities, however:

- In the Group 2 elements, the filled 2*s* orbital apparently shields the nucleus so effectively that the electron affinities are slightly endothermic.
- The Group 15 elements have rather low values, due possibly to the need to place the added electron in a half-filled *p* orbital; why the electron affinity of nitrogen should be endothermic is not clear. The vertical trend is for electron affinity to become less exothermic in successive periods owing to better shielding of the nucleus by more inner shells and the greater size of the atom, but here also there are some apparent anomalies.

3.5.5 Electronegativity

When two elements are joined in a chemical bond, the element that attracts the shared electrons more strongly is more *electronegative*. Elements with low electronegativity (the metallic elements) are said to be *electropositive*.

It is important to understand that electronegativity is properties of atoms that are chemically bound to each other; there is no way of measuring the electronegativity of an isolated atom.

Moreover, the same atom can exhibit different electronegativities in different chemical environments, so the "electronegativity of an element" is only a general guide to its chemical behaviour rather than an exact specification of its behaviour in a particular compound. Nevertheless, electronegativity is eminently useful in summarising the chemical behaviour of an element. You will make considerable use of electronegativity when you study chemical bonding and the chemistry of the individual elements.

Because there is no single definition of electronegativity, any numerical scale for measuring it must of necessity be somewhat arbitrary. Most of such scales are themselves based on atomic properties that are directly measurable and which also relate in one way or the other to electron-attracting propensity. The most widely used of these scales was devised by Linus Pauling and is related to ionisation energy and electron affinity. The Pauling scale runs from 0 to 4; the highest electron affinity, 4.0, is assigned to fluorine, while caesium has the lowest value of 0.7. Values less than about 2.2 are usually associated with electropositive or metallic character.

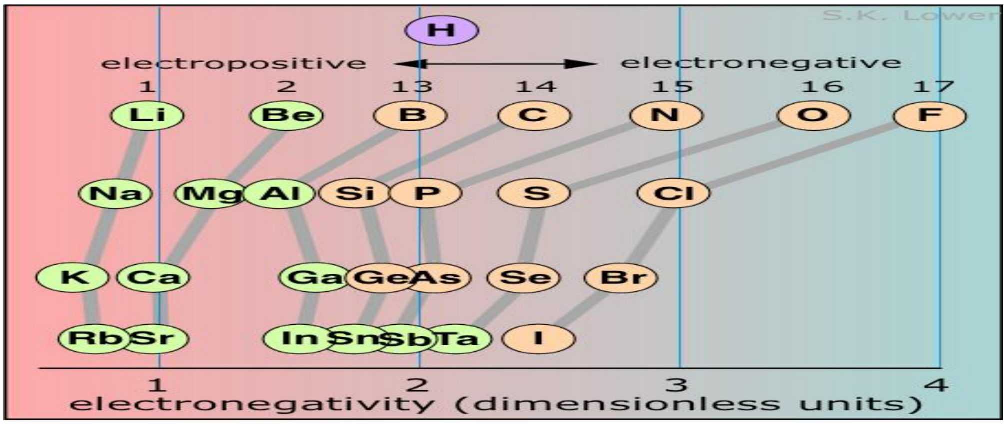


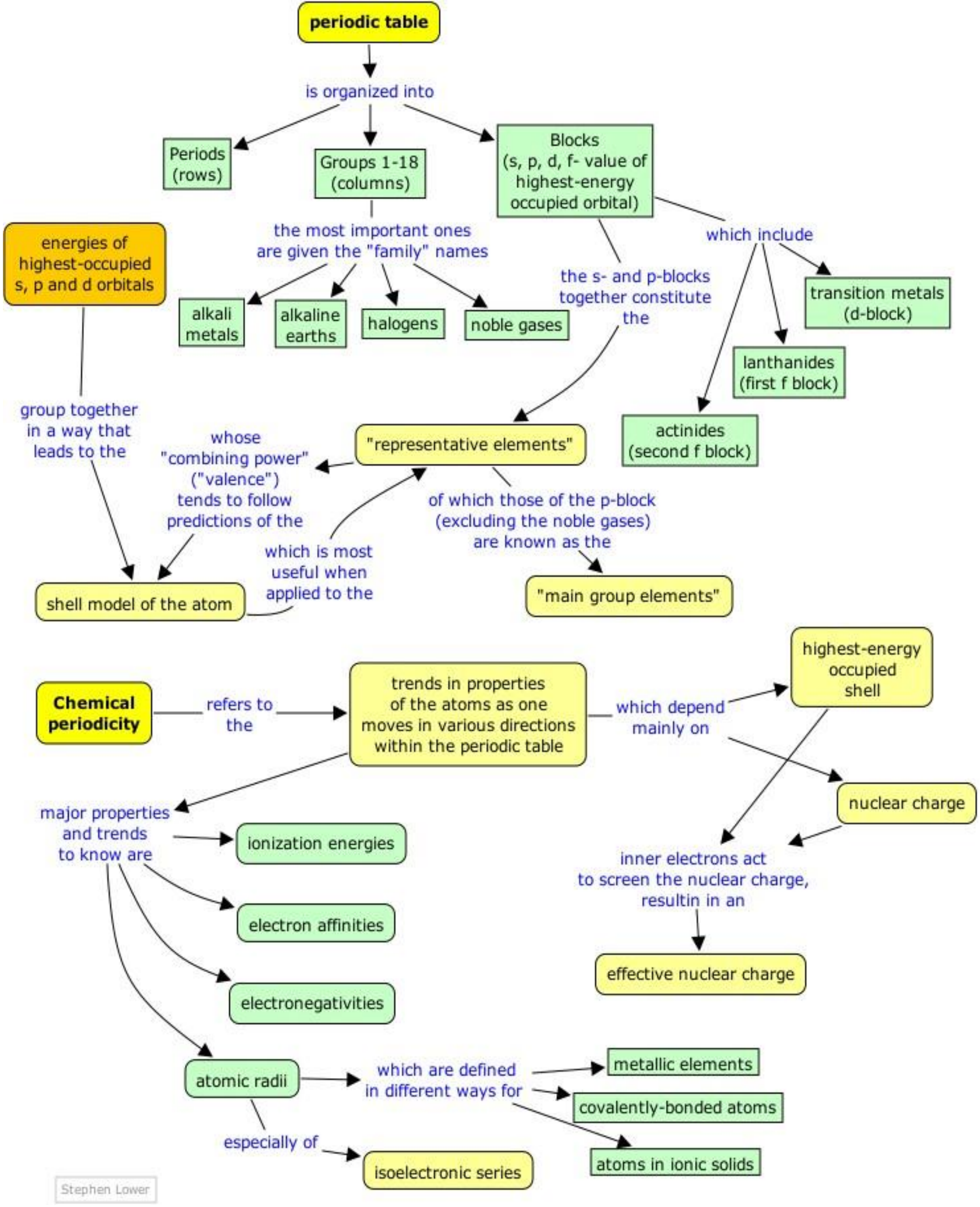
Fig. 2.7: Electronegativity Scale

In the representation of the scale shown in the above figure, the elements are arranged in rows corresponding to their locations in the periodic table. The correlation is obvious; electronegativity is associated with the higher rows and the rightmost columns.

The location of hydrogen on this scale reflects some of the significant chemical properties of this element. Although it acts like a metallic element in many respects (forming a positive ion, for example), it can also form hydride-ion (H^-) solids with the more electropositive elements, and of course its ability to share electrons with carbon and other *p*-block elements gives rise to a very rich chemistry, including of course the millions of organic compounds.

4.0 SUMMARY

The concept map below gives a summary to this unit.



5.0 CONCLUSION

Periodic table is the table of the chemical elements arranged to illustrate patterns of recurring chemical and physical properties. Elements, such as oxygen, iron, and gold, are the most basic chemical substances and cannot be broken down by chemical reactions. All other substances are formed from combinations of elements. The periodic table provides a means of arranging all the known elements and even those yet to be discovered.

6.0 TUTOR-MARKED ASSIGNMENT

i. Decide which statements are true and explain why
  a. The Na^+ ion is smaller than the K^+ ion.
  b. The Na^+ ion is smaller than the Na atom.
  c. Ionisation energies increase down the group.
  d. All the halogens have higher first ionisation energies than all the noble gases.
  e. More energy is released when an electron enters the 3p shell of chlorine than when it enters the 4p shell of bromine.
  f. The electron affinity of a cation is larger than that of the parent atom.

ii. Arrange these elements in order of increasing electronegativity: Al, Na, Si, Mg.
iii. What do you understand by the term ‘effective nuclear charge’?

7.0 REFERENCES/FURTHER READING

http://www.chem1.com/acad/webtext/atoms/atpt-6.html

Huheey, J.E. *et* al. (1993). *Inorganic Chemistry: Principles of Structure and Reactivity*. (4th ed.). New York, USA: HarperCollins.

Scerri, E. (2007). *The periodic table: Its Story and Its Significance*. Oxford: Oxford University Press.

MODULE 3

UNIT 1 IONIC BONDING

CONTENT

1.0 INTRODUCTION

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.

For example, you are familiar with the fairly benign unspectacular behaviour of common white crystalline table salt (NaCl). Salt consists of positive sodium ions (Na^+) and negative chloride ions (Cl^-). On the other hand the element sodium is a silvery gray metal composed of neutral atoms which react vigorously with water or air. Chlorine as an element is a neutral greenish-yellow, poisonous, diatomic gas (Cl_2).

The main principle to remember is that 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

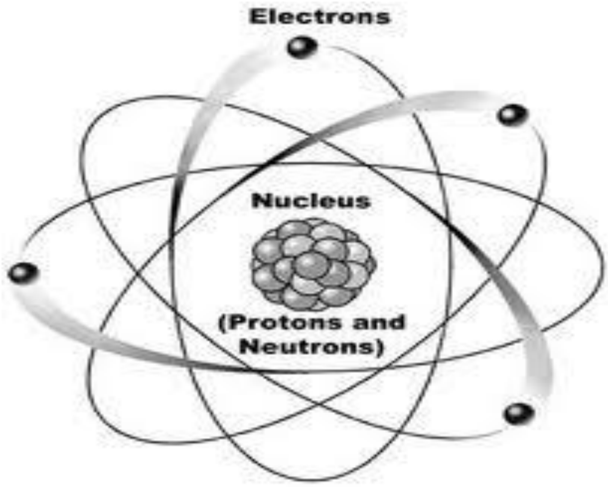
At the end of this unit, you should be able to:

- describe how an ionic bond is formed
- describe the effect of ionisation energy on the process of ionic bonding formation
- explain how the octet rule applies to atoms of metallic and nonmetallic elements
- describe how cations and anions form
- define lattice enthalpy terms
- construct a simple Born Haber cycle
- eefine lattice enthalpy terms. Construct a simple Born Haber cycle
- list three energy terms that influence the tendency for two elements to form an ionic compound
- use the Born-Haber cycle to calculate the magnitude of the lattice energies of ionic solids.

3.0 MAIN CONTENT

3.1 Basic Principles of Bonding

What are molecules made from? They are made from atoms, which are themselves made from nuclei and electrons. These building blocks carry an electrical charge: nuclei are positively charged, and electrons are negatively charged. The nuclei themselves are made up of (positively charged) protons and (neutral) neutrons. This is all summarised on the following picture:



The Atom.

Different types of atom have different numbers of protons, neutrons, and electrons. For example, **carbon** atoms have 6 protons, 6 neutrons, and 6 electrons.

Charged species interact with each other: like charges (+ and + or - and -) repel each other, opposite charges (- and +) attract each other. This well-known principle from physics is summarised by Coulomb's law:

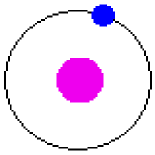
$$F = \frac{1}{4\pi\epsilon_0}\frac{q_1 q_2}{r^2}$$

(Here, F is the **force** between the two charges; ε_0 is a constant (not important here), q_1 and q_2 are the values of the charges involved, and r is the distance between them.)

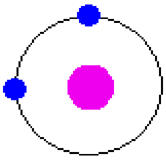
This force between charged species is central to **all** of chemistry, and in particular to all the types of bonding we will discuss.

First, it explains how atoms hold together: the negatively charged electrons are attracted to the positively charged nucleus more than they are repelled by the other electrons.

There is a fine balance between the attractive force holding the electrons close to the nucleus, and the repulsive force which tends to keep electrons away from each other. The result of this competition between attractive and repulsive charge-charge interactions is what explains the **detailed structure** of atoms. The electrons in atoms tend to form into concentric **shells**. For the hydrogen atom, with just one electron and one proton (Z = 1), the electron sits in the first shell, as shown here:



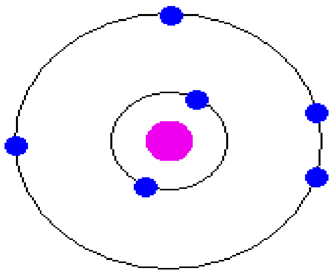
Hydrogen Atom (Z = 1)



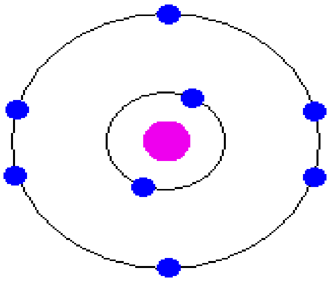
Helium Atom (Z = 2)

The Helium atom has two protons, two neutrons and 2 electrons (i.e., Z = 2). Both electrons sit in the first shell.

For elements with more electrons, there is no more room in the first shell, and so a **second shell** is occupied. This is shown below for carbon (Z = 6) and oxygen (Z = 8).

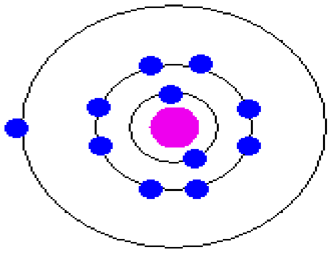


Carbon Atom (Z = 6)

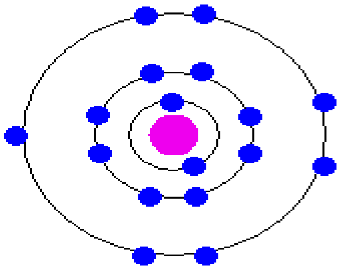


Oxygen Atom (Z = 8)

Above 10 electrons, the second shell contains eight electrons and is full. For the elements beyond (starting with sodium, Z = 11), the last electrons therefore sit in the **third shell**, as shown here for sodium and chlorine (Z = 17):



Sodium Atom (Z = 11)



Chlorine Atom (Z = 17)

This structural description leads naturally to an important property of atoms, the **octet rule**: atoms have a strong tendency to lose, gain, or share electrons if this leads to them having a complete shell of electrons around them. In other words, atoms prefer to have a total of 2, 10, or 18 electrons around them.

3.2 Ionic Bonds

Elements in the first few columns of the periodic table have a 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, easily lose one electron to form mono-positive ions, Na^+ and K^+. These ions have 10 and 18 electrons, respectively and they are quite stable according to the octet rule.

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.

Likewise, 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.

Now, imagine what will happen when one sodium atom meets one chlorine atom: the sodium atom will lose one electron to give Na^+, and the chlorine atom will gain that electron to give Cl^-. This can be represented schematically in the following way:

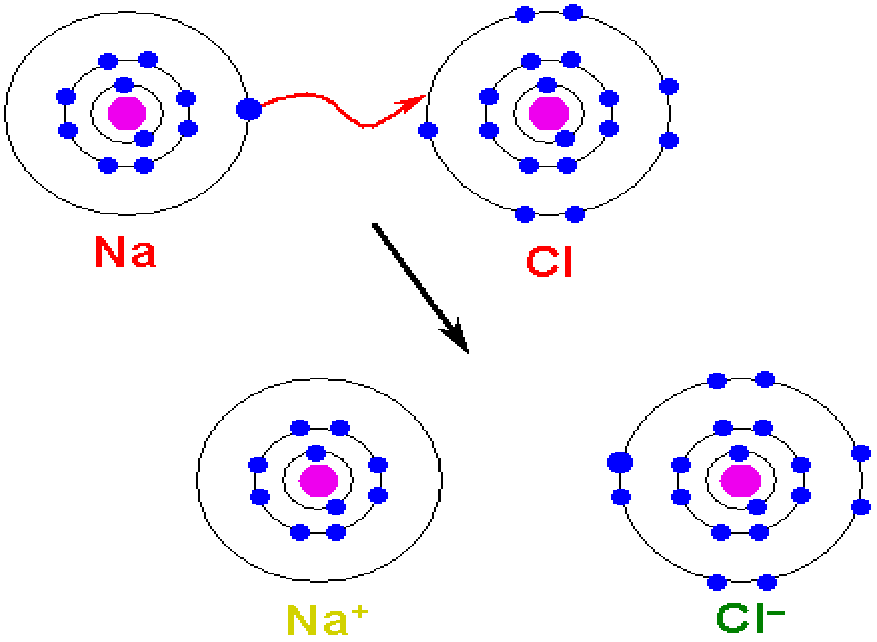
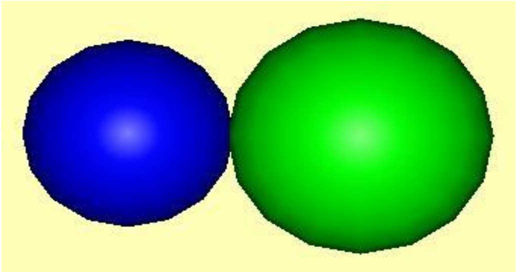
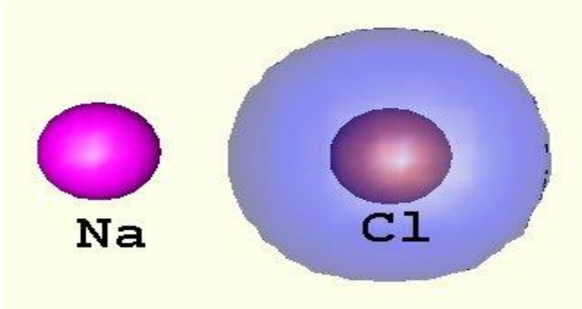


Fig. 3.1: Formation of Sodium Chloride by Ionic Bonding

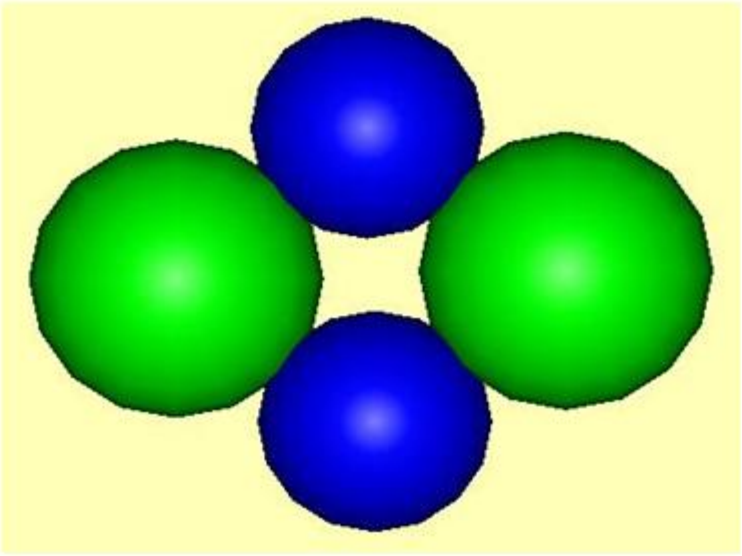
The resulting ions, which have opposite charges, will be attracted to one another, and will draw closer, until they "touch". This happens when the inner shell of electrons on the sodium ion (the smaller sphere) starts to overlap with the outer shell of electrons on the chloride anion (the bigger sphere).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



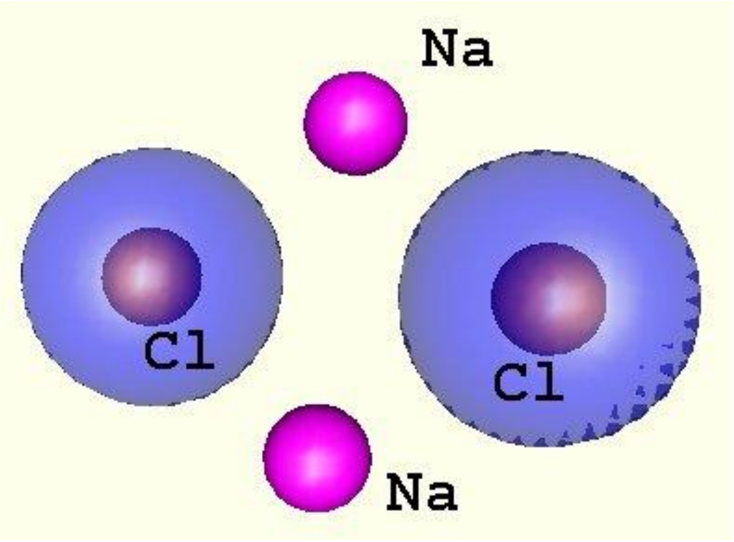
It is possible to determine where the *valence* electrons are situated in this pair of ions. They are almost entirely situated on the chlorine atom, as expected: the sodium atom has lost its only valence (3s) electron, whereas chlorine has gained an electron and has the $3s^2 3p^6$ valence configuration.



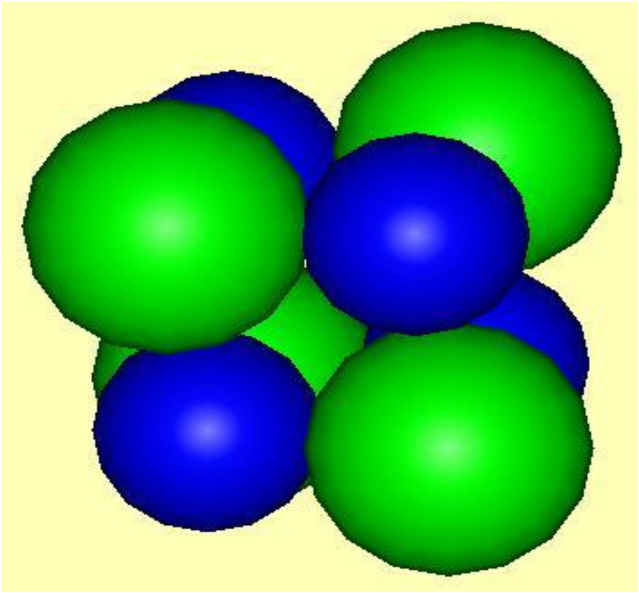
NaCl, or sodium chloride, is however more complicated than this! This is because charge-charge interaction occurs in all directions. Once an Na^+ cation has attracted a Cl^- anion in one direction, it can attract another in a different direction. So two pairs of ions such as above can come together to form a species with four ions in total, all placed so as to interact favourably with ions of opposite charge:



Here, too, all the valence electrons sit on the chlorine atoms:



And this need not stop here... The next step is to get 8 ions, 4 each of sodium and chlorine:



The stable form of sodium chloride involves a very large number of NaCl units arranged in a lattice (or regular arrangement) millions of atoms across. Because the lattice is rigid, this means that one gets a solid: the ions do not move much with respect to one another. Also, because atoms are so small, even a small crystal of salt will have billions of sodium chloride units in it! The ions are arranged so that each positive (sodium) ion is close to many negative (chloride) ions, as shown in Figure 3.2 below:

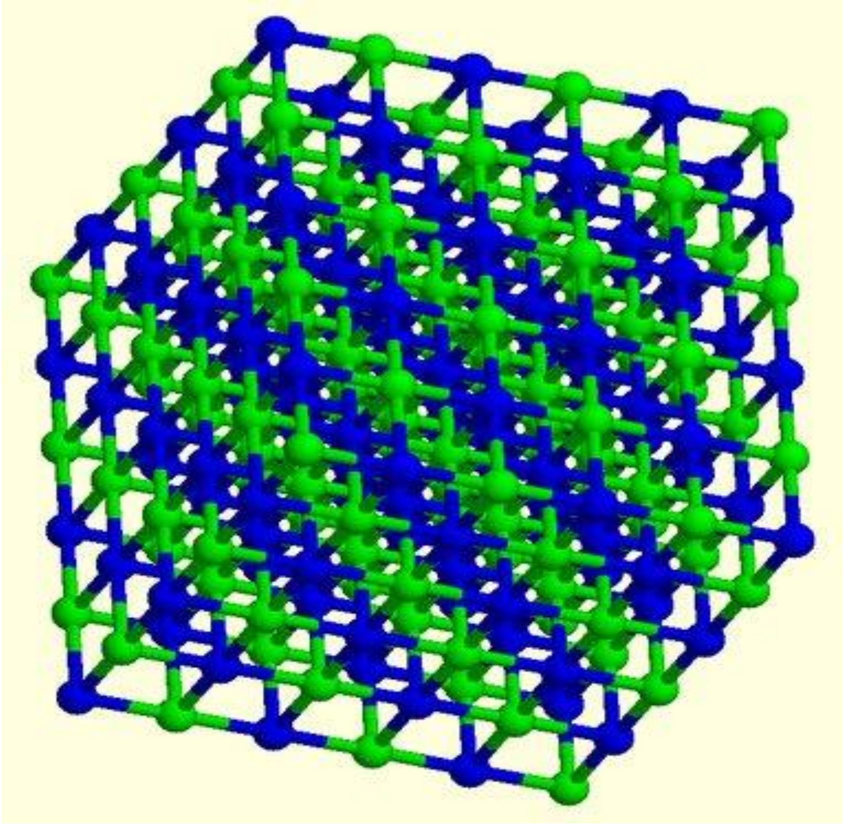


Fig. 3.2: The Arrangement of Ions such that each Positive (sodium) ion is close to many Negative (chloride) ions

Can you count how many ions each sodium is next to? And how many ions each chlorine is next to? These pairs of ions in close contact are shown with lines joining them. These lines illustrate the strong ionic bond between ions of opposite charge which are next to each other. However, you should remember that these close contacts are not the same as covalent bonds - there is no pair of electrons shared between the two atoms which are connected by the two lines. Also, there is some ionic bonding between ions which are further away from each other - ions of opposite charge always attract each other, however far they are from each other. Nevertheless, the force holding them together is largest when they are close together. The lines connecting ions in this lattice (and others below) are there to make it easier to detect the pairs of ions in close contact with each other.

Remember - atoms are very small! The distance between a sodium ion and its nearest chloride ion neighbours is about 3 ten-millionths of a millimetre (3 Å or 3×10^{-10} m). Imagine a cubic grain of salt with edges which are 3 tenths of a millimetre (3×10^{-4} m) long. That implies that there will be a line of about a million (10^6) ions along each edge. And the grain will contain $10^6 \times 10^6 \times 10^6$ (10^{18}) ions in total.

All ionic compounds adopt a similar three-dimensional structure in which the ions are close to many ions of the opposite charge.

As another example, let us consider a salt with a divalent (doubly positive) ion, for example calcium fluoride, CaF_2. This adopts the structure shown below (the calcium atoms are shown as large spheres; the fluorine atoms are smaller):

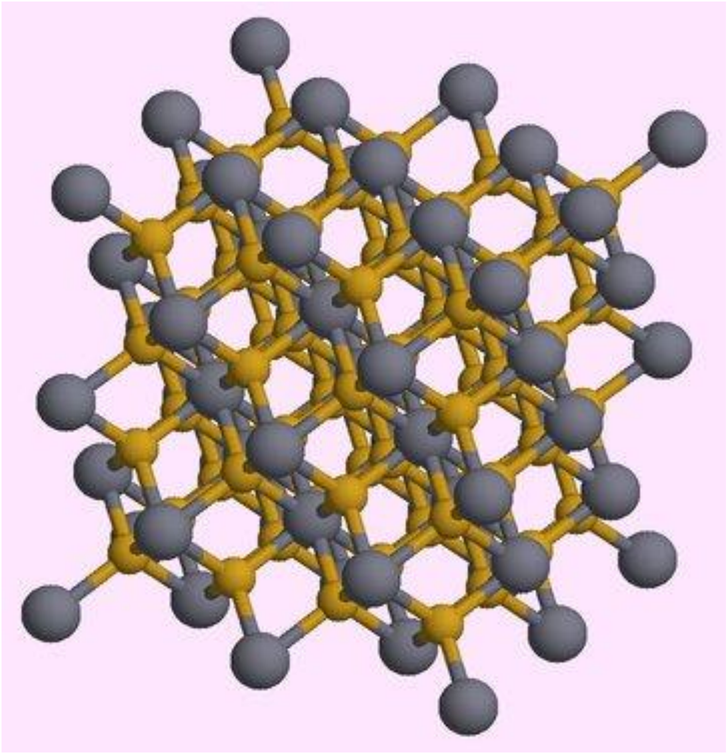


Fig. 3.3: Three-Dimensional Structure of Calcium Fluoride

Can you count how many fluoride ions each calcium is in close contact with? And how many caesium ions each fluoride ion is close to?

Experienced chemists can often predict the structure that a given ionic species will adopt, based on the nature of the ions involved. This means that it is often possible to **design** ionic compounds having certain well-defined and desirable properties. As an example, chemists have been able to make high-temperature superconductors, such as the complicated ionic compound, $YBa_2Cu_3O_4$. This solid conducts electricity with no resistance at all at low temperature (below ~ -100 degrees centigrade).

Previous superconductors only had this property at much lower temperatures. The lack of resistance makes superconductors very useful in a number of technological applications - e.g. in designing high-speed trains that levitate above the track!

3.3 Energetics of Ionic Bonding

We cannot easily measure the strength of an ionic bond, because ionic compounds do not break apart into gaseous ions:

$NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$ (will not occur!)

Born-Haber cycles are used to estimate the strength of "ionic bonds" in compounds such as NaCl. In a Born-Haber cycle, we carry out the following sequence of reactions:

Elements → Gaseous atoms → Gaseous ions → Compound
(In their atoms ions standard states)

The energy of each step except the last one can be measured experimentally. In addition, we can measure the energy of the single-step reaction below (this is the "heat of formation" of the compound):

Elements (in their standard states) ⟶ Compound

By Hess's law, the energies of the reactions in the first sequence must add up to the heat of formation (the energy of the single-step reaction).

This basic concept is not hard. The difficulty is in keeping the details straight. Ionic compounds contain two (or more) elements, each of which must be converted to gaseous atoms and then to gaseous ions. For example, here are the steps required to convert elemental calcium (a solid at room temperature) to gaseous calcium ions:

Sublime the solid calcium (convert it to a gas): $Ca(s) \rightarrow Ca(g)$

Remove one electron from each atom: $Ca(g) \rightarrow Ca^+(g) + e^-$

Remove a second electron from each atom: $Ca^+ (g) \rightarrow Ca^{2+} (g) + e^-$

Non-metals often form covalent molecules. If so, you must break the covalent bond as part of this process. Here are the steps required to convert elemental bromine (a diatomic liquid at room temperature) to gaseous bromide ions:

Vaporise the liquid bromine (convert it to a gas): $Br_2(l) \rightarrow Br_2(g)$

Break the covalent bond in Br_2: $Br_2(g) \rightarrow 2Br(g)$

Add an electron to each atom: $Br(g) + e^- \rightarrow Br^- (g)$

Your job in sorting out a Born-Haber cycle has two parts. The first is to be able to figure out exactly what reactions must occur when you convert the original element to a monatomic gas.

The second is to know how to identify the energy of each reaction type.

The reactions you might see in a Born-Haber cycle include:

i. **Heat of sublimation (ΔH_{subl}):** this is the energy required to convert a solid to a gas. For metals and most solid non-metals, sublimation produces a monatomic gas. For iodine (which is diatomic), sublimation produces $I_2(g)$.

$Na(s) \rightarrow Na(g)$ $S(s) \rightarrow S(g)$ $I_2(s) \rightarrow I_2(g)$

Heats of sublimation are always positive numbers.

ii. **Heat of vaporisation (ΔHvap):** this is the energy required to convert a liquid to a gas. The only elements for which this will come into play are bromine and mercury, which are liquids at room temperature. For bromine, vaporisation produces $Br_2(g)$.

$Hg(l) \rightarrow Hg(g)$ $Br_2(l) \rightarrow Br_2(g)$

Heats of vaporisation are always positive numbers.

iii. **Bond dissociation energy (BDE, or ΔH_{BDE}):** this is the energy required to break a covalent bond. Bond dissociation energies only come into play for the diatomic nonmetals (H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2 and At_2). In these cases, sublimation or vaporization gives us diatomic molecules, not individual atoms, so we must also break the covalent bonds in the gaseous form.

$H_2(g) \rightarrow 2\,H(g)$ $N_2(g) \rightarrow 2\,N(g)$
Bond dissociation energies are always positive numbers.

iv. **Ionisation energy (IE, or ΔH_{IE}):** this is the energy required to remove one electron from a gaseous atom. Since many ionic compounds contain metals that have lost two or more electrons, we often need to consider two or more successive ionisation energies. For example, if we need to make aluminium ions, we must remove three electrons from Al(g), so we must consider the first three ionisation energies of aluminium:

$Al(g) \rightarrow Al^+(g) + e^-$ ΔH = “first ionization energy” (IE1)

$Al^+(g) \rightarrow Al^{2+}(g) + e^-$ ΔH = “second ionization energy” (IE2)

$Al^{2+}(g) \rightarrow Al^{3+}(g) + e^-$ ΔH = “third ionization energy” (IE3)

Ionisation energies are always positive numbers, and they increase as you remove more electrons (so IE1 < IE2 < IE3 for any given element).

v. **Electron affinity (EA, or ΔH_{EA}):** this is the energy absorbed or released when you add one electron to a gaseous atom. In general, only the first electron affinity can be measured directly, because negative ions repel electrons. However, the second (and third, if necessary) electron affinity can be estimated using a variation on the Born-Haber cycle. Here are the reactions that must be considered if you need to make oxide ions.

$O(g) + e^{-} \rightarrow O^{-}(g)$ ΔH = "first electron affinity" (EA1, or simply EA)

$O^{-}(g) + e^{-} \rightarrow O^{2-}(g)$ ΔH = "second electron affinity" (EA2)

The first electron affinity is usually a negative number (a few elements have positive EA's). The second EA (and beyond) is always positive.

vi. **Crystal lattice energy (CLE, or ΔH_{CLE})**: this is the energy released when gaseous ions are converted into the solid ionic compound. For example, the lattice energy of aluminium fluoride corresponds to the following reaction:

$Al^{3+}(g) + 3F^{-}(g) \rightarrow AlF_3(s)$ ΔH = crystal lattice energy of AlF_3

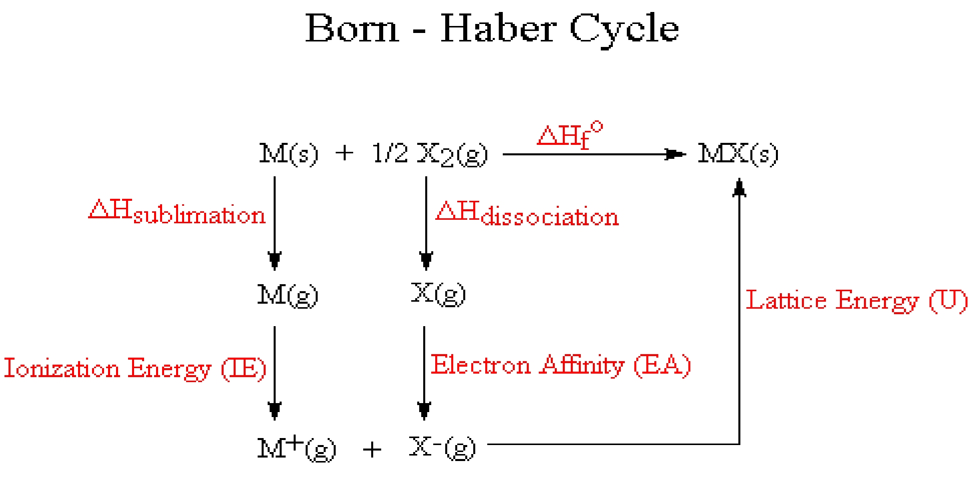
Lattice energies are always large negative numbers, ranging from around –600 to –13,000 kJ/mol.

vii. **Heat of formation (ΔH_f):** this is the energy absorbed or released when you make an ionic compound from its constituent elements (as they normally appear at room temperature and 1 atmospheric pressure). For aluminium fluoride, the corresponding reaction is:

$Al(s) + 1\frac{1}{2} F_2(g) \rightarrow AlF_3(s)$

Heats of formation are virtually always negative numbers for ionic compounds.

The diagram below is the Born-Haber cycle for the formation of an ionic compound from the reaction of an alkali metal (Li, Na, K, Rb, Cs) with a gaseous halogen (F_2, Cl_2). The Born-Haber thermochemical cycle is named after the two German physical chemists, Max Born and Fritz Haber, who first used it in 1919.

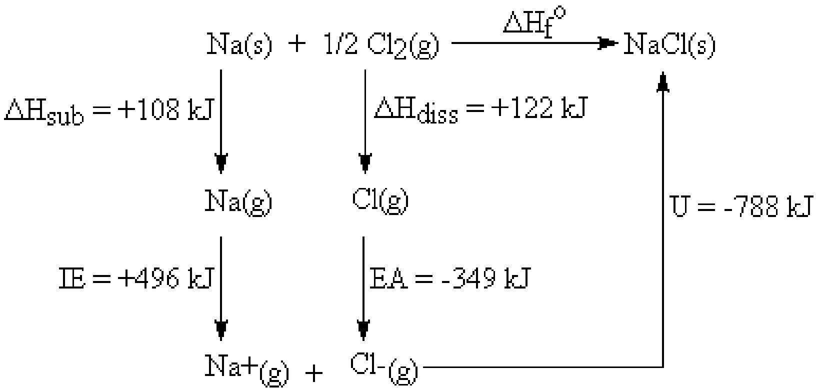


$$\Delta H_f^o = \Delta H_{sub} + IE + \Delta H_{diss} + EA + U$$

Fig. 3.4: The Born – Haber Cycle

The enthalpy change in the formation of an ionic lattice from the gaseous isolated sodium and chloride ions is -788 kJ/mole. That enthalpy change, which corresponds to the reaction $Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$, is called the lattice energy of the ionic crystal. Although the lattice energy is not directly measurable, there are various ways to estimate it from theoretical considerations and some experimental values. For all known ionic crystals, the lattice energy has a large negative value. It is ultimately the lattice energy of an ionic crystal which is responsible for the formation and stability of ionic crystal structures.

For sodium chloride, the Born - Haber cycle is:



$$\Delta H_f^o = \Delta H_{sub} + IE + \Delta H_{diss} + EA + U$$

$$\Delta H_f^o = 108 + 496 + 122 - 349 - 788 = -411 \text{ kJ/mole}$$

The concept behind the Born-Haber cycle is based on Hess' Law, which follows from the first law of thermodynamics (law of conservation of energy).

Hess's Law: If a reaction is carried out in a series of steps, the enthalpy change for the reaction will be equal to the sum of enthalpy changes for the individual steps.

3.4 The Properties of Ionic Compounds

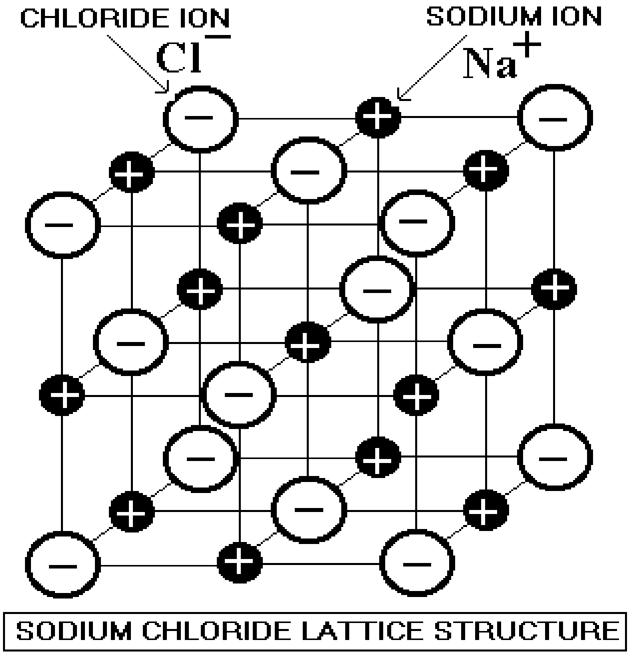


Fig. 3.5: The Lattice Structure of Sodium Chloride

i. The diagram above is typical of the giant ionic crystal structure of ionic compounds like sodium chloride and magnesium oxide.
ii. The alternate positive and negative ions in an ionic solid are arranged in an orderly way in a giant ionic lattice structure.
iii. The ionic bond is the strong electrical attraction between the positive and negative ions next to each other in the lattice.
iv. The bonding extends throughout the crystal in all directions.
v. Salts and metal oxides are typical ionic compounds.
vi. This strong bonding force is the basis of the hard structure (if brittle) and high melting and boiling points, so they are not very volatile.
vii. A relatively large amount of energy is needed to melt or boil ionic compounds. The bigger the charges on the ions the stronger the bonding attraction e.g. magnesium oxide $Mg^{2+}O^{2-}$ has a higher melting point than sodium chloride $Na^{+}Cl^{-}$.
viii. Unlike covalent molecules, ALL ionic compounds are crystalline solids at room temperature.

ix. They are hard but brittle, when stressed the bonds are broken along planes of ions which shear away. They are NOT malleable like metals.

x. Many ionic compounds are soluble in water, but not all, so do not make assumptions. Salts can dissolve in water because the ions can separate and become surrounded by water molecules which weakly bond to the ions. This reduces the attractive forces between the ions, preventing the crystal structure to exist. Evaporating the water from a salt solution will eventually allow the ionic crystal lattice to reform.

xi. The solid crystals DO NOT conduct electricity because the ions are not free to move to carry an electric current. However, if the ionic compound is melted or dissolved in water, the liquid will now conduct electricity, as the ion particles are now free.

4.0 CONCLUSION

Ionic bonds 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. Ionic bonds are very common and are exemplified by table salt, in which a sodium ion attracts a chloride ion to form Na^+Cl^- or, as usually written, NaCl. Calcium ions (Ca^{2+}) and chloride ions (Cl^-) combine in a one-to-two ratio to form calcium chloride, $CaCl_2$. The total charge on each combination of ions, NaCl and $CaCl_2$, is neutral, or zero.

6.0 TUTOR-MARKED ASSIGNMENT

i. Draw and label a Born-Haber cycle for the formation of calcium oxide.

ii. Calculate the lattice enthalpy of calcium oxide from the following data.
   a. enthalpy of atomisation of Ca(s): 178 kJ mol^{-1}
   b. first ionisation energy of Ca(g): 590 kJ mol^{-1}
   c. second ionisation energy of Ca(g): 1150 kJ mol^{-1}
   d. enthalpy of atomisation of O2(g): 249 kJ mol^{-1}
   e. first electron affinity of O(g): -141 kJ mol^{-1}
   f. second electron affinity of O(g): 844 kJ mol^{-1}
   g. enthalpy of formation of CaO(s): - 635 kJ mol^{-1}.

iii. The standard enthalpy of formation of KCl(s) is - 437 kJ mol^{-1}. In a Born-Haber cycle for the formation of KCl(s), which enthalpy change(s) are exothermic?
   a. the lattice enthalpy and the electron affinity of chlorine
   b. the electron affinity of chlorine
   c. the formation of Cl(g) from Cl_2(g)
   d. the enthalpy of atomisation of K(s) and the first ionisation energy of K(g)
   e. lattice enthalpy

7.0 REFERENCES/FURTHER READING

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UNIT 2 THE COVALENT BOND

CONTENTS

1.0 INTRODUCTION

Matter is made up of atoms and ions that experience both attractive and repulsive forces. It is the balance of these forces that result in chemical bonding within molecules, in metals, and in ionic compounds. In this unit, we shall describe the forces between particles and how these forces result in the formation of covalent bonds within molecules.

Bonding between non-metals consists of two electrons which are shared between two atoms. Using the Wave Theory, the covalent bond involves an overlap of the electron clouds from each atom. The electrons are concentrated in the region between the two atoms. In covalent bonding, the two electrons shared by the atoms are attracted to the nucleus of both atoms. Neither atom completely loses or gains electrons as in ionic bonding.

2.0 OBJECTIVES

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

- describe the nature of covalent bonds
- discuss the formation of covalent bonds
- identify the possibility if isomerism in covalent bonding
- highlight the nature of covalent solids
- explain the nature of coordinate bonding
- discuss the effect of coordinate bonding on physical properties
- state and explain the properties of covalent compounds.

3.0 MAIN CONTENT

3.1 The Covalent Bond

In unit 1 of this module, we discussed how atoms could achieve a complete shell of electrons by losing or gaining one or more electrons, to form ions. There is another way atoms can satisfy the octet rule: they can share electrons. For example, two hydrogen atoms can share their electrons, as shown below. Because each of the shared electrons then "belongs" to both atoms, both atoms then have a full shell, with two electrons. The pair of shared electrons is symbolised by the heavy line between the atoms.

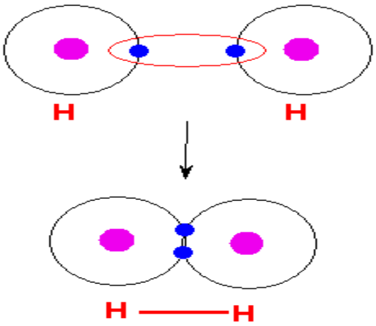


Fig. 2.1: Formation of the Hydrogen Molecule by Simple Covalent Bonding

In terms of charge-charge interactions, what happens is that the shared electrons are located between the two bonded atoms. The force attracting them to both nuclei is stronger than the repulsive force between the nuclei.

The methane (CH_4) molecule illustrates a more complex example. Each of the 4 electrons in the outermost ("valence") shell of carbon is shared with each of the hydrogen. In turn, each of the hydrogen also shares one electron with carbon. Overall, carbon "owns" 10 electrons – to satisfy the octet rule - and each hydrogen has 2 electrons. This is shown in figure 2.2:

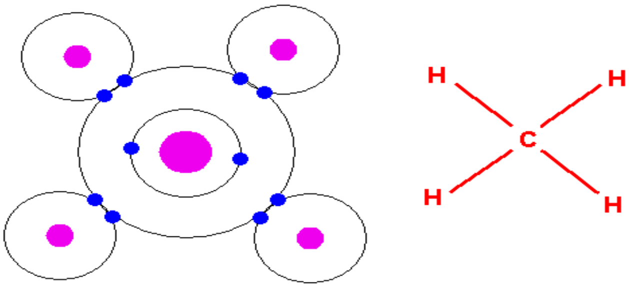


Fig. 2.2: Formation of the Methane Molecule by Simple Covalent Bonding

The experimental studies of methane molecule reveals that the four hydrogen atoms spread out evenly around the carbon atom, leading to the three-dimensional structure shown here:

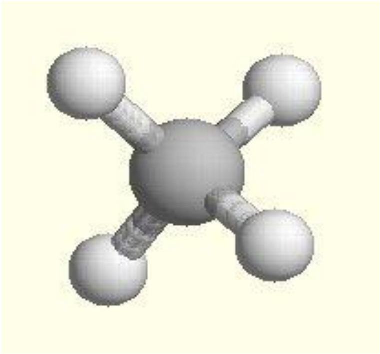


Fig. 2.3: Three-Dimensional Structure of Methane

As you would expect given that the electrons are shared, if we plot the region where the electrons sit, this is not localised on one atom, as it was for the ionic compounds, but is all over the molecule:

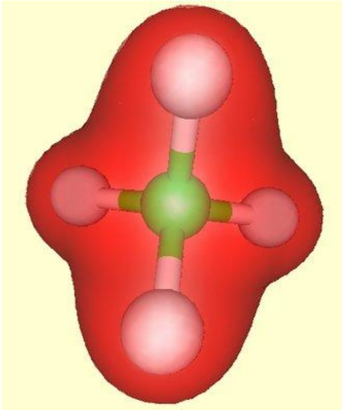


Fig. 2.4: Structure of Methane

3.2 Covalent Bonding and Isomers

As we have seen above, atoms can share electrons with others to form chemical bonds. This can also take place between two carbon atoms, to form a molecule such as ethane (C_2H_6):

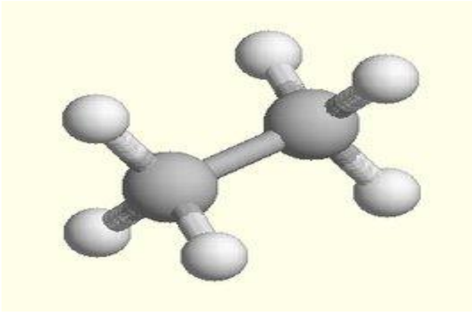


Fig. 2.5: Three-Dimensional Structure of Ethane

When we add two more carbon atoms and 4 more hydrogen atoms, to make butane (C_4H_{10}), an interesting situation arises: There are two different ways of bonding the carbons together, to form two different molecules, or isomers. For one of the isomers, the first carbon is bonded to three hydrogen atoms, and to the second carbon, which is itself bonded to another two hydrogen atoms and to the third carbon, which is bonded to the fourth carbon. In the other isomer, one of the carbons forms a bond to all three carbon atoms:

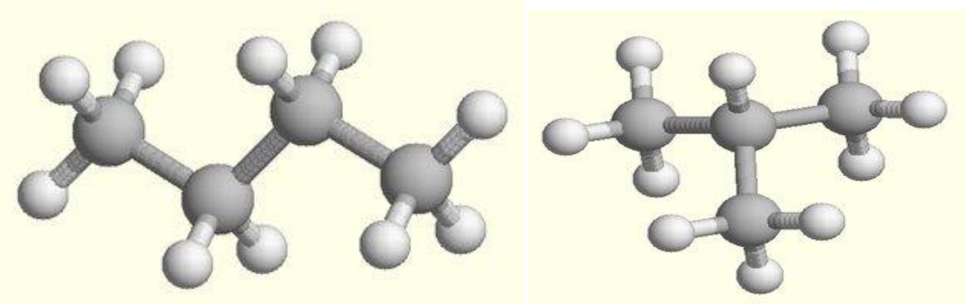


Fig. 2.6: Three-Dimensional Structures of Butane's Isomers

Larger compounds can also be formed, and they will have even more isomers. For example, this compound with 8 carbons is called isooctane, and is one of the main components of petrol for cars:

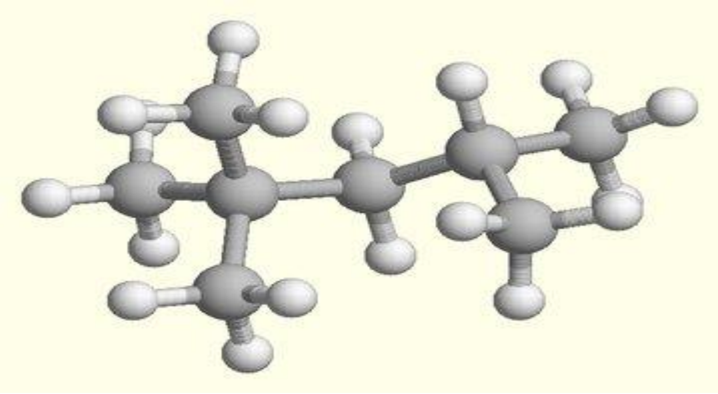


Fig. 2.7: Three-Dimensional Structure of an Isomer of Octane

Can you check that the formula for this compound is C_8H_{18}? Sketch another compound with the same formula?

Because covalent bonds can be formed in many different ways, it is possible to write down, and make many different molecules. Many of these are natural compounds, made by living animals or plants within their cells. This example shows one such molecule, cholesterol ($C_{27}H_{46}O$), which can contribute to heart disease in people whose diet is too rich in fats:

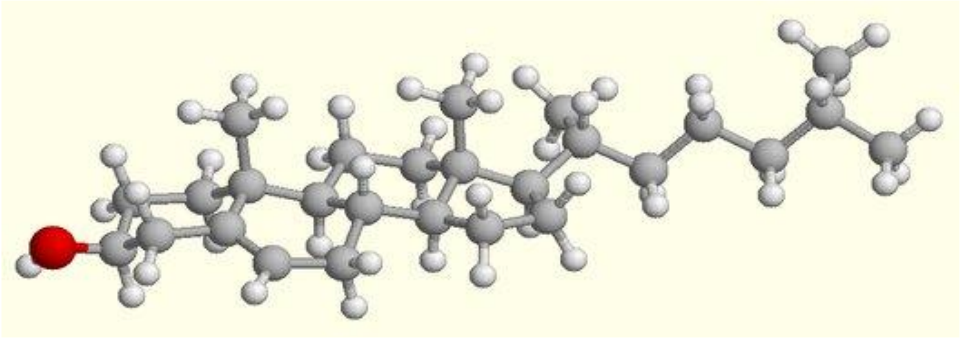


Fig.2.8: Three-Dimensional Structure of Cholesterol

Note that in this structure, two neighbouring carbon atoms appear to form only three bonds, which would go against the octet rule. In fact, these atoms bond by sharing two electrons each (a total of four electrons). In this way, they complete their electron shell like the others.

This situation is referred to as a double bond, and is shown in the pop-up window as a thicker stick between those two atoms (Can you find this bond? Check that all other carbon atoms do form four bonds).

Other compounds are synthetic, they are made by chemists. Chemists can also make the natural compounds, starting from only simple things like methane and water. The "natural" molecules made in this way are identical to the "real" natural compounds. Other synthetic molecules do not exist in nature. They can have desirable properties, for example, many medicines are made in this way. An example of a "small" medicinal molecule is aspirin, $C_9H_8O_4$, shown below. In this molecule, two bonds between carbon and oxygen are double bonds, and are shown as thicker sticks in the model.

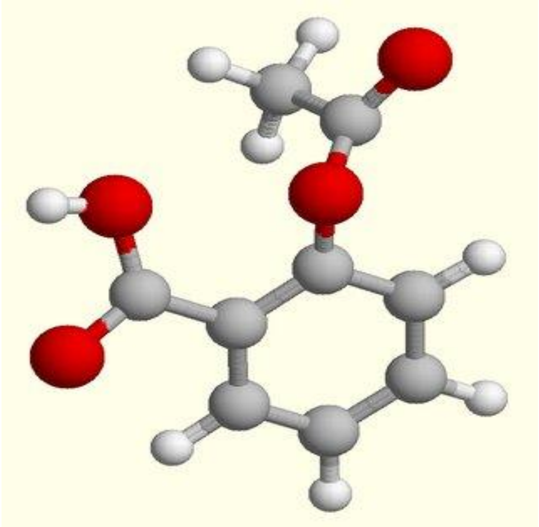


Fig. 2.9: Three-Dimensional Structure of Aspirin (Acetyl salicylic acid).

3.3 Covalent Solids

Covalent solids are formed by piling lots of covalent molecules together, and relying on their slight "stickiness" to hold the solid together, one can also form solids entirely bound together by covalent bonds. An excellent example is diamond, which is pure carbon, with each carbon atom bonding to four others, to form a huge "molecule" containing many millions of atoms. Figure 2.10 shows a part of a diamond molecule:

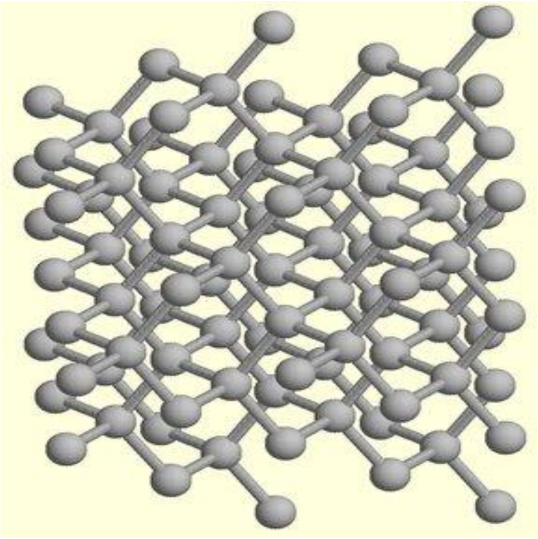


Fig. 2.10: Part of a Diamond Molecule

In diamond, all the carbon atoms share one electron with each of their four neighbouring carbon atoms. There is another form in which pure carbon can be formed: graphite. This is the main component of the "lead" in pencils. Here, instead of each carbon having four neighbours, it only has three. Each carbon shares one electron with two of its neighbours, and 2 electrons with the third neighbour. In this way, one C-C bond out of three is a double bond. The atoms all bond together in planes and the planes stack on top of one another as shown in Figure 2.11:

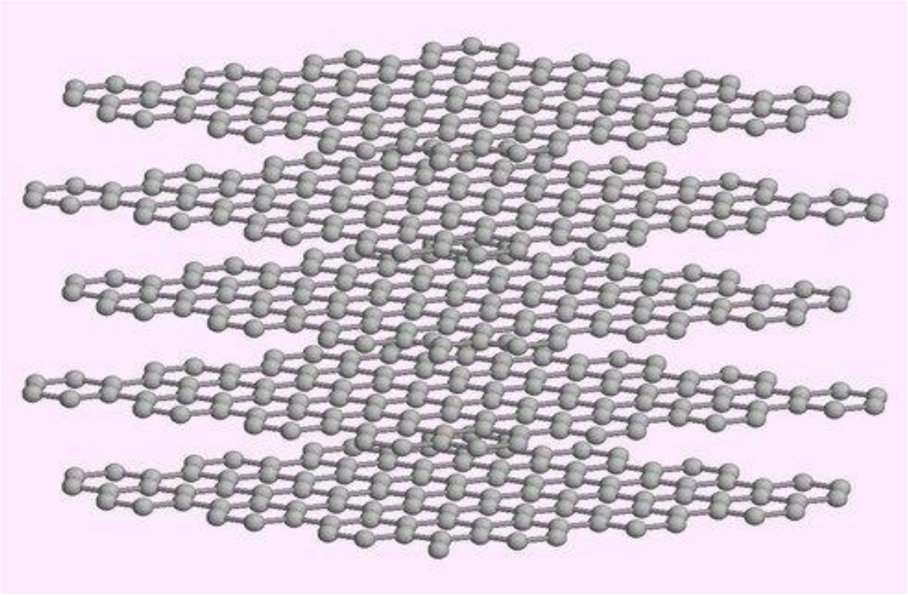


Fig. 2.11: Planes of Atoms in the Structure of Graphite

In graphite, the C-C bonds in the planes are very strong, but the force between the different planes is quite weak, and they can slip over one another. This explains the "soft" feel of graphite, and the fact that it is used as a lubricant, for example in motor oil.

Other "Big" Covalent Molecules

In solids like diamond and graphite, the different atoms all bond to one another to form one very large molecule. The atoms are bonded to each other in all directions in diamond, and in two directions (within the planes) in graphite, with no bonding in the other direction. Some important covalent molecules involve atoms bonding to each other repeatedly along just one direction, with no bonds in the others. These are called polymers, and one simple example if polyethene (also called polythene, or polyethylene). The structure of polythene is shown in Figure 2.12 (the dangling bonds at each end indicate how the bonding should really continue for thousands of atoms on each side):

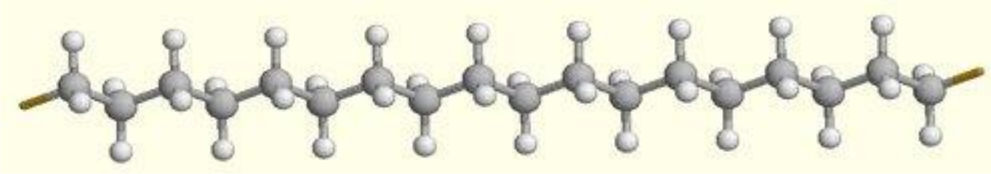


Fig. 2.12: Three-Dimensional Structure of Polythene

Polythene is what most plastic bags are made of. Other polymers include molecules such as nylon, Teflon (these, like polythene, are man-made), or cellulose (the stuff that makes wood hard), a biological polymer.

3.4 Co-ordinate (Dative Covalent) Bonding

A covalent bond is formed by two atoms sharing a pair of electrons. The atoms are held together because the electron pair is attracted by both of the nuclei.

In the formation of a simple covalent bond, each atom supplies one electron to the bond - but that does not necessary have to be the case. A co-ordinate bond (also called a dative covalent bond) is a covalent bond (a shared pair of electrons) in which both electrons come from the same atom.

For the rest of this unit, we shall use the term co-ordinate bond - but if you prefer to call it a dative covalent bond, it is acceptable.

The reaction between ammonia and hydrogen chloride

If these colourless gases are allowed to mix, a thick white smoke of solid ammonium chloride is formed.

$$NH_3 + HCl \longrightarrow NH_4Cl$$

Ammonium ions, NH_4^+, are formed by the transfer of a hydrogen ion from the hydrogen chloride to the lone pair of electrons on the ammonia molecule.

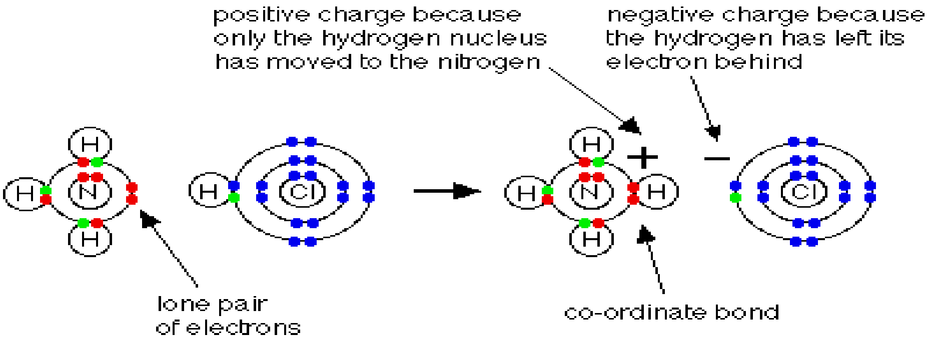


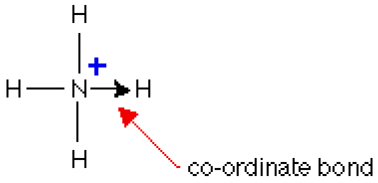
Fig. 2.13: Formation of Ammonium Chloride by Coordinate Bonding

When the ammonium ion, NH_4^+, is formed, the fourth hydrogen is attached by a dative covalent bond, because only the hydrogen's nucleus is transferred from the chlorine to the nitrogen. The hydrogen's electron is left behind on the chlorine to form a negative chloride ion.

Once the ammonium ion has been formed it is impossible to tell any difference between the dative covalent and the ordinary covalent bonds. Although the electrons are shown differently in the diagram, there is no difference between them in reality.

Representing co-ordinate bonds

In simple diagrams, a co-ordinate bond is shown by an arrow. The arrow points from the atom donating the lone pair to the atom accepting it.



Dissolving hydrogen chloride in water to make hydrochloric acid

Something similar happens. A hydrogen ion (H^+) is transferred from the chlorine to one of the lone pairs on the oxygen atom.

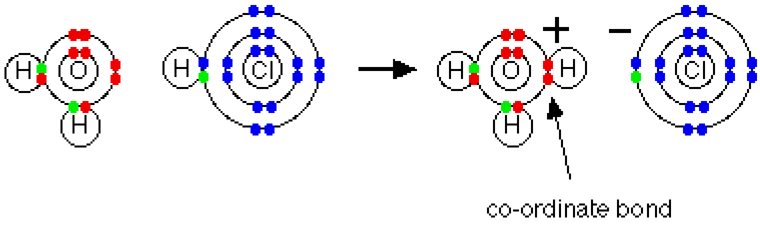


Fig. 2.14: Dissolution of Hydrogen Chloride in Water

$H_2O + HCl \longrightarrow H_3O^+ + Cl^-$

The H_3O^+ ion is variously called the hydroxonium ion, the hydronium ion or the oxonium ion.

If you write the hydrogen ion as $H^+_{(aq)}$, the "$_{(aq)}$" represents the water molecule that the hydrogen ion is attached to. When it reacts with something (an alkali, for example), the hydrogen ion simply becomes detached from the water molecule again.

Note that once the co-ordinate bond has been set up, all the hydrogen atoms attached to the oxygen are exactly equivalent. When a hydrogen ion breaks away again, it could be any of the three.

The reaction between ammonia and boron trifluoride, BF_3

If you have recently read the page on covalent bonding, you may remember boron trifluoride as a compound which does not have a noble gas structure around the boron atom. The boron only has 3 pairs of electrons in its bonding level, whereas there would be room for 4 pairs. BF_3 is described as being *electron deficient.*

The lone pair on the nitrogen of an ammonia molecule can be used to overcome that deficiency, and a compound is formed involving a co-ordinate bond.

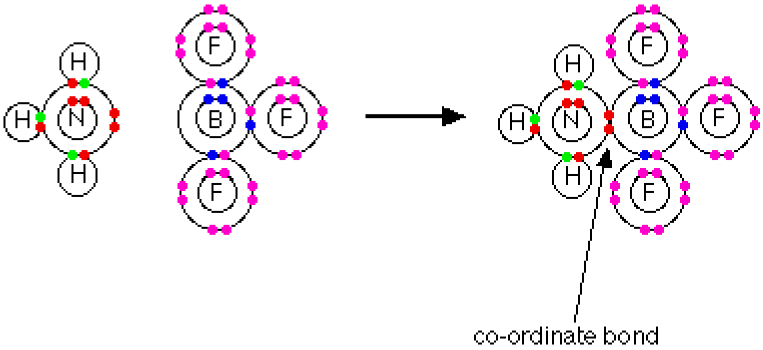
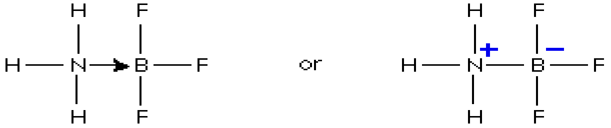


Fig. 2.15: Reaction between Ammonia and Boron Trifluoride

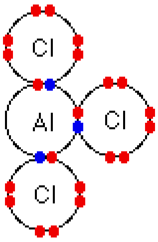
Using lines to represent the bonds, this could be drawn more simply as:



The second diagram shows another way that you might find co-ordinate bonds drawn. The nitrogen end of the bond has become positive because the electron pair has moved away from the nitrogen towards the boron - which has therefore become negative.

The structure of aluminium chloride

Aluminium chloride sublimes (turns straight from a solid to a gas) at about 180°C. If it simply contained ions, it would have a very high melting and boiling point because of the strong attractions between the positive and negative ions. The implication is that when it sublimes at this relatively low temperature, it must be covalent. The dots-and-crosses diagram shows only the outer electrons.



$AlCl_3$, like BF_3, is electron deficient. There is likely to be a similarity, because aluminium and boron are in the same group in the Periodic Table, as are fluorine and chlorine.

Measurements of the relative mass of aluminium chloride show that its formula in the vapour at the sublimation temperature is not $AlCl_3$, but Al_2Cl_6. This implies that it exists as a dimer (two molecules joined together). The bonding between the two molecules is co-ordinate, using lone pairs on the chlorine atoms. Each chlorine atom has 3 lone pairs, but only the two important ones are shown in the line diagram.

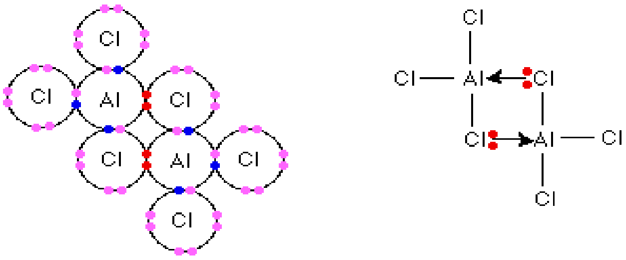


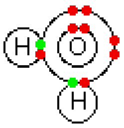
Fig. 2.16: The Structure of Aluminium Chloride

Energy is released when the two co-ordinate bonds are formed, and so the dimer is more stable than two separate $AlCl_3$ molecules.

The bonding in hydrated metal ions

Water molecules are strongly attracted to ions in solution - the water molecules clustering around the positive or negative ions. In many cases, the attractions are so great that formal bonds are made, and this is true of almost all positive metal ions. Ions with water molecules attached are described as *hydrated ions.*

Although aluminium chloride is covalent, when it dissolves in water, ions are produced. Six water molecules bond to the aluminium to give an ion with the formula $Al(H_2O)_6^{3+}$. It is called the hexaaquaaluminium ion - which translates as six ("hexa") water molecules ("aqua") wrapped around an aluminium ion.

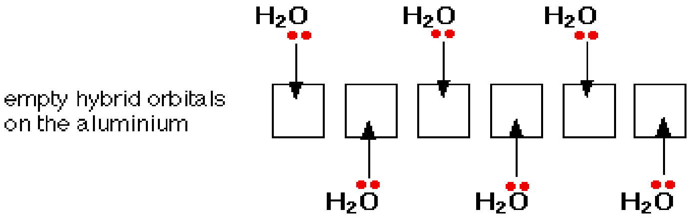


The bonding in this (and the similar ions formed by the great majority of other metals) is co-ordinate (dative covalent) using lone pairs on the water molecules.

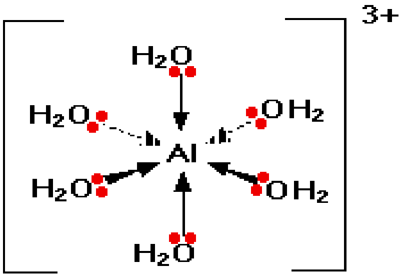
Aluminium is $1s^2 2s^2 2p^6 3s^2 3p_x^1$. When it forms an Al^{3+} ion, it loses the 3-level electrons to leave $1s^2 2s^2 2p^6$.

This implieds that all the 3-level orbitals are now empty. The aluminium re-organises (hybridises) six of these (the 3s, three 3p, and two 3d) to produce six new orbitals all with the same energy. These six hybrid orbitals accept lone pairs from six water molecules.

You might wonder why it chooses to use six orbitals rather than four or eight or whatever. Six is the maximum number of water molecules that is possible to fit around an aluminium ion (and most other metal ions). By making the maximum number of bonds, it releases most energy and so becomes most energetically stable.



Only one lone pair is shown on each water molecule. The other lone pair is pointing away from the aluminium and therefore not involved in the bonding. The resulting ion looks like this:



Because of the movement of electrons towards the centre of the ion, the 3+ charge is no longer located entirely on the aluminium, but is now spread over the whole of the ion.

Carbon monoxide, CO

Carbon monoxide can be thought of as having two ordinary covalent bonds between the carbon and the oxygen plus a co-ordinate bond using a lone pair on the oxygen atom.

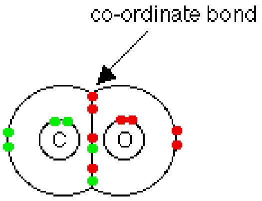


Fig. 2.17: Structure of Carbon (II) Oxide

Nitric acid, HNO_3

In this case, one of the oxygen atoms can be thought of as attaching to the nitrogen via a co-ordinate bond using the lone pair on the nitrogen atom.

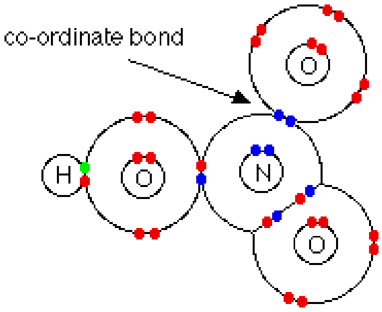


Fig. 2.18: Structure of Trioxonitrate (V) Acid

In fact, this structure is misleading because it suggests that the two oxygen atoms on the right-hand side of the diagram are joined to the nitrogen in different ways. Both bonds are actually identical in length and strength, and so the arrangement of the electrons must be identical. There is no way of showing this using a dots-and-crosses picture. The bonding involves delocalisation.

3.5 Properties of Covalent Molecules

The covalent bonds between atoms in a given molecule are very strong; as strong as ionic bonds. However, unlike ionic bonds, there is a limit to the number of covalent bonds to other atoms that a given atom can form. For example, carbon can make four bonds - not more while oxygen can form only two bonds. As a result, once each atom has made all the bonds it can make, as shown in all the molecules above, the atoms can no longer interact with other ones. For this reason, two covalent molecules barely stick together. Light molecules are therefore gases, such as methane or ethane, above, hydrogen, H_2, nitrogen, N_2 (the main component of the air we breathe, etc. Heavier molecules, such as the isooctane molecule, are liquids at room temperature, while others, for instance cholesterol, are solids.

Typical properties of simple covalent substances

1. The electrical forces of attraction, which is the chemical bond, between atoms in a molecule are usually very strong, subsequently; most covalent molecules do not change chemically on moderate heating. For instance, although a covalent molecule like iodine, I_2, is readily vapourised on heating, it **does not** break up into iodine atoms I. The I-I covalent bond is strong enough to withstand the heating and the purple vapour still consists of the same I_2 molecules as the dark coloured solid is made up of.

2. **Ease of vaporisation on heating**: The electrical attractive forces between individual molecules are weak, so the bulk material is not very strong physically and there are also consequences for the melting and boiling points.

3. These weak electrical attractions are known as intermolecular forces and are readily weakened further on heating. The effect of absorbing heat energy results in increased the thermal vibration of the molecules which weakens the intermolecular forces. In liquids, the increase in the average particle kinetic energy makes it easier for molecules to overcome the intermolecular forces and change into a gas or vapour. Consequently, small covalent

molecules tend to be volatile liquids with low boiling points, easily vapourised, or low melting point solids.

4. On heating the inter-molecular forces are easily overcome with the increased kinetic energy of the particles giving the material a low melting or boiling point and a relatively small amount of energy is needed to effect these state changes. This contrasts with the high melting points of giant covalent structures with their strong 3D network.

   Note: The weak electrical attractive forces between molecules, the so called intermolecular forces should be clearly distinguished between the strong covalent bonding between atoms in molecules (small or giant), and these are sometimes referred to as intramolecular forces (i.e. internal to the molecule).
5. Covalent structures are usually poor conductors of electricity because there are no free electrons or ions in any state to carry electric charge.
6. Most small molecules will dissolve in some solvent to form a solution. This again contrasts with giant covalent structures where the strong bond network stops solvent molecules interacting with the particles making up the material.

4.0 SUMMARY

Covalent bonds involve sharing electrons between atoms. The shared electrons "belong" to both atoms in the bond. Each atom forms the right number of bonds, such that they have filled shells. There is lots of flexibility in terms of which atom bonds to which other ones. This means that many isomeric molecules can be formed, and nature as well as chemists are skilled at designing and making new molecules with desirable properties. In most cases, only a small number of atoms are bonded together to make a molecule, and there is no bonding between atoms in one molecule and atoms of other molecules. This means that molecules are only very slightly "sticky" between themselves, and covalent compounds are either gases, or liquids, or sometimes solids. In some cases, bonding occurs to form large molecules with thousands or millions of atoms, and these can be solids.

5.0 CONCLUSION

In this unit, you have learnt that covalent bond result from the sharing of electrons by two atoms. Covalent bond was discussed in the detail with respect to its isomers; we have equally discussed the covalent solids. Dative (co-ordinate) covalent bond was equally explained with some examples.

6.0 TUTOR-MARKED ASSIGNMENT

Explain the reason for your answer in each of the followings:

i. Why are non-metals not bonded by covalent bond?
   a. They want to create new chemical compounds
   b. They want full electron shells
   c. Because it is their nature

ii. Covalent bonding is the transferring of outer electrons between non-metals.
   True or False?

iii. Nitrogen has an electron configuration of 2,8,5. Chlorine has an electron configuration of 2,8,7. How many electrons do both elements need to get full outer shell?
   a) Nitrogen needs 6; Chlorine needs 3
   b) Nitrogen needs 3; Chlorine needs 2
   c) Nitrogen needs 3; Chlorine needs 1

iv. Nitrogen and Chlorine covalently bond. What is the chemical formula?
   a) NCl_3
   b) N_3Cl
   c) NCl

v. What is an example of a diatomic molecule?
   - Sulphur and Oxygen bond to create SO_2
   - Nitrogen and Nitrogen bond to create N_3
   - Oxygen and Oxygen bond to create O_2

vi. Neon has an electron configuration of 2,8. Carbon has an electron configuration of 2,4. What will the chemical formula be?
   - C_2Ne
   - There will be no chemical formula
   - Ne_2C_2

vii. Covalent bonds do not conduct electricity
   True or False?

7.0 REFERENCES/FURTHER READING

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UNIT 3 OTHER TYPES OF BONDING

CONTENTS

1.0 INTRODUCTION

In the previous units, you have learnt about the two most important types of bonding: ionic bonding and covalent bonding. Both of these are ultimately driven by the desire that atoms have to be surrounded by a complete shell of electrons. They achieve this by respectively either gaining or losing, or sharing, one or more electrons.

Intermolecular attractions are attractions between one molecule and a neighbouring molecule. The forces of attraction which hold an individual molecule together (for example, the covalent bonds) are known as **intramolecular attractions**. These two words are so confusingly similar that it is safer to abandon one of them and never use it. The term "intramolecular" will hence, not be used again in this unit.

All molecules experience intermolecular attractions, although in some cases those attractions are very weak. Even in a gas like hydrogen, H_2, if you slow the molecules down by cooling the gas, the attractions are large enough for the molecules to stick together eventually to form a liquid and then a solid.

In hydrogen's case, the attractions are so weak that the molecules have to be cooled to 21K (-252°C) before the attractions are enough to condense the hydrogen as a liquid. Helium's intermolecular attractions are even weaker - the molecules will not stick together to form a liquid until the temperature drops to 4 K (-269°C).

2.0 OBJECTIVES

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

- classify intermolecular forces as ionic, covalent, London dispersion, dipole-dipole, or hydrogen bonding
- explain properties of material in terms of type of intermolecular forces
- predict the properties of a substance based on the dominant intermolecular forces.

3.0 MAIN CONTENT

3.1 Metallic Bonding

A metal is an element that can easily lose up to three electrons, thus forming positive ions. The lost electrons however come together to form a combined ‘sea’ or ‘cloud’ of electrons. Metals consist of a lattice of positive ions existing in a freely moving ‘sea’ of ‘cloud’ of electrons that bind them together. Electrons in the ‘sea’ do not belong to specific metal atoms and move easily throughout the assembly. Metals are well known to be solids (except for Mercury). The bonds between metals can loosely be described as **covalent bonds** (due to sharing electrons), except that the metal atoms do not just share electrons with 1, 2, 3 or 4 neighbours, as in covalent bonding, but with many atoms. The structure of the metal is determined by the fact that each atom tries to be as close to as many other atoms as possible. This is shown here for one typical metal structure (adopted, for instance, by iron at some temperatures):

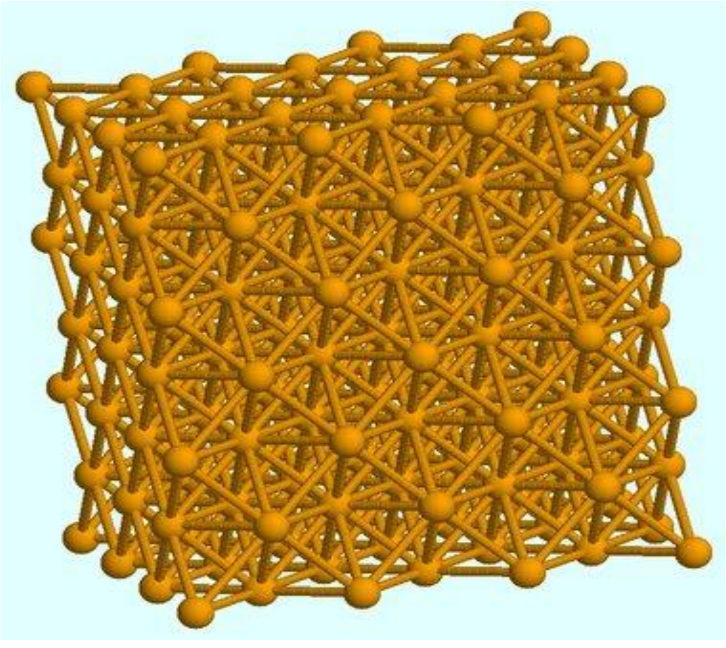

Fig. 2.17: The Structure of a Metal

Can you count how many neighbours each iron atom is bonded to? Contrast this with the structure of diamond seen previously.
Because the electrons are shared with all the neighbours, it is quite easy for the electrons in metals to move around. If each "shared" electron shifts one atom to the right or left, this leads to a net shift of charge. This occurs quite easily in metals, but much less so in ionic solids, or covalent ones, where the electrons are rigidly associated with either a particular atom or ion, or a particular pair of atoms. It is because electrons can move around so easily inside metals that the latter **conduct electricity**.

3.1.1 Explaining the Physical Properties of Metals

- This **strong bonding** generally results in **dense**, **strong materials with high melting and boiling points**.
- Metals are **good conductors of electricity** because these 'free' electrons carry the charge of an electric current when a potential difference (voltage!) is applied across a piece of metal.
- Metals are also **good conductors of heat**. This is also due to the free moving electrons; the 'hot' high kinetic energy electrons move around freely to transfer the particle kinetic energy more efficiently to 'cooler' atoms.
- Typical metals also have a **silvery surface** but remember this may be easily tarnished by corrosive oxidation in air and water.
- Unlike ionic solids, metals are very **malleable**; they can be readily bent, pressed or hammered into shape. The layers of atoms can slide over each other without fracturing the structure (Figure 2.18). The reason for this is the **mobility of the electrons**. When planes of metal atoms are 'bent' or slide the electrons can run in between the atoms and maintain a strong bonding situation. This cannot happen in ionic solids.

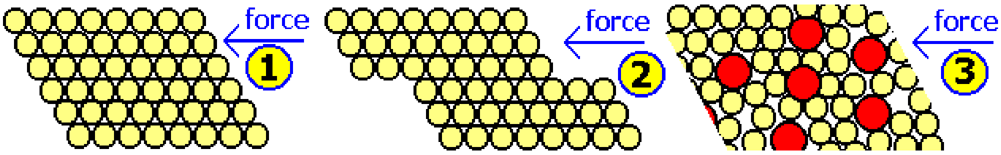

Fig. 2.18: Alloy Structure

Figure 2.18 (**1**) shows the regular arrangement of the atoms in a metal crystal and the white spaces show where the free electrons are (yellow circles actually positive metal ions).

Figure 2.18 (**2**) shows what happens when the metal is stressed by a strong force. The layers of atoms can slide over each other and the bonding is maintained as the mobile electrons keep in contact with atoms, so the metal remains intact BUT a different shape.

Figure 2.18 (**3**) shows an alloy mixture. It is NOT a compound but a physical mixing of a metal plus at least one other material (one can be another metal e.g. Ni, a non-metal e.g. C or a compound of carbon or manganese, and it can be bigger or smaller than iron atoms). Many alloys are produced to give a stronger metal. The presence of the other atoms (smaller or bigger) disrupts the symmetry of the layers and reduces the 'slip ability' of one layer next to another. The result is a stronger harder less malleable metal.

The main point about using alloys is that you can make up, and try out, all sorts of different compositions until you find the one that best suits the required purpose

3.2 Hydrogen Bonding

In covalent bonds, the electrons are shared, so that each atom gets a filled shell. When the distribution of electrons in molecules is considered in detail, it becomes apparent that the "sharing" is not always perfectly "fair": often, one of the atoms gets "more" of the shared electrons than the other does.
This occurs, in particular, when atoms such as nitrogen, fluorine, or oxygen bond to hydrogen. For example, in HF (hydrogen fluoride), the structure can be described by the following "sharing" picture:

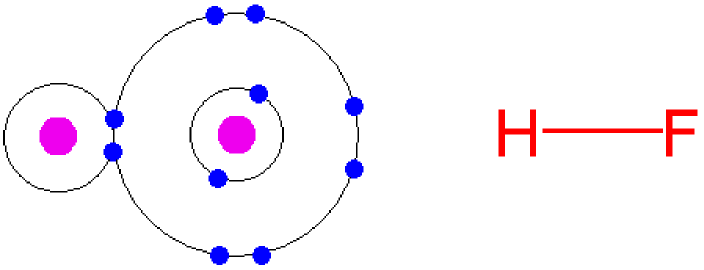

Fig.2.19: Structure of Hydrogen Fluoride

However, this structure does not tell the whole truth about the distribution of electrons in HF. Indeed, the following, "ionic" structure also respects the filled (or empty) shell rule:

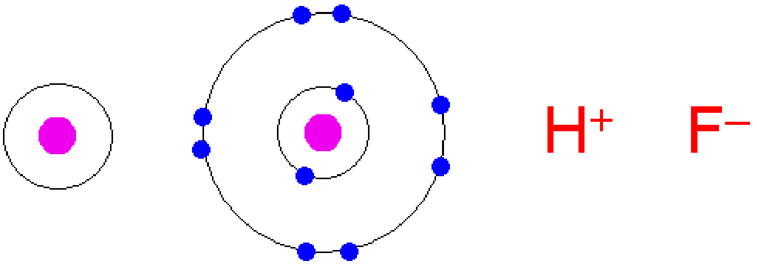

Fig. 2.20: Structure of HF

In reality, HF is described by both these structures, so that the H-F bond is **polar**, with each atom bearing a small positive (δ+) or negative (δ-) charge. When two hydrogen fluoride molecules come close to each other, the like charges attract each other, and one gets a "molecule" of di-hydrogen fluoride as shown:

Fig. 2.21: Hydrogen Bonding in Hydrogen Fluoride

The weak "bond" between the F atom and the H is called a **Hydrogen Bond**, and is shown here as the dotted green line.

Hydrogen bonds can also occur between oxygen atoms and hydrogen. One of the most important types of hydrogen bonds is of this type, and is the one occurring in water. As discussed for HF, the electrons in H_2O molecules are not evenly "shared": the oxygen atom has more of them than the hydrogen atoms. As a result, oxygen has a (partial) negative charge, and the two hydrogen atoms have a positive charge. When you have two water molecules close to another, a hydrogen atom on one of the molecules is attracted to the oxygen of the other molecule, to give a dimer. The structure of this dimer is shown here:

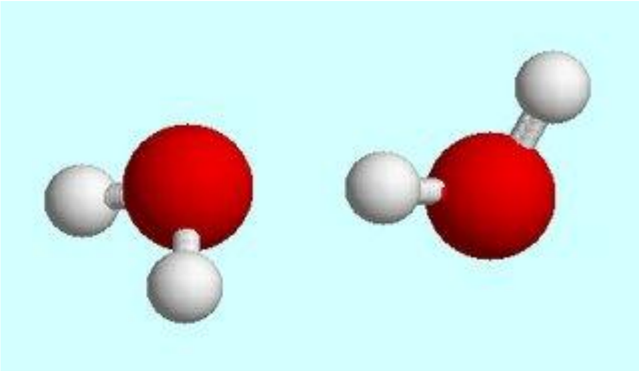

Fig. 2.22: Three-Dimensional Structure of Water

Note how the oxygen, hydrogen, and oxygen atoms involved in the hydrogen bond are arranged more or less in a straight line. This is the preferred geometry for hydrogen bonds, and explains why only one hydrogen bond can be formed in the water dimer.

Upon going to three water molecules, it is now possible to form several hydrogen bonds. This is shown here:

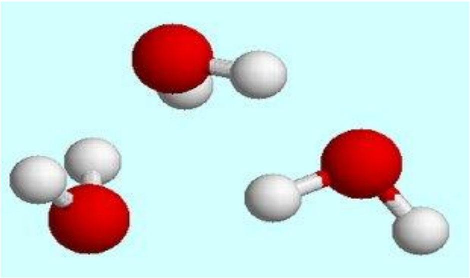

Fig. 2.23: Three Water Molecules

How many hydrogen bonds is each water molecule involved in?
In liquid water or ice, many water molecules are close to each other, and they form dense networks of hydrogen bonds. In ice, the arrangement of the water molecules with respect to each other is regular, whereas in water, it is random. Figure 2.24 shows a typical arrangement of water molecules similar to what you might find in the liquid:

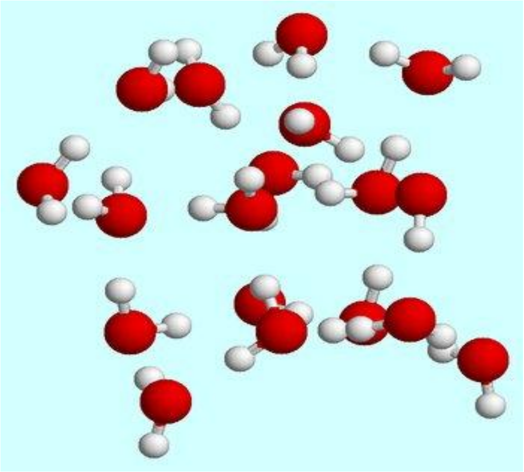

Fig. 2.24: Hydrogen Bonding in Water

Can you see some of the hydrogen bonds? These bonds are weaker than typical covalent or ionic bonds, but nevertheless strong enough to make molecules which can hydrogen bond much more "sticky" with respect to each other than are other covalent molecules with otherwise similar properties. For example, the molecular mass of water is 18, and that of nitrogen is 28, yet nitrogen is a gas down to almost -200 degrees centigrade, whereas water is a liquid up to 100 degrees!

3.2.1 Hydrogen Bonds in Biology

The cells of living things are made up of many different sorts of molecule. Two important classes of molecule are **proteins** and **nucleic acids**. In both of these molecules, parts of the (very large) molecules are involved in hydrogen bonds with other parts of the same molecules. This is very important in establishing the structure and properties of these molecules. Hydrogen bonding plays important role in the structure of

DNA (Deoxyribonucleic acid), one of the most important nucleic acids, and showing the important role of hydrogen bonding.

3.3 Other Intermolecular Forces

Intermolecular forces are forces of attraction or repulsion which act between neighbouring particles: atoms, molecules or ions. They are weak compared to the intramolecular forces, the forces which keep a molecule together. For example, the covalent bond present within HCl molecules is much stronger than the forces present between the neighbouring molecules, which exist when the molecules are sufficiently close to each other. Hydrogen bonding is an example of intermolecular forces.

3.3.1 London Dispersion Forces

London dispersion forces (LDF, also known as dispersion forces, London forces, instantaneous dipole–induced dipole forces) is a type of force acting between atoms and molecules. They are part of the van der Waals forces. The LDF is named after the German-American physicist Fritz London.

The LDF is a weak intermolecular force arising from quantum induced instantaneous polarisation multi-poles in molecules. They can therefore act between molecules without permanent multi-pole moments.

London forces are exhibited by non-polar molecules because of the correlated movements of the electrons in interacting molecules. Because the electrons from different molecules start "fleeing" and avoiding each other, electron density in a molecule becomes redistributed in proximity to another molecule, (see quantum mechanical theory of dispersion forces). This is frequently described as formation of "instantaneous dipoles" that attract each other. London forces are present between all chemical groups and usually represent the main part of the total interaction force in condensed matter, even though they are generally weaker than ionic bonds and hydrogen bonds.

This is the only attractive intermolecular force present between neutral atoms (e.g., a noble gas). Without London forces, there would be no attractive force between noble gas atoms, and they would not exist in liquid form.

London forces become stronger as the atom or molecule in question becomes larger. This is due to the increased polarisability of molecules with larger, more dispersed electron clouds. This trend is exemplified by the halogens (from smallest to largest: F_2, Cl_2, Br_2, I_2). Fluorine and chlorine are gases at room temperature, bromine is a liquid, and iodine is a solid. The London forces also become stronger with larger amounts of surface contact. Greater surface area means closer interaction between different molecules.

3.3.2 Dipole-Dipole Interactions

The non-symmetrical distribution of charge within a molecule polarises the molecule into positive and negative poles such that there exist electrostatic interactions between close molecules called a *permanent dipole-permanent dipole attraction*. Hydrogen chloride, HCl, is made up of a positively charged end and a negatively charged end such that there is charge interaction forming a weak bond between the hydrogen atom of one hydrogen chloride molecule and the chlorine end of another molecule.

Trichloromethane (chloroform), $CHCl_3$, is another example of molecules with dipole-dipole attraction where polar molecules are held together more strongly than non-polar molecules of comparable mass.
Dipole-dipole forces are:

- stronger intermolecular forces than dispersion forces
- occur between molecules that have permanent net dipoles (polar molecules), for example, dipole-dipole interactions occur between SCl_2 molecules, PCl_3 molecules and CH_3Cl molecules. If the permanent net dipole within the polar molecules results from a covalent bond between a hydrogen atom and either fluorine, oxygen or nitrogen, the resulting intermolecular force is referred to as Hydrogen Bonding.
- established if the partial positive charge on one molecule is electrostatically attracted to the partial negative charge on a neighbouring molecule.

4.0 SUMMARY

Ionic bonding and covalent bonding are not the only kinds of bond between atoms. Some important other types of bond include **metallic** bonds, and **hydrogen bonds**. These explain the properties of metals, for instance, they conduct electricity, and are very important in establishing the properties of water and living cells.

In this unit, we have been able to view the structure of a number of typical chemical compounds. You have also learnt how **structure** is dependent upon the **bonding** between atoms. You have seen examples of the two most important types of chemical bond, **ionic** bonds and **covalent** ones. You have also learnt that the overall **properties** of a compound can be related to its structure, and thus to its bonding. Finally, we have briefly examined two more types of bonding: **metallic** and **hydrogen bonding**.

5.0 CONCLUSION

In this unit, you have learnt about the following:

- metallic bonding
- the physical properties of metals
- hydrogen bonding
- hydrogen bonds in biology
- other intermolecular forces
- London dispersion forces
- dipole-dipole interactions.

6.0 TUTOR-MARKED ASSIGNMENT

i. What are dipoles?
ii. What are dipole moments?
iii. How do dipoles interact?
iv. Why do molecules attract one another?
v. How do London dispersion forces come about?
vi. What parameters cause an increase of the London dispersion forces?
vii. What is a hydrogen bond?
viii. What type of hydrogen bonds is strong?
ix. What chemical groups are hydrogen acceptors for hydrogen bonds?

7.0 REFERENCES/FURTHER READING

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UNIT 4 BONDING THEORIES AND MOLECULAR GEOMETRY

CONTENTS

1.0 INTRODUCTION

The VSEPR model is useful for predicting molecular shape and estimating bond angles, but the model is insufficient for explaining bond energy and bond strength. Two other models, namely; the ***valence bond method*** and ***molecular orbital theory*** provide a more rigorous and complex treatment of covalent bond formation that take into account bond energy and bond length. In the *valence bond method,* covalent bonds are assumed to be formed by overlaps of atomic orbitals. The type of orbitals and the extent of the orbital overlap determine the bond length and bond energy. This model also proposes the occurrence of *hybridisations* of atomic orbitals.

2.0 OBJECTIVES

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

- describe covalent bonding in terms of the valence bond theory
- explain covalent bonding in terms of the molecular orbital theory
- use the VSEPR theory to predict the shape of covalently bonded molecules or polyatomic ions
- sketch the basic molecular shapes
- predict the approximate bond angles based on molecular structure and space that lone pairs, single and multiple bonds use
- distinguish between the predicted orientations of electron pairs around the central atom(s) and the predicted shape of the molecule
- determine if a molecular or polyatomic ion is polar or non-polar, given a molecular formula and periodic table
- describe why orbital hybridisation is necessary for covalent bonding
- use the molecular structure predicted by VSEPR to determine the orbital hybridisation of a central atom(s) in a molecule or polyatomic ion.

3.0 MAIN CONTENT

3.1 Valence Bond Theory

The valence bond theory states that "a covalent bond is formed by the overlap of two singly occupied atomic orbitals."

In Valence Bond Theory (VBT), bonding is viewed as occurring by the overlap of two atomic orbitals, one from each atom. Each atom's orbital contains a single electron and a bond is formed by the electrons, now paired in overlapping orbitals, holding the two nuclei together. Every covalent bond has a characteristic bond strength and bond length. The bond length is defined as the distance between the two nuclei.

As an example, the covalent bond in hydrogen fluoride is adequately described by the overlap of the two singly occupied atomic orbitals on each atom, as indicated in Figure 4.1.

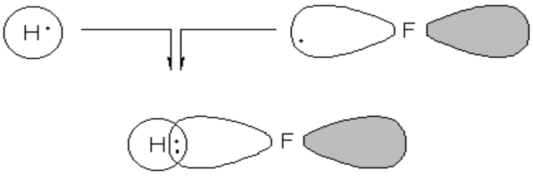


Fig. 4.1: The Covalent Bond in Hydrogen Fluoride is Formed by the Overlap of the Singly Occupied Hydrogen 1s Orbital and the Singly Occupied Fluorine 2p$_z$ Orbital

Bond strength is defined as the amount of energy needed to homolytically break a bond (each of the nuclei takes one of the two electrons from the bond). A normal carbon-chlorine bond has a bond length of 1.78 Angstroms (1.78 X 10^{-10} meters) and bond strength of (339 kJ/mol or 81 kcal/mol). Valence Bond Theory is useful for understanding the basic idea behind covalent bond formation. However, it fails to explain the chemical bonding in simple organic molecules like methane (CH_4). The electronic configuration of carbon, $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$, clearly indicates that carbon has only two singly occupied orbitals ($2p_y$ and $2p_z$); therefore, carbon should only form two chemical bonds if this theory were strictly correct. We know that carbon has a tendency to form four bonds, so something must be wrong with this theory.

In Molecular Orbital Theory (MOT), bonding is explained in terms of the mathematical combination of atomic orbitals to form molecular orbitals. The newly formed orbitals are called molecular orbitals because they belong to the entire molecule. The combination of two atomic orbitals leads to two molecular orbitals, a bonding molecular orbital and an antibonding molecular orbital.

3.2 Molecular Orbital Theory

Molecular Orbital Theory states that: a covalent bond is formed when the atomic orbitals of two interacting species combine to form an equivalent number of new molecular orbitals, so named because these new molecular orbitals encompass the entire molecule. These molecular orbitals are formed by the mathematical addition/subtraction of various atomic orbitals.

As an example, the covalent bond in hydrogen gas is completely described by the combination of the two 1s atomic orbitals on each hydrogen atom. The new molecular orbitals (psi 1 and psi 2) are the result of the combination of the atomic orbitals in both an additive and subtractive sense as indicated in Figure 4.2. Psi 1 is called a bonding molecular orbital, because electron density is centered between the two nuclei. Psi 2 is called an anti-bonding orbital, because a node exists in the space between the two nuclei. As you will note from Figure 1, only the bonding molecular orbital is fully occupied, thus forming the covalent bond.

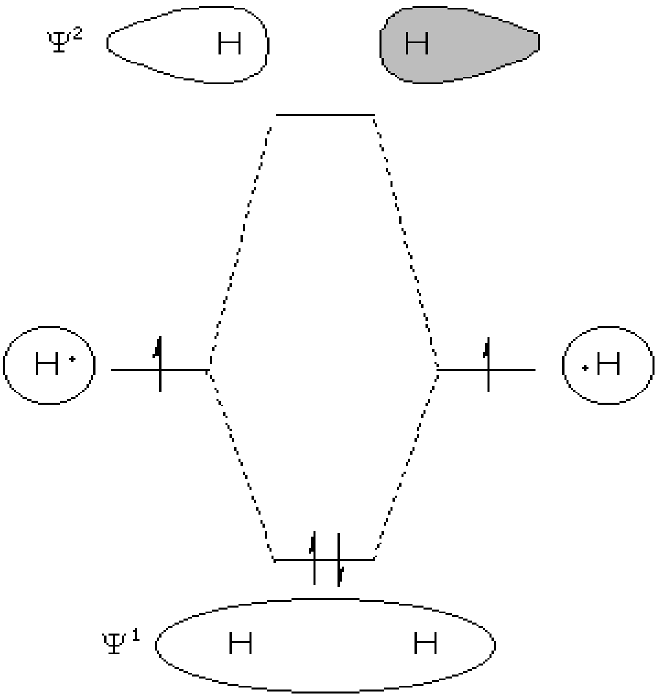


Fig. 4.2: The Covalent Bond in Hydrogen Gas is Formed by the Combination of the Atomic Orbitals from Each Hydrogen Atom

Molecular Orbital Theory provides the most accurate picture of covalent chemical bonding to date. However, describing the molecular orbitals for even simple organic molecules like methane (CH_4) precludes the use of this theory in any practical sense.

3.3 Hybridisation

The VBT and MOT cannot successfully bond in organic molecules like methane (CH_4). In order to explain such bonding situation, the concept of hybridisation has been introduced.

Hybridisation theory states that: *a covalent bond is formed by the overlap of two singly occupied hybrid or atomic orbitals. Hybrid atomic orbitals are created by mixing together atomic orbitals to form an equal number of new hybrid atomic orbitals.*

Hybrid orbitals are usually formed by mixing together 2s and 2p orbitals. Depending upon the number of 2p orbitals included, one can form sp, sp^2, and sp^3 hybrid orbitals.

An sp hybrid orbital is formed by mixing together the 2s and $2p_x$ atomic orbitals as shown in Figure 4.1. This will form 2 sp hybrid orbitals that are oriented with the major lobe of each pointing in opposite directions.

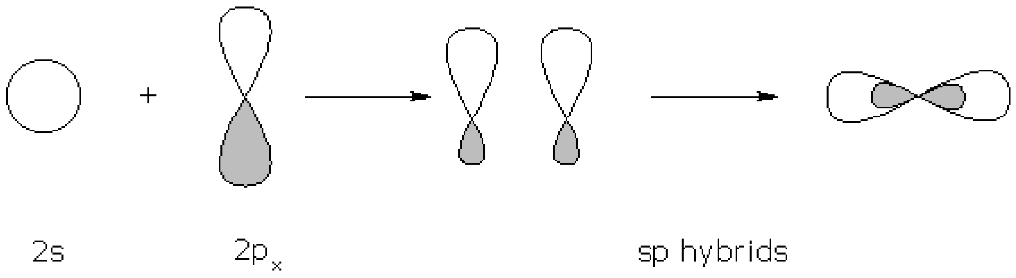


Fig. 4.3: Hybrid Orbitals formed by the Combination of 2s and $2p_x$ Atomic Orbitals

An sp^2 hybrid orbital is formed by mixing together the 2s, $2p_x$, and $2p_y$ atomic orbitals as shown in Figure 4.4. This will form 3 sp^2 hybrid orbitals that are oriented with the major lobe of each pointing in a triangular fashion.

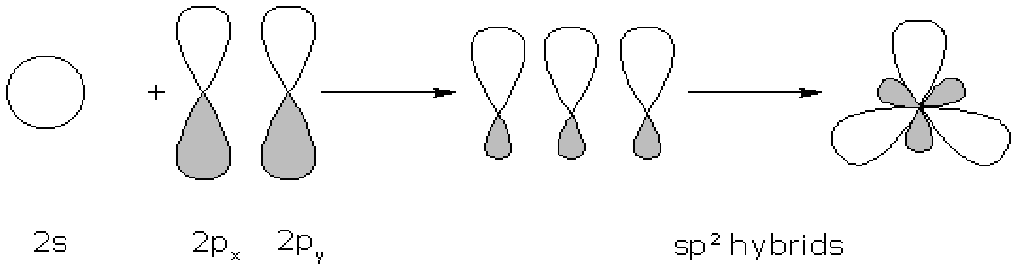


Fig. 4.4: Hybrid Orbitals formed by the Combination of 2s, $2p_x$, and $2p_y$ Atomic Orbitals

An sp^3 hybrid orbital is formed by mixing together the 2s, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals as shown in Figure 4.5. This will form 4 sp^3 hybrid orbitals that are oriented with the major lobe of each pointing in a tetrahedral fashion.

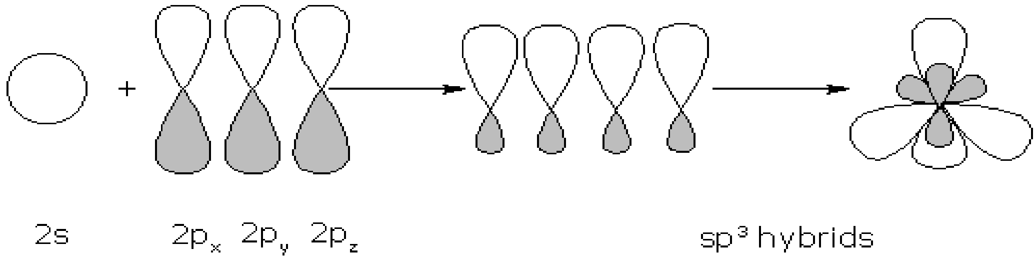


Fig. 4.5: Hybrid Orbitals formed by the Combination of 2s, $2p_x$, $2p_y$, and $2p_z$ Atomic Orbitals

How are hybrid orbitals used? Well, consider methane (CH_4). We know that carbon has 4 bonds, so we will use sp^3 hybrid orbitals to overlap with the 1s orbitals of each hydrogen atom. Figure 4.6 describes the process. Using this method, we can accurately describe the bonding in methane as being tetrahedral.

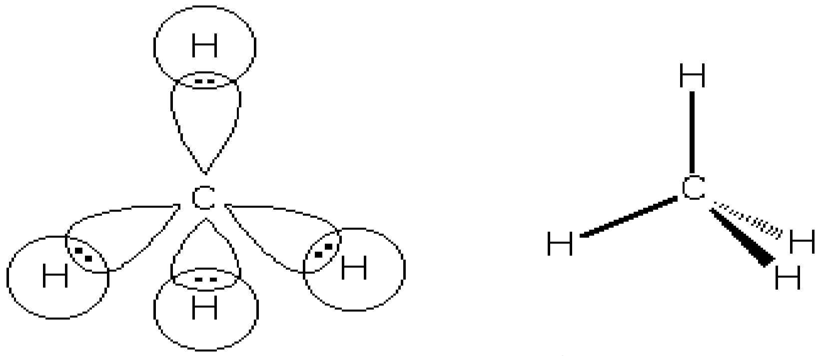


Fig. 4.6: Bonding in Methane using sp^3 Hybrid Orbitals

We can also use hybridisation theory to describe multiple bonds. Take ethene (C_2H_4) as an example. Each carbon atom has three atoms attached to it; therefore, we require 3 sp^2 hybrid orbitals to account for the hydrogen attachments. The singly occupied, unhybridised $2p_z$ orbital on each carbon will overlap, in a sideways manner, to provide the double bond. Figure 4.7 indicates this:

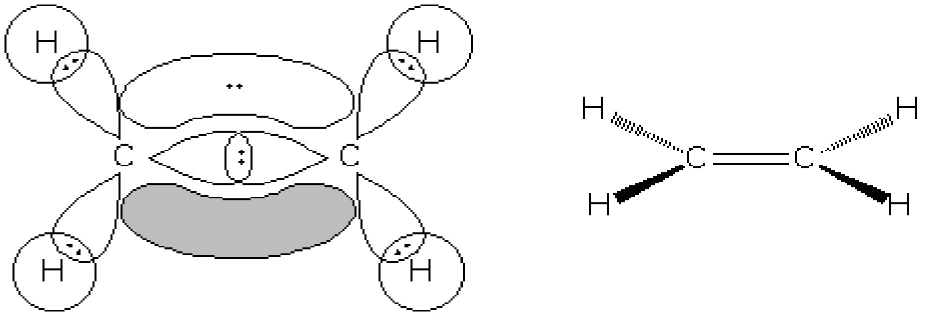


Fig. 4.7: Bonding in Ethene using sp^2 Hybrid Orbitals

Hybridisation theory provides a useful picture of covalent chemical bonding. It allows us to accurately predict the 3-dimensional shapes of molecules, as well as the correct valency for each atom. Hybridisation theory also gives us useful information about the relative acidity of organic molecules based upon the percentages character of a hybrid orbital.

3.4 Lewis Structures

Lewis structures (also known as Lewis dot diagrams, electron dot diagrams, and electron dot structures) are diagrams that show the bonding between atoms of a molecule and the lone pairs of electrons that may exist in the molecule. A Lewis structure can be drawn for any covalently bonded molecule, as well as coordination compounds. The Lewis structure was named after Gilbert Newton Lewis, who introduced it in his 1916 article *The Atom and the Molecule.* They are similar to electron dot diagrams in that the valence electrons in lone pairs are represented as dots, but they also contain lines to represent shared pairs in a chemical bond (single, double, triple, etc.).

Lewis structures show each atom and its position in the structure of the molecule using its chemical symbol. Lines are drawn between atoms that are bonded to one another (pairs of dots can be used instead of lines). Excess electrons that form lone pairs are represented as pairs of dots, and are placed next to the atoms.

Although many of the elements react by gaining, losing or sharing electrons until they have achieved a valence shell electron configuration with a full octet (8) of electrons, there are many noteworthy exceptions to the 'octet rule'. Hydrogen (H) conforms instead to a duet rule wherein it fills its first (and outermost) shell with just two electrons or empties it completely. Some compounds like boron trifluoride have incomplete orbitals while other such as sulphur hexafluoride, have a valence shell with more than eight electrons.

3.4.1 Writing Lewis Structures by Trial and Error

The Lewis structure of a compound can be generated by trial and error. We start by writing symbols that contain the correct number of valence electrons for the atoms in the molecule. We then combine electrons to form covalent bonds until we come up with a Lewis structure in which all of the elements (with the exception of the hydrogen atoms) have an octet of valence electrons.

Example: Let us apply the trial and error approach to generating the Lewis structure of carbon dioxide, CO_2. We start by determining the number of valence electrons on each atom from the electron configurations of the elements. Carbon has four valence electrons, and oxygen has six.

C: [He] $2s^2\ 2p^2$
O: [He] $2s^2\ 2p^4$

We can symbolise this information as shown at the top of the figure below. We now combine one electron from each atom to form covalent bonds between the atoms. When this is done, each oxygen atom has a total of seven valence electrons and the carbon atom has a total of six valence electrons. Because none of these atoms have an octet of valence electrons, we combine another electron on each atom to form two more bonds. The result is a Lewis structure in which each atom has an octet of valence electrons.

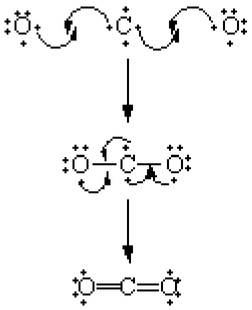


Fig. 4.8: Lewis Structure of Carbon (IV) Oxide

3.4.2 A Step-by-Step Approach to Writing Lewis Structures

The trial-and-error method for writing Lewis structures can be time consuming. For all but the simplest molecules, the following step-by-step process is faster.

Step 1: Determine the total number of valence electrons
Step 2: Write the skeleton structure of the molecule
Step 3: Use two valence electrons to form each bond in the skeleton structure
Step 4: Try to satisfy the octets of the atoms by distributing the remaining valence electrons as nonbonding electrons.

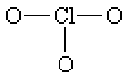
The first step in this process involves calculating the number of valence electrons in the molecule or ion. For a neutral molecule this is nothing more than the sum of the valence electrons on each atom. If the molecule carries an electric charge, we add one electron for each negative charge or subtract an electron for each positive charge.

Example: Let us determine the number of valence electrons in the chlorate (ClO_3^-) ion.

A chlorine atom (Group VIIA) has seven valence electrons and each oxygen atom (Group VIA) has six valence electrons. Because the chlorate ion has a charge of -1, this ion contains one more electron than a neutral ClO_3 molecule. Thus, the ClO_3^- ion has a total of 26 valence electrons.

ClO_3^-: $7 + 3(6) + 1 = 26$

The second step in this process involves deciding which atoms in the molecule are connected by covalent bonds. The formula of the compound often provides a hint as to the skeleton structure. The formula for the chlorate ion, for example, suggests the following skeleton structure.



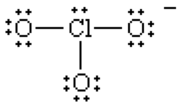
$O-\underset{O}{Cl}-O$

The third step assumes that the skeleton structure of the molecule is held together by covalent bonds. The valence electrons are therefore divided into two categories: **bonding electrons** and **nonbonding electrons**. Because it takes two electrons to form a covalent bond, we can calculate the number of nonbonding electrons in the molecule by subtracting two electrons from the total number of valence electrons for each bond in the skeleton structure.

There are three covalent bonds in the most reasonable skeleton structure for the chlorate ion. As a result, six of the 26 valence electrons must be used as bonding electrons. This leaves 20 nonbonding electrons in the valence shell.

26 valence electrons
- 6 valence electrons
20 non-bonding electrons

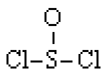
The nonbonding valence electrons are now used to satisfy the octets of the atoms in the molecule. Each oxygen atom in the ClO_3^- ion already has two electrons — the electrons in the Cl-O covalent bond. Because each oxygen atom needs six nonbonding electrons to satisfy its octet, it takes 18 nonbonding electrons to satisfy the three oxygen atoms. This leaves one pair of nonbonding electrons, which can be used to fill the octet of the central atom.



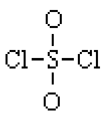
3.4.3 Drawing Skeleton Structures

The most difficult part of the four-step process in the previous section is writing the skeleton structure of the molecule. As a general rule, the less electronegative element is at the center of the molecule.

Example: The formulas of thionyl chloride ($SOCl_2$) and sulphuryl chloride (SO_2Cl_2) can be translated into the following skeleton structures.



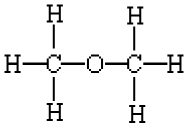
$Cl-\overset{O}{S}-Cl$



$Cl-\underset{O}{\overset{O}{S}}-Cl$

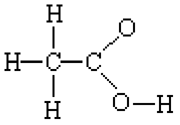
It is also useful to recognise that the formulas for complex molecules are often written in a way that hints at the skeleton structure of the molecule.

Example: Dimethyl ether is often written as CH_3OCH_3, which translates into the following skeleton structure:



Finally, it is useful to recognise that many compounds that are acids contain O-H bonds.

Example: The formula of acetic acid is often written as CH_3CO_2H, because this molecule contains the following skeleton structure.



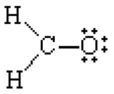
3.4.5 Molecules that Contain Too Many or Too Few Electrons

Occasionally, we encounter a molecule that does not seem to have enough valence electrons. If we cannot get a satisfactory Lewis structure by sharing a single pair of electrons, it may be possible to achieve this goal by sharing two or even three pairs of electrons.

Example: Consider formaldehyde (H_2CO) which contains 12 valence electrons.

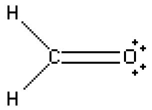
H_2CO: 2(1) + 4 + 6 = 12

The formula of this molecule suggests the following skeleton structure.



There are three covalent bonds in this skeletal structure, which means that six valence electrons must be used as bonding electrons. This leaves six nonbonding electrons. It is impossible, however, to satisfy the octets of the atoms in this molecule with only six nonbonding electrons. When the nonbonding electrons are used to satisfy the octet of the oxygen atom, the carbon atom has a total of only six valence electrons.

We therefore assume that the carbon and oxygen atoms share two pairs of electrons. There are now four bonds in the skeleton structure, which leaves only four nonbonding electrons. This is enough, however, to satisfy the octets of the carbon and oxygen atoms.

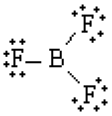


Every once in a while, we encounter a molecule for which it is impossible to write a satisfactory Lewis structure.

Example: Consider boron trifluoride (BF_3) which contains 24 valence electrons.

BF_3: 3 + 3(7) = 24

There are three covalent bonds in the most reasonable skeleton structure for the molecule. Because it takes six electrons to form the skeleton structure, there are 18 nonbonding valence electrons. Each fluorine atom needs six nonbonding electrons to satisfy its octet. Thus, all of the nonbonding electrons are consumed by the three fluorine atoms. As a result, we run out of electrons while the boron atom has only six valence electrons.



The elements that form strong double or triple bonds are C, N, O, P, and S. Because neither boron nor fluorine falls in this category, we have to stop with what appears to be an unsatisfactory Lewis structure.

Too Many Electrons

It is also possible to encounter a molecule that seems to have too many valence electrons. When that happens, we expand the valence shell of the central atom.

Example: Consider the Lewis structure for sulphur tetrafluoride (SF_4) which contains 34 valence electrons.

SF_4: 6 + 4(7) = 34

There are four covalent bonds in the skeleton structure for SF_4. Because this requires using eight valence electrons to form the covalent bonds that hold the molecule together, there are 26 nonbonding valence electrons.

Each fluorine atom needs six nonbonding electrons to satisfy its octet. Because there are four of these atoms, so we need 24 nonbonding electrons for this purpose. But there are 26 nonbonding electrons in this molecule. We have already satisfied the octets for all five atoms, and we still have one more pair of valence electrons. We therefore expand the valence shell of the sulphur atom to hold more than eight electrons.

This raises an interesting question: How does the sulphur atom in SF_4 hold 10 electrons in its valence shell? The electron configuration for a neutral sulphur atom seems to suggest that it takes eight electrons to fill the 3*s* and 3*p* orbitals in the valence shell of this atom. But let us examine, once again, the selection rules for atomic orbitals.

According to these rules, the $n = 3$ shell of orbitals contains 3*s*, 3*p*, and 3*d* orbitals. Because the 3*d* orbitals on a neutral sulphur atom are all empty, one of these orbitals can be used to hold the extra pair of electrons on the sulphur atom in SF_4.

$$\text{S: [Ne] } 3s^2\ 3p^4\ 3d^0$$

3.4.6 Resonance Hybrids

For some molecules and ions, it is difficult to determine which lone pairs should be moved to form double or triple bonds. This is sometimes the case when multiple atoms of the same type surround the central atom, and is especially common for polyatomic ions.

When this situation occurs, the molecule's Lewis structure is said to be a resonance structure, and the molecule exists as a resonance hybrid. Each of the different possibilities is superimposed on the others, and the molecule is considered to have a Lewis structure equivalent to an average of these states.

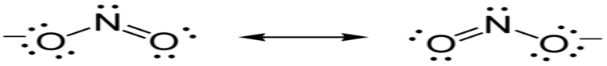
The nitrate ion (NO_3^-), for instance, must form a double bond between nitrogen and one of the oxygen’s to satisfy the octet rule for nitrogen. However, because the molecule is symmetrical, it does not matter which of the oxygen’s forms the double bond. In this case, there are three possible resonance structures. Expressing resonance when drawing Lewis structures may be done either by drawing each of the possible resonance forms and placing double-headed arrows between them or by using dashed lines to represent the partial bonds.

When comparing resonance structures for the same molecule, usually those with the fewest formal charges contribute more to the overall resonance hybrid. When formal charges are necessary, resonance structures that have negative charges on the more electronegative elements and positive charges on the less electronegative elements are favoured.

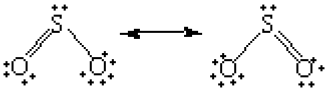
The resonance structure should not be interpreted to indicate the molecule switches between forms, but the molecule acts as the average of multiple forms.

The formula of the nitrite ion is NO_2^-.

- **Step one:** Nitrogen is the least electronegative atom, so it is the central atom by multiple criteria.
- **Step two: Count valence electrons**. Nitrogen has 5 valence electrons; each oxygen has 6, for a total of (6 × 2) + 5 = 17. The ion has a charge of −1, which indicates an extra electron, so the total number of electrons is 18.
- **Step three: Place ion pairs.** Each oxygen must be bonded to the nitrogen, which uses four electrons — two in each bond. The 14 remaining electrons should initially be placed as 7 lone pairs. Each oxygen may take a maximum of 3 lone pairs, giving each oxygen 8 electrons including the bonding pair. The 7th lone pair must be placed on the nitrogen atom.
- **Step four: Satisfy the octet rule.** Both oxygen atoms currently have 8 electrons assigned to them. The nitrogen atom has only 6 electrons assigned to it. One of the lone pairs on an oxygen atom must form a double bond, but either atom will work equally well. We therefore must have a resonance structure.
- **Step five: Tie up loose ends.** Two Lewis structures must be drawn: one with each oxygen atom double-bonded to the nitrogen atom. The second oxygen atom in each structure will be single-bonded to the nitrogen atom. Place brackets around each structure, and add the charge (−) to the upper right outside the brackets. Draw a double-headed arrow between the two resonance forms.



Two Lewis structures can be written for sulphur dioxide.



The only difference between these Lewis structures is the identity of the oxygen atom to which the double bond is formed. As a result, they must be equally satisfactory representations of the molecule.

Interestingly enough, neither of these structures is correct. The two Lewis structures suggest that one of the sulphur-oxygen bonds is stronger than the other. There is no difference between the lengths of the two bonds in SO_2, however, which suggests that the two sulphur-oxygen bonds are equally strong.

When we can write more than one satisfactory Lewis structure, the molecule is an average, or **resonance hybrid**, of these structures. The meaning of the term *resonance* can be best understood by an analogy. In music, the notes in a chord are often said to resonate — they mix to give something that is more than the sum of its parts. In a similar sense, the two Lewis structures for the SO_2 molecule are in resonance. They mix to give a hybrid that is more than the sum of its components. The fact that SO_2 is a resonance hybrid of two Lewis structures is indicated by writing a double-headed arrow between these Lewis structures, as shown in the figure above.

3.4.7 Formal Charge

It is sometimes useful to calculate the **formal charge** on each atom in a Lewis structure. The first step in this calculation involves dividing the electrons in each covalent bond between the atoms that form the bond. The number of valence electrons formally assigned to each atom is then compared with the number of valence electrons on a neutral atom of the element. If the atom has more valence electrons than a neutral atom, it is assumed to carry a formal negative charge. If it has fewer valence electrons, it is assigned a formal positive charge.

In terms of Lewis structures, formal charge is used in the description, comparison and assessment of likely topological and resonance structures[6] by determining the apparent electronic charge of each atom within, based upon its electron dot structure assuming exclusive covalency or non-polar bonding. It has uses in determining possible electron re-configuration when referring to reaction mechanisms, and often results in the same sign as the partial charge of the atom, with exceptions. In general, the formal charge of an atom can be calculated using the following formula, assuming non-standard definitions for the mark-up used:

$$C_f = N_v - U_e - B_n$$

Where:

- C_f is the formal charge
- N_v represents the number of valence electrons in a free atom of the element
- U_e represents the number of unshared electrons on the atom
- B_n represents the total number of bonds the atom has with another.

The formal charge of an atom is computed as the difference between the number of valence electrons that a neutral atom would have and the number of electrons that belong to it in the Lewis structure. Electrons in covalent bonds are split equally between the atoms involved in the bond. The total of the formal charges on an ion should be equal to the charge on the ion, and the total of the formal charges on a neutral molecule should be equal to zero.

3.5 Shapes of Molecules

3.5.1 The Valence Shell Electron Pair Repulsion Theory

In order to predict the geometry of molecules, *Nyholm* and *Gillespie* developed a qualitative model known as Valence Shell Electron Pair Repulsion Theory **(*VSEPR Theory*)**. The theory is a way of predicting the shape of a molecule based on the number of bonding and lone pairs of electrons in a polyatomic species.

It is based on the fact that these electrons pairs interact and repel each other due the electrostatic repulsion. In doing so, they adopt a spatial arrangement such that they are as far apart as possible and the electrostatic repulsion is minimised.

The basic assumptions of this theory are summarised below:

1. The electron pairs in the valence shell around the central atom of a molecule repel each other and tend to orient in space so as to minimise the repulsions and maximise the distance between them.
2. There are two types of valence shell electron pairs viz., (i) Bond pairs and (ii) Lone pairs.

   Bond pairs are shared by two atoms and are attracted by two nuclei. Hence, they occupy less space and cause less repulsion.

   Lone pairs are not involved in bond formation and are in attraction with only one nucleus. Hence, they occupy more space. As a result, the lone pairs cause more repulsion.

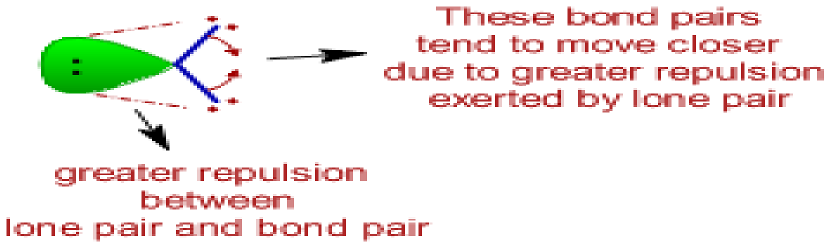
   The *order of repulsion* between different types of electron pairs is as follows:

   Lone pair - Lone pair > Lone Pair - Bond pair > Bond pair - Bond pair

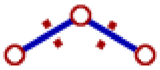
Note: The bond pairs are usually represented by a solid line, whereas the lone pairs are represented by a lobe with two electrons.

3. In VSEPR theory, the multiple bonds are treated as if they were single bonds. The electron pairs in multiple bonds are treated collectively as a single super pair.

   The repulsion caused by bonds increases with increase in the number of bonded pairs between two atoms i.e., a triple bond causes more repulsion than a double bond which in turn causes more repulsion than a single bond.
4. The shape of a molecule can be predicted from the number and type of valence shell electron pairs around the central atom.
   When the valence shell of central atom contains only bond pairs, the molecule assumes a symmetrical geometry due to even repulsions between them.
   However the symmetry is distorted when there are also lone pairs along with bond pairs due to uneven repulsion forces.
5. **Primary and secondary effects on bond angle and shape:**
   (i) The **bond angle** decreases due to the presence of lone pairs, which cause more repulsion on the bond pairs and as a result the bond pairs tend to come closer.

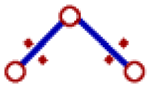


   (ii) The repulsion between electron pairs increases with increase in electronegativity of central atom and hence the bond angle increases. The electronegative central atom attracts the bonding electrons toward itself, thereby shortening the distance between them. As a result, electron pair repulsion increases; hence the bonds tend to move away from each other.



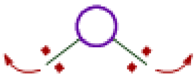
The bond pairs tend to move away from each other since the distance between them is shortened as they are more localized on more electronegative central atom.

However the bond angle decreases when the electronegativities of peripheral atoms are more than that of central atom. There is increase in the distance between bond pairs since they are now closer to peripheral atoms. As a result, inter-electronic repulsions are reduced, and the bond angle is decreased.

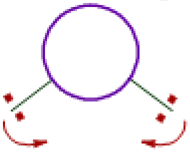


The bond pairs tend to come closer since the distance between them is increased as they are more localised on more electronegative peripheral atoms.

(iii) The bond angle decreases with increase in the size of central atom.

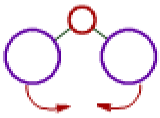


On smaller central atoms the bond pairs are closer and hence tend to move away from each other so as to minimise repulsion. Hence bond angle will be more.

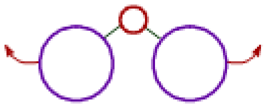


On bigger central atoms, the bond pairs are more distant from each other and hence there is less repulsion. Hence they tend to move closer, thus decreasing the bond angle.

However the bond angle increases with increase in the size of peripheral atoms, which surround the central atom.



There is less repulsion between smaller peripheral atoms and they can move closer to each other and thus decrease the bond angle.



There is a greater repulsion between bigger peripheral atoms and hence they tend to move away from each other. Thus bond angle increases.

3.5.2 Relation between Number and Type of Valence Electron Pairs with the Shape of Molecule

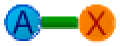
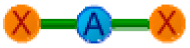
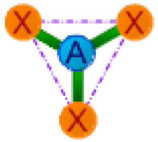
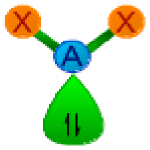
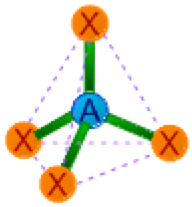
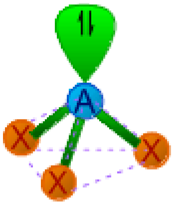
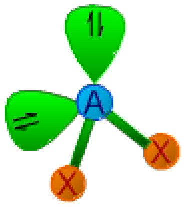
The shape of molecule and the approximate bond angles can be predicted from the number and type of electron pairs in the valence shell of central atom as tabulated in table 4.1.

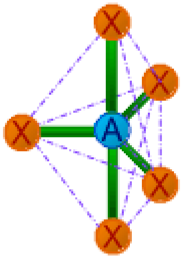
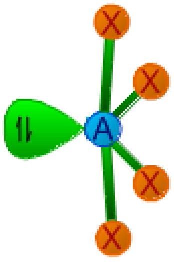
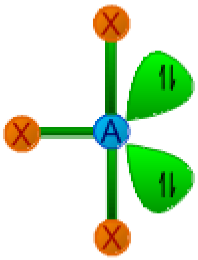
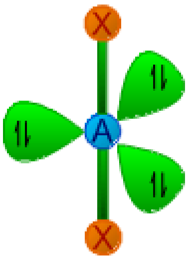
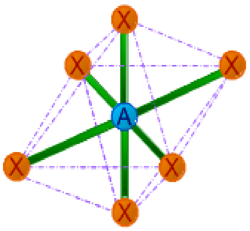
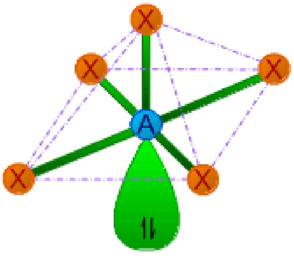
In table 4.1, the molecule is represented by "AXE" notation, where
A = Central atom
X = Peripheral atom bonded to the central atom either by a single bond or by multiple bond; indicating a bond pair.

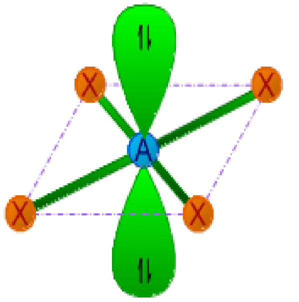
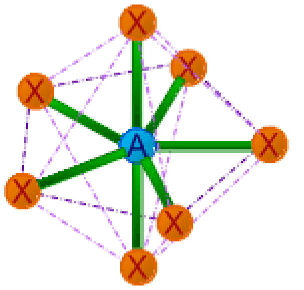
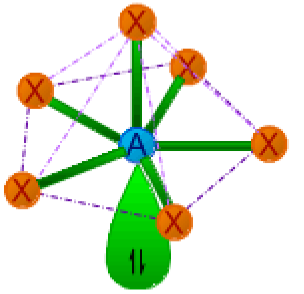
E = Lone pair

Note:
* The sum of number of peripheral atoms (**X**) and number of lone pairs (**E**) is also known as **steric number**.

Table 4.1: Relation between Number and Type of Valence Electron Pairs with the Shape of Molecule

Steric number	Number of Bond pairs	Number of Lone pairs	Formula	Shape of molecule		Approx. Bond angles	Examples
1	1	0	AX	Linear		-	ClF, BrF, BrCl, HF, O_2
2	2	0	AX_2	Linear		180^o	$BeCl_2$, $HgCl_2$, CO_2
3	3	0	AX_3	Trigonal planar		120^o	BF_3, CO_3^{2-}, NO_3^-, SO_3
	2	1	AX_2E	Angular		120^o	SO_2, $SnCl_2$, O_3, NSF, NO_2^-
4	4	0	AX_4	Tetrahedral		109^o 28'	CH_4, $SiCl_4$, NH_4^+, PO_4^{3-}, SO_4^{2-}, ClO_4^-
	3	1	AX_3E	Trigonal pyramidal		around 109^o 28'	NH_3, PCl_3, XeO_3
	2	2	AX_2E_2	Angular		around 109^o 28'	H_2O, SCl_2, Cl_2O, OF_2

5	5	0	AX_5	Trigonal bipyramidal		120^o & 90^o	PCl_5, SOF_4
	4	1	AX_4E	See saw or distorted tetrahedral		-	SF_4, $TeCl_4$
	3	2	AX_3E_2	T-Shape		90^o	ClF_3, BrF_3, $BrCl_3$
	2	3	AX_2E_3	Linear		180^o	XeF_2, I_3^-
6	6	0	AX_6	Octahedral		90^o	SF_6
	5	1	AX_5E	Square pyramidal		90^o	ClF_5, BrF_5, ICl_5

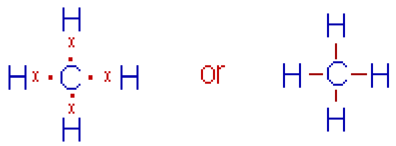
	4	2	AX_4E_2	Square planar		90^o	XeF_4
7	7	0	AX_7	Pentagonal bipyramidal		72^o & 90^o	IF_7
	6	1	AX_6E	Pentagonal pyramidal		around 72^o & 90^o	$XeOF_5^-$, IOF_5^{2-}

3.5.3 Steps involved in predicting the Shapes of Molecules using VSEPR Theory

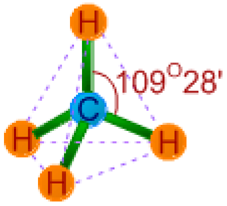
- The first step in determination of shape of a molecule is to write the Lewis dot structure of the molecule.
- Then find out the number of bond pairs and lone pairs in the valence shell of central atom.
  While counting the number of bond pairs, treat multiple bonds as if they were single bonds. Thus electron pairs in multiple bonds are to be treated collectively as a single super pair.
- Use the above table to predict the shape of molecule based on steric number and the number of bond pairs and lone pairs.

3.5.4 Applications and Illustrations of VSEPR Theory Methane (CH_4)

The Lewis structure of methane molecule is:



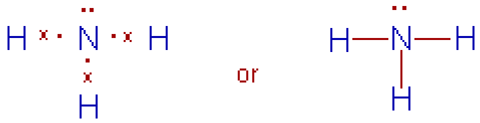
- There are four bond pairs around the central carbon atom in its valence shell. Hence it has tetrahedral shape with 109^o 28' of bond angles.



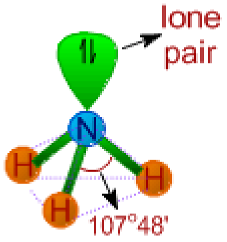
Tetrahedral shape of Methane molecule

Ammonia (NH_3):

The Lewis structure of ammonia indicates there are three bond pairs and one lone pair around the central nitrogen atom.



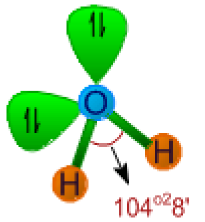
- Since the steric number is 4, its structure is based on tetrahedral geometry. However, its shape is pyramidal with a lone pair on nitrogen atom.
- The bond angle is decreased from 109^o 28' to 107^o 48' due to repulsion caused by lone pair on the bond pairs.



Pyramidal shape of Ammonia molecule

Water (H_2O)

It is evident from the Lewis structure of water molecule; there are two bond pairs and two lone pairs in the valence shell of oxygen. Hence its structure is based on tetrahedral geometry. However its shape is angular with two lone pairs on oxygen.

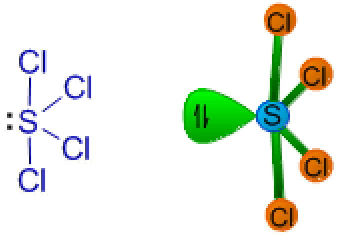


Angular shape of Water molecule

The bond angle is decreased to 104° 28' due to repulsions caused by lone pairs on bond pairs. It can be noted that the bond angle decreases with increase in the number of lone pairs on the central atom.

Sulphur tetrachloride (SCl_4):

Since there are four bond pairs and one lone pair around sulfur in its valence shell, the structure of SCl_4 is based on trigonal bipyramidal geometry. It has seesaw shape with a lone pair occupying the equatorial position.



seesaw shape of SCl_4

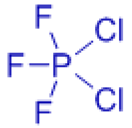
The angles between P-Cl_{axial} and P-$Cl_{equatorial}$ are less than 90° due to repulsion exerted by the lone pair. The angle between P-$Cl_{equatorial}$ bonds also decreases from its usual value, 120°.

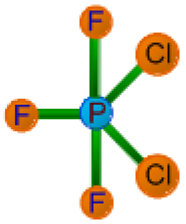
The lone pair occupies the equatorial position to minimize the repulsions.

Note: Usually the lone pairs, bulky groups and less electronegative atoms tend to occupy equatorial position to minimize repulsions. This is because they experience repulsion only from two groups at 90°, when they occupy the equatorial positions. However the repulsion will be more when they occupy axial positions, since they encounter three groups at 90°.

PF_3Cl_2:

There are only 5 bond pairs on phosphorus atom. Hence it has trigonal bipyramidal shape. The chlorine atoms occupy the equatorial positions to minimize the repulsions since they are not only bulkier and also less electronegative than fluorine atoms.



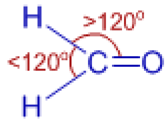


The bond pair of P-Cl is slightly closer towards the P atom when compared to the bond pair of P-F, since the chlorine atoms are comparatively less electronegative than fluorine atoms. Hence there is comparatively more negative charge accumulation towards P atom, which makes the P-Cl bonds to experience more repulsion than P-F bonds. Hence, they orient in equatorial positions at 120^o to minimiSe repulsions.

Note that, here we are comparing the polarity of P-Cl bond with P-F bond. But one should keep in mind that the bond pair of P-Cl bond is still closer to Cl, since it is more electronegative than P atom.

Formaldehyde (HCHO):
There are three bond pairs around the central carbon atom. The double bond between C and O is considered as a single super pair. Hence, the shape of the molecule is trigonal planar and the bond angles are expected to be equal to 120^o.

However, the C=O exerts more repulsion on the C-H bond pairs. Hence the ∠H-C-H bond angle will be less than 120^o and the ∠H-C-O is greater than 120^o.



4.0 CONCLUSION

The molecular orbital theory is based on the wave-mechanic model and it assumes that when atoms combine to form a molecule, their orbitals combine mathematically to form *molecular orbitals*. The number of molecular orbitals formed is equal to the total number or atomic orbitals that are linearly combined to form the molecular orbitals. The molecular orbital theory also determines bond orders and the occurrence of paramagnetism. For example, molecular orbital theory explains why O_2 molecule is paramagnetic, a property that could not be explained with the Lewis structure or valence bond method.

5.0 SUMMARY

According to the valence bond theory, a covalent bond is formed between the two atoms by the overlap of half-filled valence atomic orbitals of each atom containing one unpaired electron. A valence bond structure is similar to a Lewis structure, but where a single Lewis structure cannot be written, several valence bond structures are used.

Molecular orbital theory is a method for determining molecular structure in which electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei in the whole molecule.

In chemistry, hybridisation is the concept of mixing atomic orbitals to form new *hybrid orbitals* suitable for the qualitative description of atomic bonding properties. Hybridised orbitals are very useful in the explanation of the shape of molecular orbitals for molecules. It is an integral part of valence bond theory. Although sometimes taught together with the valence shell electron-pair repulsion (VSEPR) theory, valence bond and hybridisation are in fact not related to the VSEPR model.

Lewis structures (also known as Lewis dot diagrams, electron dot diagrams, and electron dot structures) are diagrams that show the bonding between atoms of a molecule and the lone pairs of electrons that may exist in the molecule.

6.0 TUTOR-MARKED ASSIGNMENT

Choose the correct options and explain your answer in each case.

i. For a molecule with the formula AB_2 the molecular shape is __________.
   a. linear or trigonal planar
   b. linear or bent
   c. linear or T-shaped
   d. T-shaped

ii. According to VSEPR theory, if there are five electron domains in the valence shell of an atom, they will be arranged in a(n) __________ geometry.
   a. octahedral
   b. trigonal bipyramidal
   c. tetrahedral
   d. trigonal planar

iii. The electron-domain geometry and molecular geometry of iodine trichloride are__________ and __________ respectively.
   a. trigonal bipyramidal, trigonal planar
   b. tetrahedral, trigonal pyramidal
   c. trigonal bipyramidal, T-shaped
   d. octahedral, trigonal planar

viii. The hybridisation of orbitals on the central atom in a molecule is sp. The electron domain geometry around this central atom is __________.
   a. octahedral
   b. linear
   c. trigonal planar
   d. tetrahedral

ix. In counting the electron domains around the central atom in VSEPR theory, a__________ is not included.
   a. nonbonding pair of electrons
   b. single covalent bond
   c. core level electron pair
   d. double covalent bond

x. Which one of the following statements is **false**?
   a. Valence bond theory and molecular orbital theory can be described as two different views of the same thing.
   b. When one considers the molecular orbitals resulting from the overlap of any two specific atomic orbitals, the bonding orbitals are always lower in energy than the antibonding orbitals.
   c. Molecular orbitals are generally described as being more delocalised than hybridised atomic orbitals.
   d. One of the shortcomings of molecular orbital theory is its inability to account for a triple bond in the nitrogen molecule, N_2.
   e. One of the shortcomings of valence bond theory is its inability to account for the paramagnetism of the oxygen molecule, O_2.

xi. Antibonding molecular orbitals are produced by
   a. constructive interaction of atomic orbitals.
   b. destructive interaction of atomic orbitals.
   c. the overlap of the atomic orbitals of two negative ions
   d. all of these
   e. none of these

7.0 REFERENCES/FURTHER READING

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