CHEMISTRY DEPARTMENT
EDO UNIVERSITY
IYHAMO, EDO STATE, NIGERIA

Semester / Session: First Semester 2018/2019
Course Code: CHM 111
Course Title: Introductory Chemistry I
Course Credit: 3
Course Duration: 3 Hours of Lecture per Week
Day of the Week: Wednesday (8.00 - 11.00am)
Course Lecturer: Dr. (Mrs.). Maliki M.
Lecturers' Office Hours: Dr. (Mrs.). Maliki M. Monday 12:00-2:00pm.

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Alternative Email: ellpetangmaliki@yahoo.com

Intended Learning Outcomes

At the completion of this course, students are expected to:

1. Understand the atomic structure and the use of the mole concept in quantitative chemical calculations.
2. Calculate and utilize solution concentration units such as molarity.
3. Demonstrate understanding of the basic features of the periodic table and be able to identify and name elements and ions.
4. Demonstrate understanding of the reactivity of elements based on their position in the periodic table.
5. Understand the concept of hybridisation and prediction of hybrid structure of simple compounds
6. Balance chemical equations, identify basic types of chemical reactions and predict the outcome of these reactions.
7. Apply the gas laws to predict behavior of gases and its application in quantitative problems.
8. Apply the concepts of chemical equilibrium and solve simple quantitative equilibrium calculations
9. Understand stoichiometric relationships involved in reactions.
10. Understand radioactive chemistry and its applications

COURSE DETAILS:

Week 1-2:*Atomic theory and Nature of atoms.*
Week 3:*Introduction to the periodic table: properties and Electronic configuration.*

Week 4*: Stoichiometry: formulae and Equations, Volumetric analysis, redox precipitation and complexation reactions.*
Week 5: *States of matter: Gases, Liquids and solids. Gas laws, General gas equations*
Week 6: *Chemistry of elements in group 1, 2 and 3*
Week 7:*Electrochemistry and The Nernst equation.*
Week 8:*Chemical equilibrium*
Week 9:*Introduction to solution Chemistry:*
Week 10*:Introduction to nuclear reactions: Radioactivity.*
Week 11: *Revision*
Week 12: *Exam*

RESOURCES

- **Course lecture Notes: http://www.edouniversity.edu.ng/oer**
- **Books:**

- Atkins, P. and Jones, L. (1997). Chemistry: molecules, matter and change, 3rd. Freeman
- Hottzclaw, H.F. and Robinson, W.R. (Ed). (1988). College Chemistry with Qualitative
- Analysis (8th Ed.) Massachusetts, Toronto: D.C. Health and Company
- Earl, B. and Wilford L.D.R (Eds). (2001). GCSE Chemistry (Revised Ed.). London: John Murry (Publishers) Ltd.
- Earl, B. And Wilford, L.D. R. (2001). Further advanced chemistry. London: John Murray (Publishers) Ltd.
- Ndiokwere, C.I. and Ukhun, M.E. (2006). First year University inorganic and physical chemistry, revised edition. Mindex publishing
- Philip Mathew (1992). Advanced Chemistry, 2nd edition. University press, united kingdom

<u>Course Requirements, Examination and Grading:</u>

This is a core course for all Chemistry major students and required for all student in the faculties of Sciences, Engineering and Medical Sciences. Students Attendance, assignment, presentation and mid-semester test will form the continuous assessment and a final written examination. A minimum of 70% attendance is required to write final examination. Where necessary, practical tests may be given to students which will be graded and form part of the continuous assessment. The grades will be distributed as given below;

Continuous assessments (Test, Assignments, Group work etc.): 30%

Final Examination:	70%
Total Score:	100%

General Course Outline:

Atomic theory and Nature of atoms. Introduction to the periodic table: properties and Electronic configuration. Stoichiometry: formulae and Equations, Volumetric analysis, redox precipitation and complexation reactions. States of matter: Gases, Liquids and solids. Gas laws. General gas equations. Electrochemistry and Redox reactions. Chemical Kinetics, rate orders and rate laws. Chemical equilibrium, Nuclear Chemistry and Radioactivity.

CHAPTER1

ATOMIC THEORY AND NATURE OF ATOMS

Chemistry studies the composition of matter and the changes it undergoes. Matter has been defined as anything that has weight and can occupy space. All materials are made up of matter.

For centuries, philosopher, chemist and physicist tried to answer the question of what matter was made up of using a variety of experiments and observations.

1.1 THE EARLY IDEAS OF THE ATOM

In 440BC a Greek philosopher named Democritus came up with a conceived idea that matter was composed of very tiny and indestructible particles. He stated that these particles were the smallest unit of matter which he called **atomos** – meaning indivisible in Greek. The theory was not generally accepted because it was a mere philosophy (guess). In 1803, John Dalton proposed the atomic theory as follows:

1. All elements are composed of atoms and atoms are indivisible and indestructible particles
2. Atoms of the same elements are exactly alike (identical) in size, shape, mass and chemistry. While atoms of different elements are different.
3. Atoms combine with atoms of other elements in simple whole-number ratios to form chemical compounds.

Dalton's atomic theory became one of the foundations of chemistry and the dawn of quantitative analysis, because soon after the theory, scientific investigation became rapid. Curiosity and the urge to understand the world became increased.

1.2 JOSEPH JOHN THOMSON ATOMIC MODEL

Discovery of the electrons

In 1897, J.J. Thomson discovered the electrons while investigating the electrical conductivity of gases at very low pressure. In his experiment, a very high potential difference (pd) was placed across a glass tube containing gas at a very low pressure. At that experimental condition, a glow coming from the negative terminal was observed and it was attracted to the anode. A hole in the anode allowed the rays to pass through and hit the end of the glass tube's surface. The rays was deflected to the north pole by the magnetic field in the glass tube. The beam hit the fluorescent screen at the positively charged plate, when it was exposed to an electric field. However, in the absence of both the magnetic and electrical field or when both fields are on such that the fields cancels each other influence, the beam was not deflected, it travelled in a straight line and hit the fluorescent screen at point directly opposite the source.

Thomson concluded that the special ray must be negatively charged because it was attracted to the positively charged plate and moved away from the negatively charge plate. His conclusion was supported by the electromagnetic theory which state that a moving charged body behaves like a magnet which interact with the electric and magnetic field through which it passes. From his experiment, Thompson was also able to show that the ray was the same irrespective of the type of gas in the tube or the type of metal used as the electrodes, stating that the ray must be inside every atom. The glass tube Thompson used in his experiment is also called the cathode ray tube, while the negatively charged ray that he discovered are now known as electrons.

Properties of the cathode rays;

1. They are identical irrespective of cathodes (different metals) or gas used in the experiment, all produced same results.
2. The rays are deflected by magnetic and electric fields.
3. The rays produced some chemical reactions similar to those produced by light.
4. They travel in a straight line when it is not interfered with.

Also, from J.J. Thompson's investigation he showed that at ordinary pressure gases are electrical insulators, but at pressure below 0.01amt, when subjected to a high voltage, gases break down and conduct electricity.

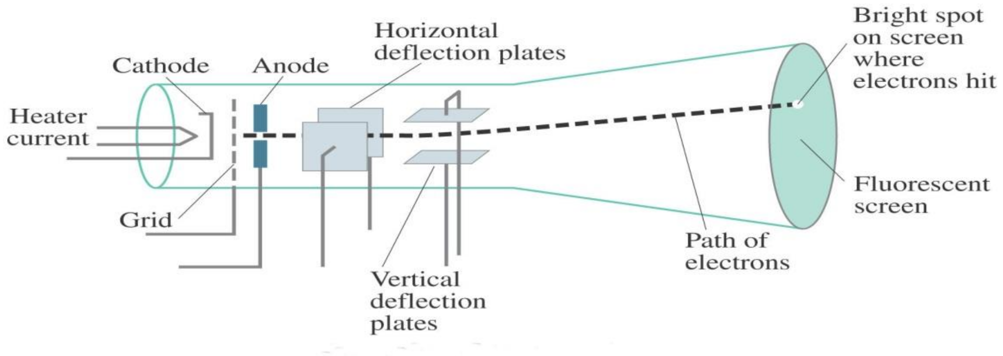
Based on the knowledge he obtained from the cathode ray experiment- that is the effect of electric and magnetic field on negatively charged particles, J.J. Thompson was able to derive the ratio of electric charge to mass of an electron as -1.76 X10^8 C/g. Where C = Coulomb. Also, a scientist called R.A. Millikan conducted a number of experiments in 1916 and found the charge of an electron to be -1.60 X 10^{-19}C. Finally, the mass of the electron was calculated from the data obtained by J.J. Thompson's and R.A. Millikan.

$$\text{Mass of an electron} = \frac{\text{charge}}{\text{Charge/mass}}$$

$$= \frac{-1.60 \times 10^{-19}}{-1.76 \times 10^{8}\ \text{C/g.}}$$

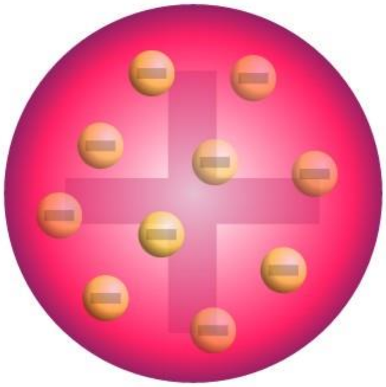
$$9.09\text{x}\ 10^{-28}\text{g}$$

FIGURE 1.1 THE CATHODE RAY TUBE



By the early 1900s,it became clear that ccathode rays have identical properties regardless of the element used to produce them. Also, that all elements must contain negatively charged electrons and atoms are neutral. Therefore, there must be positive particles in the atom to balance the negative charge of the electrons. Thus J.J. Thompson later proposed a revised model for the atom called the plum pudding model. This is shown in figure 1.2. He describe an atom as a uniform positive shpere of matter (the dough) in which negatively charged electrons (raisins) were stucked.

FIGURE 1.2 THE PLUM – PUDDING MODEL



1.3 RUTHERFORD EXPERIMENT

Discovery of the nucleus

In 1910, Hans Gieger and Ernest Marsden under the supervision of Ernest (later Lord) Rutherford discovered the nucleus. Streams of positively charged particles were fired at a thin sheet of gold (gold foil). Rutherford's team observed that most of the alpha particles passed through the gold foil without any deflection at all, while a few of the particles (1:800) were highly deflected through quite large angle. Sometimes also, but less frequently, α-particles would bounce back in the direction from which it came. This observation conflicted with Thompson's model, because it was anticipated that since the positive charge in the Thomson's atom was evenly spread out, the beam (α-particle) should have easily passed through the foil with little or no deflection. Based on this observation, Rutherford proposed that most of the particles passed through the foil without any deflection because the atom consisted of largely empty spaces and does not interact much with the α-particles. However, occasionally one of the α-particle interacted with the very dense positively charged center which he called the nucleus and the very large repulsion of this positive charged particle and the nucleus resulted in the large deviation in the path of the α-particles, even to the extent of deflecting the α-particle along the direction from which it came. This model was clearly different from Thompson's.

Rutherford's model though very useful, it could not adequately explain the arrangement of electrons round the nucleus nor did it answer the question of what prevented the electrons from falling into the nucleus. This is because unlike charges attract and according to classical physics a moving charged body continually loses energy while it spirals inwards and finally collapses into the middle. Rutherford model of an atom fail to explain why electron in a given atoms do not collapse into the nucleus when in motion and could not explain the position and arrangement of electrons around the nucleus.

FIGURE 1.3 RUTHERFORD EXPERIMENT (EXPECTED AND ACTUAL RESULT)

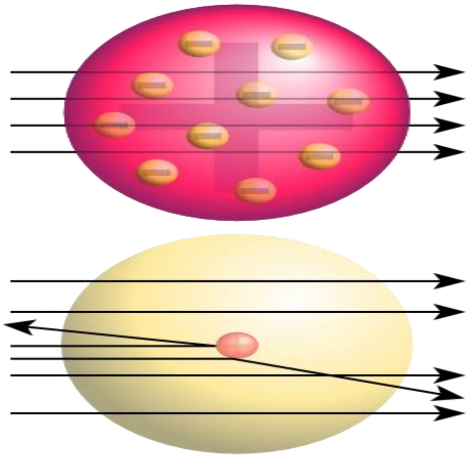
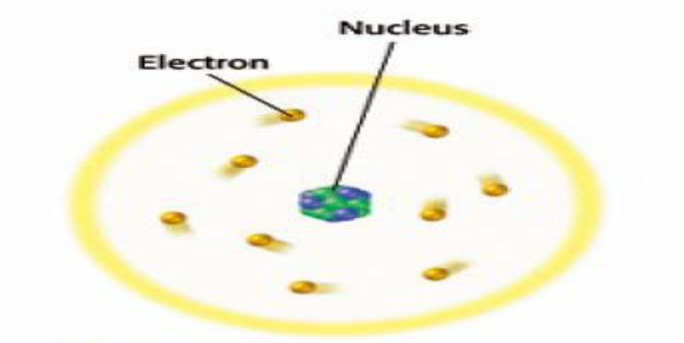


FIGURE 1.4 RUTHERFORD'S MODEL



1.4 CHADWICK EXPERIMENT

Discovery of the neutrons

After a series of experiments were conducted it was suspected that another type of subatomic particle exists. For example, experimental observations show that the mass of an oxygen atom was 16 times larger than the proton and oxygen has only eight positive charges, therefore, accounting for the remaining mass of the atom became a puzzle.

This puzzle was unraveled by James Chadwick in 1932. In his experiment, Chadwick bombarded a sheet of beryllium foil with alpha-particles and unknown radiation was produced. The result from the experiment showed that the particles emitted from beryllium consisted of electrically neutral particles with mass slightly higher than the proton.

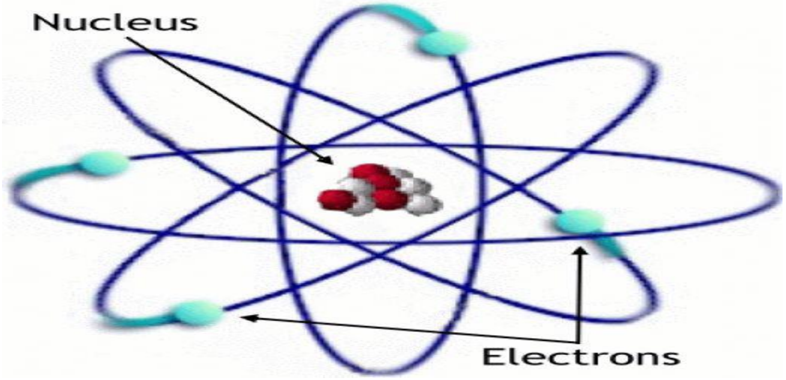
1.5 THE MODERN ATOMIC MODELS

Two atomic models are in use today, they are; the Bohr atomic model and the quantum mechanical model. Of these two models, the Bohr model is simpler and relatively easy to understand. However, because of some shortcomings of the Bohr model, the quantum mechanical model is more valid.

1.5.1THE BOHR'S MODEL OF THE ATOM

In 1913, a Danish physicist Niels Bohr (1885 – 1962) proposed an improvement to Rutherford's model. Bohr explained the arrangement of electrons in an atom and provided answers to what prevented the electrons from falling into the nucleus. He proposed that although the electrons are negatively charged and the nucleus positively charged, the movement of the electrons in definite concentric circular path around nucleus prevented the electrons from collapsing into the nucleus. The concentric circular path (orbit) that the electron orbits is much like the planet orbit around the sun. The orbits are located at certain fixed distances from the nucleus. Bohr based is explanation of the atomic model and the electronic energy levels of atoms on the experimental observation of the emission spectrum of light by atoms.

FIGURE 1.5 THE BOHR'S ATOMIC MODEL



1.5.2 ELECTROMAGNETIC SPECTRUM

Bohr based his explanations on the electromagnetic spectrum. When a white light source or emitted radiation is passed through a prism, the light splits from its source into series of coloured bands called spectrum. Atoms also give rise to spectrum called the atomic spectrum. Electromagnetic spectrum is the entire distribution of electromagnetic radiation according to frequency and wavelength. It is the entire range of lights that exist and they all travel at the same speed of light in vacuum (3×10^8 m/s).

Atoms of an element absorb energy when heated, by passing its gas or vapour through an electric discharge, the atoms become excited and the electron are promoted to a higher energy level. On falling to their lower energy states lose energy and emit light. The colours are characteristics of the element, for example hydrogen is red, and sodium is orange and so on.

Each line in an emission corresponds to a discrete (separate) wavelength, frequency and energy and thus the pattern of lines in the spectrum of each element is unique (like a finger print) to that element and thus can be used in the qualitative and quantitative identification of elements. Since the wavelength of the emission spectrum tells us what the sample is and the intensity of each wavelength can tell us how much of the element is present.

Since all electromagnetic radiation have the same speed (i.e. speed is constant), then frequency of radiation relating to spectral line of wavelength (λ) is giving by the equation;

$$f = \frac{c}{\lambda}$$

$$f\lambda = c$$

As can be seen from the equation, the wavelength of light increases as the frequency decreases

f (or v) = frequency of radiation express as hertz (Hz) is equivalent to cycle "per second"
c = speed of light (3×10^8 m/s.)
λ = wavelength

The work of Max Planck has also showed that electromagnetic radiation may be regarded as stream of particles called photon. The energy carried by a photon is related to its frequency by the expression;

$E = hf$
but $f = \frac{c}{\lambda}$

Therefore, $E = \frac{hc}{\lambda}$

Where h = Planck's constant with a value of 6.63×10^{-34} j-sec. A single photon carries one quantum of energy.

Example1.1 Calculate the frequency of radiation having a wave length of 6.5×10^{-7}meters.

Solution: $f = \frac{c}{\lambda}$

$c = 3 \times 10^8$m/s
$\lambda = 6.5 \times 10^{-7}$m

$$f = \frac{3 \times 108}{6.5 \times 10{-}7\text{m}} = 4.6 \times 10^{14} \text{ hertz}$$

Example1.2 Calculate the frequency and energy of a photon having a wave length of 1. 7µm.

Solution: $f = \frac{c}{\lambda}$

$c = 3 \times 10^8$m/s
1micrometer = 10^{-6}m
1.7micrometer = 1.7×10^{-6}m

$\lambda = 1.7 \times 10^{-6}$m

$f = \frac{3X\ 10^8}{1.7\ X\ 10^{-6}}$ = 1.77 x 10^{14} hertz

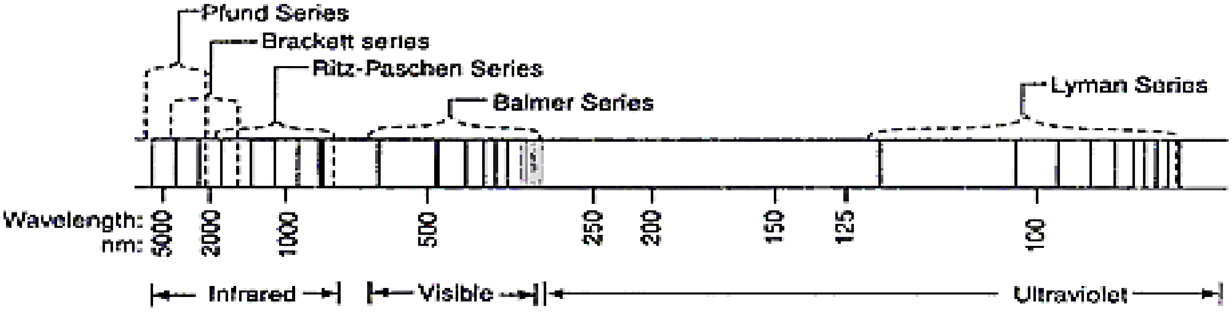
E = hf
f = 1.77 X 10^{14} hertz
h = 6.63 X 10^{-34} j-sec

E = 1.77 X 10^{14} X 6.63 X 10^{-34}
E= 1.174 X10^{-19}j

1.5.3 BOHR'S MODEL OF THE HYDROGEN ATOM

Bohr based his theory of the hydrogen atom on the electromagnetic spectrum that hydrogen produces. At room temperature, hydrogen gas does not emit light but when electricity is passed through a discharge tube containing hydrogen gas, the molecules break down into atoms and the tube glows with a reddish pink light. The emission spectrum reveals that the atom emits radiation in the form of lines. Several series of discrete lines with each corresponding to a different wavelength in the electromagnetic spectrum are observed. Figure 1.7 shows the emission spectrum of atomic hydrogen.

FIGURE 1.6: THE ATOMIC HYDROGEN SPECTRUM, SHOWING THE FIRST FIVE SERIES OF THE SPECTRAL LINES.



It can be observed from the spectrum that the intensity and distance between the lines decreases as the frequency increases after which a continuum is observed. That is the lines in each series become more closely spaced at increase frequency (decreasing wavelength)

The wave length (λ) of the radiation is related to the frequency (f) by the equation

$$\lambda = \frac{c}{f}$$

f (or v) = frequency of radiation express as hertz (Hz) is equivalent to cycle "per second"
c = speed of light (3 x 10^8 m/s.)
λ = wavelength (m)

In spectroscopy, frequency is expressed as wave number (∇) and the wave number is the reciprocal of wave length. $\nabla = \left(\frac{1}{\lambda}\right)$ m^{-1}

Calculating the wavelength of the spectral lines of the hydrogen atom is done by using an expression giving by Rydberg and therefore known as Rydberg equation:

$$\text{Frequency } (\nabla) = \left(\frac{1}{\lambda}\right) = R\left(\frac{1}{n1^2} - \frac{1}{n2^2}\right)$$

Where:
n_1= quantum number corresponding to the initial energy level (Start).
n_2=quantum number corresponding to the final energy level.
R is the Rydberg Ritz constants= 10967876m^{-1}

TABLE1.1 THE FIVE SERIES OF LINES IN THE SPECTRUM OF HYDROGEN ATOM

Order	Series	Converge toward	n_1	n_2
First series	Lyman series.	Ultraviolet region.	**1**	**2,3,4,5,------∞**
Second series	Balmer series	Visible region	**2**	**3,4,5,6,------∞**
Third series	Paschen series	Infrared region	**3**	**4,5,6,7,------∞**
Fourth series	Brackette.	Infrared region	**4**	**5,6,7,8,------∞**
Fifth series	Pfund series	Infrared region	**5**	**6,7,8,9,------∞**

It is required that $n_2 > n_1$ and *n* values are all integral up to infinity.

Example1.3 Calculate the wavelength of the first, second and third lines in the Lymer series

Solution: Frequency $(\nabla) = \left(\frac{1}{\lambda}\right) = R\left(\frac{1}{n1^2} - \frac{1}{n2^2}\right)$

For the Lymer series, $n_1 = 1$ therefore, the first line have $n_2 = 2$, the second line has $n_2 = 3$ and the third line has $n_2 = 4$. Substituting these values into the Rydberg equation we have;

First line: $\left(\frac{1}{\lambda}\right) = R\left(\frac{1}{n1^2} - \frac{1}{n2^2}\right)$

$$\frac{1}{\lambda} = 10967876\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

$$\frac{1}{\lambda} = 10967876\left(\frac{1}{1} - \frac{1}{4}\right)$$

$$\frac{1}{\lambda} = 10967876 \text{ X } 0.75$$

$$\frac{1}{\lambda} = 8225907\text{m}^{-1}$$

$$\lambda = \left(\frac{1}{82259.07525}\right) = 1.216 \text{ X } 10^{-7}\text{m}$$

Second line: $\left(\frac{1}{\lambda}\right) = R\left(\frac{1}{n1^2} - \frac{1}{n2^2}\right)$

$$\frac{1}{\lambda} = 10967876\left(\frac{1}{1^2} - \frac{1}{3^2}\right)$$

$\frac{1}{\lambda} = 10967876\left(\frac{1}{1} - \frac{1}{9}\right)$

$\frac{1}{\lambda} = 10967876 X\ 0.89$

$\frac{1}{\lambda} = 9761409.64 m^{-1}$

$\lambda = \left(\frac{1}{9761409.64}\right) = 1.024\ X\ 10^{-7} m$

Third line: $\left(\frac{1}{\lambda}\right) = R\left(\frac{1}{n1^2} - \frac{1}{n2^2}\right)$

$\frac{1}{\lambda} = 10967876\left(\frac{1}{1^2} - \frac{1}{4^2}\right)$

$\frac{1}{\lambda} = 10967876\left(\frac{1}{1} - \frac{1}{16}\right)$

$\frac{1}{\lambda} = 10967876\left(\frac{15}{16}\right)$

$\frac{1}{\lambda} = 10967876 X\ 0.9375$

$\frac{1}{\lambda} = 10282383.75\ m^{-1}$

$\lambda = \left(\frac{1}{10282383.75}\right) = 9.73\ X\ 10^{-8} m$

Example1.4 Calculate wavelengths and the energy of transition of the second and third lines in the Balmer series of a hydrogen atom. h = Planck's constant = $6.63\ X\ 10^{-34}$ j/sec, c = speed of light 3×10^8 m/s

Solution: Frequency (∇) = $\left(\frac{1}{\lambda}\right) = R\left(\frac{1}{n1^2} - \frac{1}{n2^2}\right)$

For the Balmer series, $n_1 = 2$ therefore, the second line has $n_2 = 4$ and the third line has $n_2 = 5$. Substituting these values into the Rydberg equation we have;

Second line: $\left(\frac{1}{\lambda}\right) = R\left(\frac{1}{n1^2} - \frac{1}{n2^2}\right)$

$\frac{1}{\lambda} = 10967876\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$

$\frac{1}{\lambda} = 10967876\left(\frac{1}{4} - \frac{1}{16}\right)$

$\frac{1}{\lambda} = 10967876\left(\frac{4-1}{16}\right)$

$\frac{1}{\lambda} = 10967876\left(\frac{3}{16}\right)$

$\frac{1}{\lambda} = 10967876\text{X } 0.1875$

$\frac{1}{\lambda} = 2056476.75 \text{ m}^{-1}$

$\lambda = \left(\frac{1}{2056476.75}\right) = 4.863 \text{ X } 10^{-7}\text{m}$

Energy of transition $E = \frac{hC}{\lambda}$

$E = \left(\frac{6.63 \text{ X } 10^{-34} X\ 3X10^{8}}{4.863 \text{ X } 10-7}\right) = 4.01 \text{ x}10^{-19}\text{j}$

Third line: $\left(\frac{1}{\lambda}\right) = R\left(\frac{1}{n1^2} - \frac{1}{n2^2}\right)$

$\frac{1}{\lambda} = 10967876\left(\frac{1}{2^2} - \frac{1}{5^2}\right)$

$\frac{1}{\lambda} = 10967876\left(\frac{1}{4} - \frac{1}{25}\right)$

$\frac{1}{\lambda} = 10967876\left(\frac{25-4}{100}\right)$

$\frac{1}{\lambda} = 10967876\left(\frac{21}{100}\right)$

$\frac{1}{\lambda} = 10967876 \text{ X } 0.21$

$\frac{1}{\lambda} = 2303253.96 \text{ m}^{-1}$

$\lambda = \left(\frac{1}{2303253.96}\right) = 4.34 \text{ X } 10^{-7} \text{ m}$

Energy of transition $E = \frac{hC}{\lambda}$

$E = \left(\frac{6.63 \text{ X } 10^{-34} X\ 3X10^{8}}{4.34 \text{ X } 10-7}\right) = 4.58 \text{ x}10^{-19}\text{j}$

1.5.4 BOHR'S POSTULATE

The summaries of Bohr's postulates are as follow:-

1. The electron moves in circular orbits at different energies around the nucleus.

2. The radius of the orbit is quantized. That is orbits are at definite distances from the nucleus.

3. The electron revolve only in the orbit which have fixed value of energy, thus an electron in an atom can have only definite or discrete value of energy.

4. As long as the electron remains in a particular orbit, it neither loses nor gain energy. These orbits are known as stationary state or ground state.

5. If an electron in the ground state (stationary state) with energy E_i, is given sufficient energy and goes into another allowed orbit, with energy E_f, radiation will be emitted, with energy and frequency. $hf = E_i - E_f$

1.5.5 THE LIMITATIONS OF BOHR'S ATOMIC MODEL:-

1. It can only explain the line spectrum of an atom with one electron, such as, H atom, He^+, Li^{2+}, Be^{3+} etc. but unable to explain the line spectra of atoms with more than one electron.

2. It cannot explain the splitting of spectra lines in magnetic field known as ZEEMAN EFFECT.

3. Bohr's model is unable to explain the splitting of spectra lines in an electric field and the phenomenon is known as STARK EFFECT.

4. Bohr's model is also unable to explain Heisenberg's uncertainty principles.

1.6 SUBATOMIC PARTICLES

Research studies conducted by Thompson, Chadwick, Rutherford and others reveals that the atom consist of smaller particles. Also, scientist have been able to discover hundreds of subatomic particles, however three of these particles; the Proton, Neutron and Electron are of interest to the chemist.

1.6.1 THE NUCLEUS

The nucleus is the center of the atom and although the size is small compared to the size of the electron, it accounts for 99.9% the mass of an atom because the proton and neutron are found in the nucleons. The proton and neutron are called nucleon because they are found in the nucleus of an atom.

1.6.2 PROTONS, NEUTRON AND ELECTRON

Protons are found in the nucleus of an atom, a proton has a charge of +1, and it is about 1840 times heavier than an electron. Every atom has a specific proton number which tells us the name of the element. An atom chemical identity is determined by its number of protons. A proton is what is left after hydrogen atom losses its single electron.

The neutrons are found in the nucleus. It carries no charge i.e. it is a neutral particle. A neutron like the proton is considered to have a mass of l amu. The neutrons do not take part in chemical reaction under normal condition.

Electrons are found outside the nucleus, an electron has a charge of -1. The mass of an electron is negligible. An electron is approximately $\frac{1}{1840}$ the mass of the proton.

TABLE 1.2: THE SUBATOMIC PARTICLES

Particle	Symbol	Mass (g)	Relative electrical charge	Approximate relative mass (a m u)
Electron	e^-	9.091×10^{-28}	1-	$\frac{1}{1840}$
Proton	p^+	1.67252×10^{-24}	1+	1
Neutron	n^0	1.67495×10^{-24}	0	1

Note: amu is atomic mass unit

Atoms of an element are electrically neutral, that is they have equal number of protons and electrons. However, an atom can lose or gain electrons to become an ion. If it gains electron, it becomes negatively charged and is called an anion. If it losses an electron it becomes positively charged and is called a cation.

1.7 ATOMIC NUMBER AND MASS NUMBER

The proton number is referred to as the atomic number. The atomic number is the whole number that increases across each row of the periodic table from left to right. The sum total of the number of protons and neutrons in the nucleus of an atom is the mass number. If an element X is represented thus: ${}^{A}_{Z}X$.

A = Mass number
Z = Atomic number. Therefore
A-Z = Neutron number

1.8 THE RELATIVE ATOMIC MASS

The mass number of an atom cannot be weighed directly because it is very small; however experimental methods are used to determine the mass of one atom relative to another.

The internationally agreed standard is an atom of carbon-12. This is an isotope of carbon with six protons and six neutrons, having a mass of 12 atomic mass unit (amu). Based on this standard, 1amu is exactly equal to one- twelfth the mass of one carbon-12 atom ($\frac{1}{12th}$, the mass of carbon 12). It is because the actual masses of the proton and neutron are very small that for practical purpose, the atomic mass unit (amu) is used.

Mass of one carbon-12 atom = 12 atomic mass unit therefore,

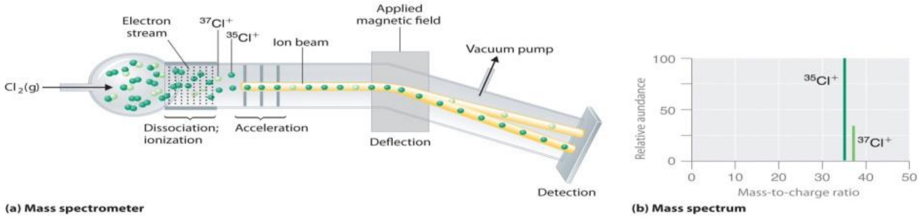
$$1 \text{ atomic mass unit} = \frac{\text{mass of one carbon}-12 \text{ atom}}{12}$$

The atomic mass unit is related to the number of protons and neutrons. It has nearly the same value as the mass number.

1.9 THE MASS SPECTROMETER

The process of producing and analysing spectra is called spectroscopy and the instrument for analysing the spectra is called a spectrometer. The mass spectrometer is an instrument designed to separate atoms of slightly different masses. First the sample to be separated is vapourized so as to allow it to move through the machine. The vapourized sample is then hit with high energy electrons, knocking off one or more electrons thus converting the atoms into positively charged ions. The ions are accelerated to a higher speed by an electric and magnetic field; also because ions are charged particles they can be deflected by an electric and magnetic field. The degree of deflection is thus dependent on the mass to charge ratio. The masses of each particle are determined by measuring the exact strength of the field and the degree of deflection of the particles in the mass spectrometer. Different elements have different mass which corresponds to a different deflection. Figure 1.7 shows the mass spectrometer

FIGURE 1.7: THE MASS SPECTROMETER



(a) Mass spectrometer **(b) Mass spectrum**

1.10 MASS SPECTRA AND ISOTOPES

The proton number (atomic number) tells us what an element is. Every element has its specific number of proton; however the number of neutrons and electrons may vary. For example carbon 12 has a proton number of 6 and a neutron number of 6 but carbon 14 has a proton number of 6 but a neutron number of 8 with a mass number of 14. This phenomenon is known as isotopy. Carbon 12 and carbon 14 are known as isotopes of carbon. Thus isotopy is defined as a phenomenon in which an element has the same number of proton but different number of neutrons. In other words isotopy is the existence of an element with the same atomic number but different mass number.

If an element X is represented thus: $^{A}_{Z}X$

A = the mass number (values are different for isotopes)
Z = the atomic number. (Values are same for isotopes) Therefore,
A-Z = Neutron number

Majority of elements found in nature are a mixture of isotopes. For example hydrogen has three isotopes namely: hydrogen $^{1}_{1}H$, deuterium $^{2}_{1}H$ and tritium $^{3}_{1}H$, which is unstable and disintegrates. Almost all hydrogen exists as hydrogen with no neutron. Also, Bromine exists in nature as ${}^{79}_{35}\text{Br}$ and bromine ${}^{81}_{35}\text{Br}$. A mass spectrometer is used to find out the masses of these isotopes using the carbon -12 scale and the proportion of each isotope. Any naturally occurring sample of bromine contains approximately 50.52% of ${}^{79}_{35}\text{Br}$, and 49.48% of ${}^{81}_{35}\text{Br}$

1.12 CALCULATING RELATIVE ATOMIC MASSES FROM SPECTRA

The mass spectrum of an element will show the presence of isotopes. From the relative heights of the peaks, we can work out the relative atomic mass of the element.

Example 4.3: Calculate the relative atomic mass of bromine from the mass spectra of bromine

Solution: Relative abundance of ${}^{79}_{35}\text{Br}$ = 50.52%
Relative abundance of ${}^{81}_{35}\text{Br}$ = 49.48%

$$\text{Relative atomic mass} = \frac{79\ x\ 50.52}{100} + \frac{81\ x\ 49.48}{100}$$

$$= \frac{3991.08}{100} + \frac{4007.88}{100}$$

$$= 39.9108 + 40.0788$$

$$= 79.9896\ 9 \approx 80$$

1.13 USES OF ISOTOPES

Isotopes have a wide range of uses and it has been used in various aspects of life and nature.

Medicine: Isotopes have been used in the field of medicine as tracers; these are substances containing a radioactive Isotope of an atom. These tracers are taken up by the organs to be monitored. For example, Iodine – 131 has been used to study the thyroid function.

Biology: Phosphorus – 32 has been used to study intake of nutrients in plants.

Power Generation: The fission of uranium 235 and the fusion of H – 3 have been used to create-explosives.

History and Archaeology: Carbon – 1.4 has been used by historians and archaeologist in determining the ages of ancient remains, such as rocks, bones, plants and so on. This technique is known as radiocarbon dating.

PRACTICE QUESTIONS

1. Refute Dalton's Theory of "indivisible" atom using J.J. Thompson's and Rutherford Model of the atom.

2. A line spectrum in the hydrogen atom has a wavelength corresponding to 4.57×10^{-7}m. Calculate the frequency and the energy associated with this transition.

3. Calculate the energy of a photon of radiation having a frequency of 3.54×10^{14} hertz.

4. Differentiate between the following;

   i. The spectra line of white light and the spectral lines of elements.
   ii. Ground state of an electron and the excited state

5. Give reasons for the following:
   (i) The nucleus accounts for the mass of an atom.
   (ii) The number of protons tells us the name of the element.
   (iii) Atomic masses unlike the atomic numbers are not whole numbers.

6. (a) Complete the table below:

Atom or ion of element	**A**	**B**	**C**	**D**	**E**
Mass number	10	-	39	-	19
Number of proton	5	7	-	20	9
Number of neutron	-	7	20	20	-

7. What is the atomic mass of chlorine, if $^{35}_{17}Cl$ has a relative abundance of 75% and $^{37}_{17}Cl$ has a relative abundance of 25%

8. Calculate the wavelength the frequency and energy of the lines in the Balmer series when n_2 = 3 and 5

9. The wave number of a line in the Lyman series is 10282383.75m^{-1}

i. Calculate the frequency and energy of the series

iii. Which line in the series is it?

Assume that the atomic mass of an element(X) is 25.77. X has three isotopes; 74.7% of $^{26}_{13}$X, 24.7% of $^{a}_{13}$X and 0.6% of $^{28}_{13}$X . Calculate for the value of a

CHAPTER 2

THE PERIODIC TABLE

2.1 HISTORY OF THE PERIODIC TABLE

The first classification of elements that became the basis of the present day classification was done by a Russian chemist called Dimitri Medelev. In 1869 Mendeleev arranged the elements in increasing atomic weight to form a periodic table. He pointed out that element with similar properties kept reoccurring at regular intervals or periods, ignoring the fact that some elements do not follow that order. Mendeleev placed elements with similar properties in horizontal rows, he called group, while the periods were vertically arranged. He equally left space in his periodic table for elements that were not discovered yet. Apart from spaces left in Mendeleev periodic table, his arrangement is different from the modern arrangement of the periodic table.

From his work, Mendeleev proposed a periodic law which states that the properties of the elements and their compounds vary in a periodic way according to their atomic weight Mendeleev's work was based on the fact that he believed that the only property of an element which does not change in cause of a chemical combination was its atomic weight. But this is not true, as it was later discovered from Moseley' s work that the atomic number was the only property in an element that does not change in cause of a chemical combination.

2.3 MODERN PERIODIC LAW

Henry Moseley was able to reveal the atomic numbers of several elements from his study of X-ray emitted by elements in a discharge tube. Based on his new discovery and the inconsistencies in the Mendeleev periodic table, Moseley suggested that the elements should be arranged in order of increasing atomic number instead of atomic mass in the periodic table. Moseley also proposed the modern periodic law, which states that the properties of the elements vary in a periodic way according to their atomic numbers.

2.3 INFORMATION FORM THE PERIOD TABLE

In the modern periodic table, classification of elements gives.

1. Elements with similar physical and chemical properties are placed on the same vertical row called group or family
2. Elements are placed in horizontal row called periods in increasing atomic numbers from left where the metals are located to the right with the non-metals
3. The table show the symbol of each element, its atomic number its atomic mass and in some occasion the element's electronic configuration
4. The table relates the electronic configuration with the electronic structure and properties of the element.
5. It shows at a glance the exact period and group an element belongs.
6. The periodic table is divided into 8 groups of elements and 7 periods, with the transition metals between the group 2 and 3 elements.
7. The periodic table shows the division of elements into metals on the left side and non-metals on the right hand side of the table.

TABLE 2.1VALENCE SHELL ELECTRONIC CONFIGURATIONS FOR EACH GROUP

H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca						
s^1	s^2	s^2p^1	s^2p^2	s^2p^3	s^2p^4	s^2p^5	s^2p^6

2.4 REACTIVITY TREND IN THE PERIODIC TABLE

With regards to chemical reactivity, a reaction occurs when element loss, gain or share their valence electrons with another element or specie. The ease with which elements loss, gain or share electrons in a chemical reaction measure their reactivity.

Reactivity increases down a metallic group as successive members of the same group increases by one additional energy level of electrons. Since metals react by loss of electrons, the metals down the metallic group lose electrons easier than those on top. Therefore lithium is less reactive than sodium and sodium less reactive than potassium.

On the other hand, non-metals react by gain of electrons, a process called electronegativity. The more electronegative element is one which gains electrons more easily and is more reactive. Reactivity (electronegativity) reduces down the group as successive members of the group increases by one additional energy level of electrons and an increased distance between the valence electrons and the positive nuclear pull. This makes it more difficult for the positive nucleus to attract neighboring electrons into the valence energy level, thereby reducing reactivity as we go down the group. Using the group seven elements as an illustration, fluorine is more reactive followed by chlorine, bromine than iodine.

The period cuts across all the groups in the periodic table. As one moves across a particular period from left to right, there is increase electronegativity of the element. Since the element advance toward elements with more electronegative properties

2.5 GROUP OF ELEMENTS

In going down a particular group, it is observed that the elements have similar chemical properties. This property is directly related to the electronic configuration as each group of elements has the same number of valence electrons.

2.5.1 GROUP 1 ELEMENT

They are the most electropositive metals. They have one valence electron which they loss in cause of a chemical reaction.

The members are generally referred to as alkali metals because their hydroxides are soluble. They react vigorously with cold water, forming an alkali solution and liberating hydrogen gas.

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

2.5.2 GROUP 2 ELEMENTS

The Group 2 elements are also called the alkaline earth metals. They are less electropositive than the group one metals.

They react by loss of two electrons thus divalent.
They react with cold water mildly, given a basic solution that is less soluble than the group 1 elements.

$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$

2.5.3 GROUP 3 ELEMENTS

They are metals which are less electropositive than the Group 1 and 2 elements. They react by loss of their three valence electrons, thus they are trivalent.

2.5.4 GROUP 4 ELEMENTS

They exhibit non-metallic properties and they are tetravalent because they have four valence electrons. They form covalent bond by sharing of electrons. There is a gradual change from non-metallic properties to metallic properties as one move down the group. They exhibit two oxidation state which are +2 and + 4 oxidation state. The +2 oxidation state increases while the +4 oxidation state decreases on going down the group.

2.5.5 GROUP 5 ELEMENTS

They are non-metals and show two common valences of 3 and 5. They react by gain of electrons. Their oxides combine with water to form acid.

2.5.6 GROUP 6 ELEMENTS

Element in group 6 are non-metals. There are electron acceptors and are oxidizing in nature. They have six valence electrons and require two electrons to reach the octet electron configuration

2.5.7 GROUP 7 ELEMENTS

The elements in Group 7 are known as the halogen which means salt former. They are the most reactive non-metals known. They are so reactive that they cannot exist free in nature. They react by gain of one electron.

2.5.8 GROUP 8 ELEMENTS

These elements are also called the noble gases. They are unreactive.

2.5.9 TRANSITION ELEMENTS/METALS

These elements occupy the space between the Group 2 and Group 3 elements on the fourth and fifth period. They are the element with an incomplete d-orbital.

Also we have the special transition metals on the sixth and seventh periods.

1. The lanthanides series; these are the fourteen elements after lanthanum with atomic number from 58-71 in the sixth periods. Members successively add one electron to the 4f sub shell.
2. The actinides series: These are the fourteen elements after actinium with atomic number from 90-103 in the seventh, periods. Members successively add one electron to the 5f sub shell.

2.6 PERIODIC PROPERTIES IN THE PERIODIC TABLE

The period properties in the periodic table are all related to the forces of attraction between the positive nucleus and the negative electrons. These properties include.

1. Ionization energy
2. Electronegativity
3. Electron affinity
4. Atomic radius
5. Ionic radius

2.6.1. Ionizations energy

This is the energy required to remove the most loosely held valence electron or outermost energy level electron of an atom in the gas phase, to form ions. The ionization energy increases across the period and decreases down the group. This is because as the group decend, the energy level increases successively, meaning an increased distanced between the positive nucleus and the outer energy level electrons. The resultant effect is reduced effective nuclear pull on the outermost energy level electrons, making the valence electrons easier to remove with reduced energy.

Ionization energy increases along a period as we go from left to right. Along the period, the energy level remains the same as electrons are added one after another. This causes shrinkage in size as the outer energy level electrons becomes more attracted to the positive nucleus, making it more difficult for electrons to be removed. If the valence electrons become more difficult to remove, it then means more energy is required (ionization energy) for electron removal. The table2.2 below summarizes changes in the first ionization energies.

2.6.2. ELECTRONEGATIVITY

This is the measure of the ability of an atom to attract electrons when it is in a molecule. In another word, when two atoms are covalently bonded, sharing a pair of electrons, the atom that has the ability to attract more of the shared electron pairs is the more electronegative.

Electronegativity increase across the period from left to right. This is because electrons are added to a constant energy level one after another, with no screening or shielding effect. This causes shrinkage in size as the valence electrons become more attracted to the positive nuclear pull, therefore increasing the ability of the atom to attract electrons. As an illustration, in a bond between carbon and oxygen, oxygen will be more able to attract the shared pair of electron carbon.

Electronegativity decreases down the group as repeatedly energy level of electrons is added. The inner energy levels then shield the outer energy level from the attractive pull of the positive nucleus, thus making it difficult for the atom to attract a shared pair of electrons.

Table 2.3 below summarizes the electronegativity values given on the Pauling's scale using a value of 4.0 for fluorine.

TABLE 2.2SUMMARY OF FIRST IONIZATION ENERGY DOWN THE GROUPS AND ACROSS PERIODS

H 1.3							He 2.4
Li 0.5	Be 0.9	B 0.8	C 1.1	N 1.4	O 1.5	F 1.7	Ne 2.2
Na 0.5	Mg 0.7	Al 0.6	Si 0.8	P 1.0	S 1.0	Cl 1.3	Ar 1.5
K 0.4	Ca 0.6						

TABLE 2.3SUMMARIES OF ELECTRONEGATIVITY TRENDS, DOWN THE GROUP AND ACROSS THE PERIOD

H 2.2							He
Li 1.0	Be 1.5	B 2.0	C 2.6	N 3.1	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2	Al 1.5	Si 1.9	P 2.2	S 2.6	Cl 3.2	Ar
K 0.8	Ca 1.0						

Note that electronegativity values are not assigned to the noble gases because they commonly donot share electrons

2.6.3. ELECTRON AFFINITY

This is the energy released when an electron is added to a neutral atom in gaseous state to form gaseous ion.

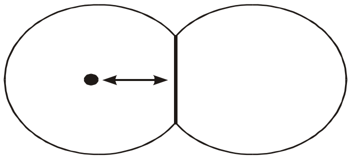
Electron affinity decreases down the group as it become more difficult for electrons to add to an atom. So, less energy will be released in the cause of the reaction as more energy will be used up.

Electron affinity increases with increase in atomic number along the period as the ease for an electron to add to a neutral atom becomes less and less difficult. Therefore using less energy for the reaction and releasing more energy.

2.3.4 ATOMIC RADIUS

An atom does not have a definite diameter; radius, **circumference** or volume because of its wave-like nature. Therefore, its size expressed as its radius is done in three different ways, all in unit of nanometer (nm)

- **i. Covalent atomic radius**: This is the distance from the nucleus to the valence shell when the sharing of electrons covalently bonds the atom. When the covalent bond involves identical atoms e.g. $H_2$and O_2, the atomic radius is half the distance between the two nuclei



- **ii. Vander Waals radius:** This is half the distance between two nuclei when measured from their closest point, when no bond is formed.

- **iii. Atomic radius of metals:** This is the distance between nuclei of atom when arranged in a metal-like crystalline structure.

Atomic radius decrease across a period with increasing atomic number from left to right while it increases down the group. Table2.4 below give a summary of the trend in atomic radius.

TABLE 2.4ATOMIC RADIUS TREND DOWN THE GROUP AND ACROSS THE PERIOD

H 0.030							He
Li 0.123	Be 0.089	B 0.088	C 0.077	N 0.070	O 0.064	F 0.064	Ne
Na 0.157	Mg 0.136	Al 0.125	Si 0.117	P 0.110	S 0.104	Cl 0.099	Ar
K 0.203	Ca 0.174						

Atomic radius values are not given to the noble gases because they do not form covalent bonds.

2.3.5. IONIC RADIUS

Just like the atoms, ions also have a wave like property which makes their size difficult to ascertain. Ions are formed when atom gain or lose electron(s). The ionic radius is the effective distance between the nucleus of the ions and its outer energy level. Usually, ions have eight electrons in the outer energy level.

Metals react by the loss of all their valence electrons, forming positive ions called cation since all the outer energy level electrons are lost the energy level is lost as well, causing the radius of the ion to become smaller that the initial atom. Also, greater positive change exerts a greater attractive force on the electrons, thus causing shrinkage in size

Non-metals on the other hand, react by gain of electrons forming negative ions called anion. The radius of the ion formed becomes bigger than the initial atom. This is because the electron gained fill up the energy level, resulting to a greater negative charge. This reduces the attractive pull of the positive nucleus on the outer energy level electrons. Ionic radius just like atomic radius increases down the group. But it reduces across the metallic period while it increases across the non-metallic period.

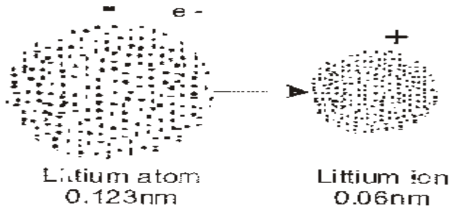


TABLE 2.5 SUMMARY OF THE IONIC RADIUS TREND DOWN THE GROUP AND ACROSS THE PERIOD.

H 0.021							He
Li 0.060	Be 0.031	B 0.020	C 0.015	N 0.017	O 0.140	F 0.136	Ne
Na 0.095	Mg 0.065	Al 0.050	Si 0.041	P 0.212	S 0.184	Cl 0.181	Ar
K 0.133	Ca 0.099						

→ **Reduces** ← **Increases**

Generally,

1. The ionic radii of positive ions are smaller than their corresponding atomic radii because increase in positive charge will have a greater nuclear attractive pull on the valence electrons, causing shrinkage in size.
2 The ionic radii of negative ions are bigger than their corresponding atomic radii because increase in negative charge will have a reduced nuclear attractive pull on the valence electrons. Also the increased electrons will have repelling effect on each other causing

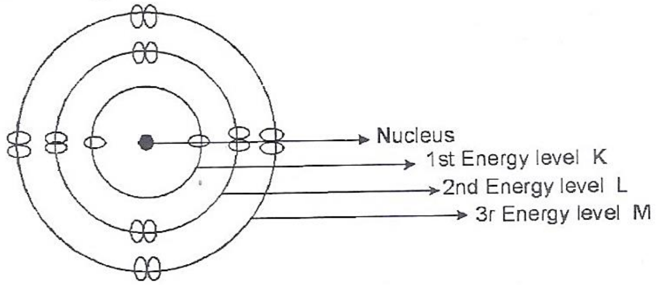
increase in size.

3 For Isoelectronic series (ions and atoms with the same number of electrons), ionic radius decreases as atomic number increase.

ELECTRONIC CONFIGURATION

The electron configuration of an atom is the representation of the arrangement of electrons distributed among the orbital shells and subshells in its ground state. The physical and chemical properties of elements are related to their unique electronic configurations. The valence electrons (electrons in the outermost shell) are the determining factor for the unique chemistry of the element. Electrons fill up the orbital with lower energy level first before occupying orbitals of higher energy level. Also, the first orbital or shell will accommodate a maximum of two electrons after which subsequent orbitals would accommodate a maximum of eight electrons each. Figure 2.1 shows the electronic configuration of argon with 18 electrons However, because of some shortcomings of the Bohr's model, the quantum mechanical model is now more valid. The will be treated in the next chapter.

Example 2.1. Do the electronic configuration of argon (atomic number =18).



PRACTICE QUESTIONS

1 a. How is Mendeleev periodic law different from the modern periodic law

b. Mention three information you can get from the periodic table

2. Define the follow and explain their trend down the group and across the period in the periodic table;

   i. Electronegativity
   ii. Atomic radius
   iii. Ionisation energy

3Which noble gas and halogen belong to the third period?

4 List the following atoms in order of increasing electronegativity; K, Al, S, CI, and F

5. List the following in order of reactivity Na, K, Be, and Ca.

6. In the following bonded pairs of atoms, state in each case the atom that attracts more of bond to itself (a) H: Br (b) Na:CI (c) Mg and Mg^{2}+ (d) CI and CI- (e) K and Ca

7. Identify the atom or ion with the larger radius in each of the following pair

(a) S and O
(b) H and Li
(c) Mg and Mg^{2}
(d) Cl and Cl^{-+}
(e) K and Ca

8. Place the following isoelectronic species in order of increasing atomic radii and explain. Na+, $Mg^{2+,}$ Al^{3+}, $Si^{4+}N^{3-}$, $0^{2-.}$ F^{-}, Ne

9. Where in the periodic table of the first 20 elements would you expect to find;

(a) The most reactive metals

(b). The most reactive nonmetals

(c). The least reactive metals

(d) The least reactive nonmetals

CHAPTER 3

THE WAVE MECHANICAL MODEL

The wave mechanical model (also called the quantum mechanical model) involves the use of mathematical equation to describe the arrangement and motion of electrons in atoms.

According to Albert Einstein, light has both wave and particle like character.That is, matter has a dual nature. A French physicist took up the idea that very small particles such as electrons might also display wave properties.

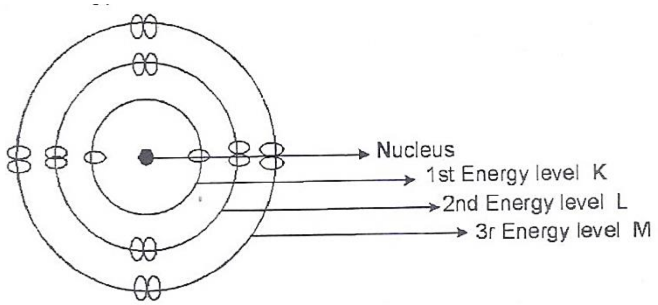
In 1926, the Austrian Physicist – Erwin Schrodinger formulated wave-equation to describe the location and energy of electrons. He incorporated the Bohr, Louis de Broglie and the Heisenberg uncertainty principle concept and developed the wave mechanical model (Quantum mechanical model). Unlike the Bohr model, the wave mechanical model does not propose that electrons are localized in fixed orbits. In fact it does not define the exact location (orbit) of an electron around a nucleus. It describes the probability of finding can electron in a certain position at any time. If we assume a cloud of electron round the nucleus, the cloud would be most dense where we have a greater probability of finding an electron. Such regions where we could find an electron is called an “orbital”. The electron cloud defines the shape of the orbital.

3.1 ENERGY LEVELS OF AN ATOM

Electrons are arranged in energy level. As we have already known, electrons do not move in fixed path, the Bohr orbit should not be confused with orbitals.

Electrons with the lowest energy level are found nearer the nucleus while electrons with higher energy are successively found further away from the nucleus depending on the energy level of the electron. Each energy level referred to as orbitals have a maximum number of electrons they can hold, the first energy level which is closest to the nucleus can hold not more than two electrons. Let us consider the illustration below.

Figure 3.1: Energy level of an atom



3.2 QUANTUM NUMBERS

Quantum numbers are numbers used to completely describe the properties of the electrons around a nucleus. These properties can be described in terms of four quantum numbers. There are:

Principal quantum number: (n)

This describes the distance of an electron from the nucleus. The number is the same with that given by Bohr. It describes the size and energy of the orbital. Principal quantum number (n) is assigned values of integral numbers ranging from n = l, 2, 3, 4 and so on to∞. The number of electrons that can occupy a given energy level is given by $2n^2$. Orbitals with the same n-value are said to belong to the same energy level or the same shell.

Azimuthal or subsidiary or angular momentum quantum number: (C**)**.

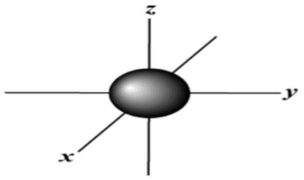
This number determines the shape of the subshells. The principal quantum energy shell is divided into sub energy shells. Each sub shell corresponds to several electron cloud space. The energy of the subshells increases as the value of increases. Azimuthal quantum number has integral values ranging from C = 0, 1 2, 3 to n-1. The subshells are designated as s, p, d, f and so on. The subshells all have different energies. The energy of the subshells are in this order s<p<d<f.

Table 3.1Summary of subshells, number of orbitals, shape of orbitals and their maximum number of electrons

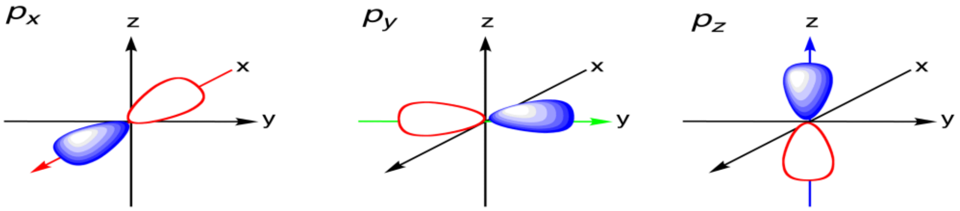
Subshell	Number of Orbitals	Shape of Orbitals	Maximum No. of Electrons
S	1	Spherical	2
P	3	Dumbbell	6
D	5	Double Dumbbell	10
F	7	Complex	14

Figure 3.2: **Shape of Orbitals**

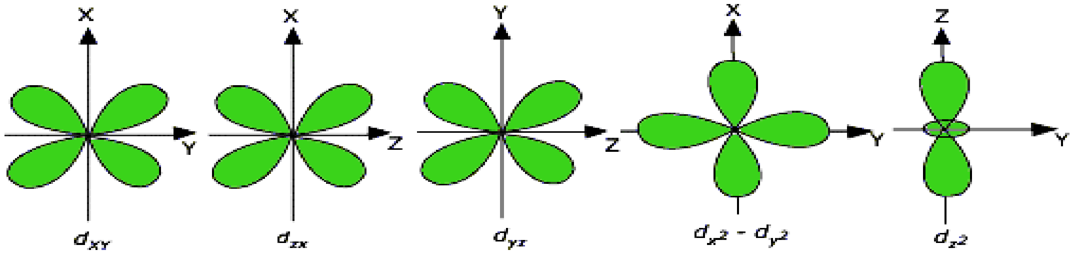
(a) The one s-orbitals



(b) The three p-orbitals



(c) The five d-orbitals



Magnetic Quantum Number (m): Magnetic Quantum Number (m): This specifies the permitted orientation in space for an electron cloud. It gives the number of orbital types in an energy level. And it has integral values of m = -ℓ --- 0 --- +ℓ. That is, the number of orbital in a sub shell is given by 2ℓ + l.

When ℓ = 0, m = 0, which means that there is only one orientation, which is a spherical distribution (s-sub level or s-orbital).When ℓ = I, then m = -l, 0, + 1, that is there are three permitted orientation. The axes of these dumb-bells shaped orbital lie at 90° to each other. They are designated as P_x, P_y and P_z as shown in Fig. 3.2b, corresponding to major charge concentration along each of the three Cartesian coordinates.

Table 3.2: Relationship between Quantum Numbers and Atomic orbital

Principal Quantum No. (n)	Subsidiary Quantum No. (n)	Number of Sublevels	Number of Orbital m = 2ℓ + 1	Atomic Orbital	Number of Electron
1	0	1	1	1s	2
2	0 1	2	1 3	2s 2p	8
3	0 1 2	3	1 3 5	3s 3p 3d	18
4	0 1 2 3	4	1 3 5 7	4s 4p 4d 4f	32

Table 3.2 shows the first four energy levels in the quantum mechanical model of the atom.

Spin quantum number(s): This does not arise from Schrodinger equation but comes from other consideration. It gives the direction of electron spin on its axis. It has two values: + $\frac{1}{2}$ and - $\frac{1}{2}$. This means that an electron in a particular orbital has two permitted orientation of spin on its own axis, opposite to one another s = + $\frac{1}{2}$ (for electron spinning in clockwise direction) and s = - $\frac{1}{2}$ (for anticlockwise direction).

All the orbitals in a particular sub-shell are of equal energy. As seen in Figure 5.3. The energy gap between successive shells gets smaller as the principal quantum number increases. This explains why the 3d orbital which is an orbital in an inner shell is at a higher energy level than the 4s orbital in the next shell further away from the nucleus but lower than the 4p orbitals.

Example 3.1: How many orbitals do we have in the second principal level n = 2?

Solution: The second principal energy level has 2 sub-shells: 2s and 2p orbitals. The 2s sub-shell has one orbital, and the 2p sub-shell has 3 orbita1's so in all, we have four orbitals in the second principal level.

Can you write the number of orbitals in:
- (i) The fourth energy level n = 4
- (ii) The 4s orbital

3.3 ELECTRONIC CONFIGURATION OF ELEMENTS

Electron configuration of an element is the arrangement of electrons in its atomic orbital when it is at the ground state. In order to understand how electrons are arranged in orbitals. It is necessary to understand some basic principles. These principles are discussed below;

3.3.1 HEISENBERG UNCERTAINTY PRINCIPLE

This principle states that it is impossible to know simultaneously at the same time the exact position and momentum of small particles like electrons.

3.3.2 PAULI'S EXCLUSION PRINCIPLE

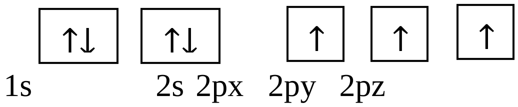
This principle states that in an atom of many electrons, no two electrons in that atom can behave identically or have the same set of all the four quantum numbers. That is, even if the principal quantum number, subsidiary quantum number and the magnetic quantum number, are identical. The spin quantum number must have opposite spin on its axis. That is the spin must be clockwise and anticlockwise.

This is used to represent an electron and its direction of spin $\boxed{\uparrow}$

While an orbital containing an electron pair is represented as $\boxed{\uparrow\downarrow}$

3.3.3 HUND'S RULE

This states that electrons will singly occupy orbitals of equal energy (degenerate orbitals) until all the orbitals contain one electron each with parallel spins before pairing with opposite spin.



3.3.4 AUFBAU'S PRINCIPLE OR BUILDING - UP PRINCIPLE

The Aufbau's principle is:

1. Electrons go into orbital with the lowest energy before occupying higher energy level.

2. The Pauli's exclusion principle (two versions).
   (a) It is impossible for two electrons in the same orbital to have the same or identical spin quantum number.
   (b) An orbital can contain a maximum of two electrons.
3. Electrons will fill a set of degenerate orbital singly with parallel spin before pairing with opposite spin.

Finally, electron structures are shown by writing down the list of orbitals, with number of electrons in each orbital shown as a superscript e.g. the 9 electrons in a fluorine atom can be arranged in the order $1s^2\ 2s^2\ 2p^5$. This order is referred to as electronic configuration of F.

By following the arrows in figure 3.4 below, it will help you work out the correct order of orbitals in the electron structures and thus write the electronic configuration of elements once you know the atomic number

Figure 3.4: Order of orbitals in the electron structures.

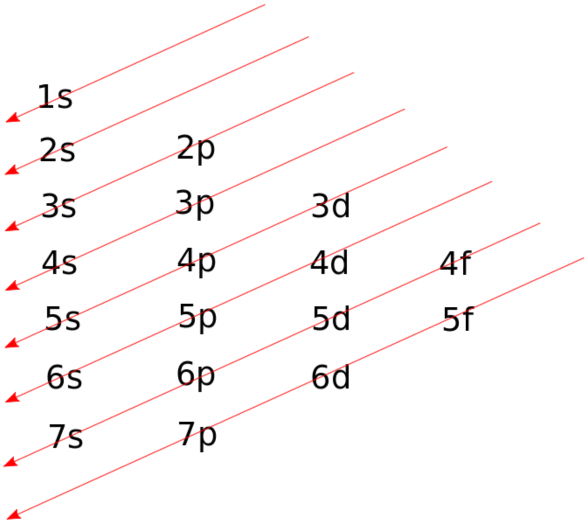


Table 3.3: The electronic configuration of the first 10 elements of the periodic table

Atomic	Element	Electronic configuration
1	H	$1s^1$
2	He	$1s^2$
3	Li	$1s^2\ 2s^1$
4	Be	$1s^2\ 2s^2$
5	B	$1s^2\ 2s^2\ 2p^1$

6	C	$1s^2\ 2s^2\ 2p^2$
7	N	$1s^2\ 2s^2\ 2p^3$
8	O	$1s^2\ 2s^2\ 2p^4$
9	F	$1s^2\ 2s^2\ 2p^5$
10	Ne	$1s^2\ 2s^2\ 2p^6$

From the table above, Helium and Neon both have their outermost *s* orbital and *p* orbital filled. This makes them very stable and they are referred to as noble gases. The next element sodium begins the filling of the next energy level n = 3.

The electronic configuration of Neon $1s^2\ 2s^2 2p^6$can also be represented in a box diagram as:

1s	2s		2p	
↑↓	↑↓	↑↓	↑↓	↑↓

In Neon all the orbitals are filled.

Sodium has atomic number of 11, so the electronic configuration is written as $ls^2\ 2s^3\ 2p^6\ 3s^1$ The 3s orbital has one unpaired electron.

Magnesium has atomic number of 12, its electronic configuration is written as $ls^2\ 2s^2\ 2p^6\ 3s^2$

Aluminum has atomic number of 13, its electronic configuration is written as $ls^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

Silicon is the next with atomic number of 14, its electronic configuration is written as $ls^2\ 2s^2\ 2p^6\ 3s^2 3p^2$

One electron is added to the 3p orbitals as atomic number of the elements increases until the 3p orbitals of Argon with atomic number 18 is completely filled. The next element is potassium, the electrons do not enter the 3d orbital instead it goes into the 4s orbital because the energy of the 3d orbital is slightly higher than that of the 4s orbital but lower than the 4p orbital. It then follows that the 4s orbital has to be completely filled before the 3d orbitals are filled. It then follows that the electronic configuration of K is written as $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$

Perfectly half-filled or completely filled orbitals confer stability on atoms. Since atoms strive towards stability, an atom like Cr would prefer to have a half filled 3d orbital and the electronic configuration which is supposed to be $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^4$ then becomes $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$

3.5 HYBRIDIZATION OF ATOMIC ORBITAL

Some atoms form covalent bonds that are different from what their electronic configuration suggests. When these bonds are formed between atoms, there is a change in the nature of the Atomic Orbitals in each atom. This peculiar bonding character can be explained with the concept called **hybridization**. It involves combining a number of orbitals to create a set of an equal number of new orbitals, where each of the new hybrid orbitals has properties which are an average of those of the orbitals from which they were created.

Thus, hybridization is a process whereby the orbitals of an atom (usually a central atom) interact to get a set of equivalent orbital called the HYBRID ORBITAL. Hybridization can also be defined as the mixing or overlapping of orbital of an atom to give a set of equivalent orbitals known as hybrid orbital. The hybrid orbital shows characteristics of both atomic orbitals.

A number of different types of hybrid orbitals are known for elements. These hybrid orbitals and the shape of the resulting molecules are given in table 3.4 below. However, only a few of the hybrid orbitals will be discussed here.

Table 3.4: hybrid orbitals types in coordination compounds

Atomic Orbitals	Hybrid Type	Numbers of Orbitals	Structure
Sp	sp	2	Linear
Sd	sd	2	Linear
spp	sp^2	3	Trigonal planar
sppp	sp^3	4	Tetrahedral
dspp	dsp^2	4	Square planar
dsppp	dsp^3	5	Trigonal bipyramid
sppdd	sp^2d^2	5	Square-base bipyramid
ddsppp	d^2sp^3	6	Octahedral
spppdd	sp^3d^2	6	Octahedral

3.5.1 sp-HYBRIDISATION

In considering the shape of a hybridized orbital, the electronic configuration of the central atom must be known. Let's consider $BeCl_2$; the central atom is Be, and its ground state electronic configuration is;

Be = $1s^2$ $2s^2$

Beryllium has to be excited to generate orbitals to accommodate the two chlorine atoms. Thus if energy is supplied to raise one of the 2s electrons to a higher energy level the excited state electronic configuration of Be will be;

Be* = $1s^2$ $2s^1$ $2p^1$

More specifically, the electronic configuration of the excited beryllium atom can be written as;

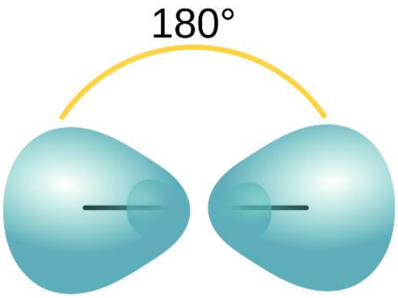
$$\text{Be}^* = \underset{1s^2}{\uparrow\downarrow} \quad \underset{2s^1}{\uparrow} \quad \underset{2px^1\ 2py\ 2pz}{\uparrow}$$

And the excited state valence shell electronic configuration is;

Be* = ↑ ↑
$2s^1$ $2px^1$ 2py 2pz

The two chlorine atoms will be accommodated in the 2s and 2px orbitals created as a result of the excitation. One would expect that one chlorine atom would occupy the $2s^1$ orbital while the other would occupy $2px^1$ orbital, making two non-equivalent $BeCl_2$ hybrids. However, the two $BeCl_2$ bonds formed are identical in every respect, indicating that the 2s and 2p orbitals mixed (hybridized) to form two equivalent sp hybrids orbital.

Also, because one s and one p orbital are used in the hybridization, the shape of the molecule will be a linear geometry.



3.5.2 sp2-HYBRIDISATION

For this, we are going to consider boron trifloride (BF_3). Here the central atom is boron (B) and its ground state (i.e. the lowest energy state) electronic configuration of boron is;

B = $1s^2$ $2s^2$ $2p^1$

Boron has to be excited to generate orbitals to accommodate all the three fluorine atoms. Thus if energy is supplied to raise one of the 2s electrons to a higher energy level the excited state electronic configuration of Be will be;

B*=$1s^2$ $2s^1$ $2p^2$

But more specifically, the electronic configuration of the excited beryllium atom can be written as;

B* = ↑↓ ↑ ↑ ↑

$1s^2$ $2s^1$ $2px^1$ 2py 2pz

And the excited state valence shell electronic configuration is:

B* = ↑ ↑ ↑
$2s^1$ $2px^1$ 2py 2pz

The three fluorine atoms will be accommodated in the $2s^1$, $2px^1$ and $2py^1$ orbital created as a result of the excitation. One would expected three non- equivalent BF_3 hybrids. However, the three BF_3 bonds formed are identical in every respect, indicating that the 2s, 2px and 2py orbitals mixed (hybridized) to form three equivalent sp^2 hybrids orbital.

Also, because one s and two p (sp^2) orbitals were used in the hybridization the shape of the molecule will be a triangular planar. The three sp^2 orbitals lie in a plane with an angle 120° between any two.

3.5.3 Sp^3-HYBRIDISATION

Here, we will be considering methane (CH_4). The central atom is carbon (C) and its ground state (i.e. the lowest energy state) electronic configuration is:

$C = 1s^2\ 2s^2\ 2p^2$

Carbon has to be excited to generate orbitals to accommodate the four hydrogen atoms. Thus if energy is supplied to raise one of the 2s electrons and one of the 2p electrons to a higher energy level,the excited state electronic configuration of C will be;

$C^* = 1s^2\ 2s^1\ 2p^3$

But more specifically, the electronic configuration of the excited carbon atom can be written as;

$C^* = \uparrow\downarrow \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow$

$1s^2 \quad 2s^1 \quad 2px^1 \quad 2py \quad 2pz$

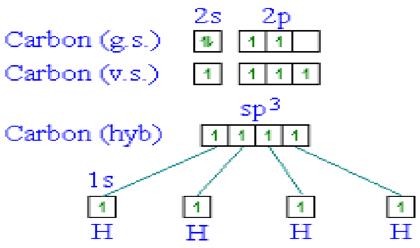
And the excited state valence shell electronic configuration is;

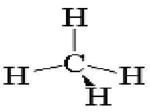
$C^* = \uparrow \quad \uparrow \quad \uparrow \quad \uparrow$

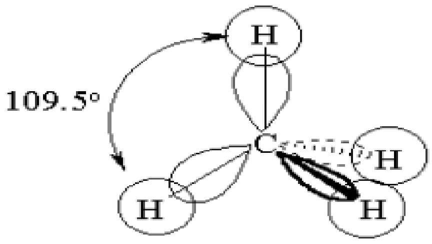
$2s^1 \quad 2px^1 \quad 2py \quad 2pz$

The four hydrogen atoms will be accommodated in the $2s^1$, $2px^1$, $2py^1$ and 2pz orbitals created as a result of the excitation. Four CH_4 bonds are formed which are identical in every respect, indicating that the 2s, 2px, 2py and 2pz orbitals mixed (hybridized) to form the four equivalent sp^3 hybrids orbital.

Also, because one s and three p (sp^3) orbitals were used in the hybridization, the shape of the molecule will be a tetrahedral. All the hydrogen carbon hydrogen angles are 109.5°







It is interesting to note that hybrid formed by only using the *s* and the *p* (i.e. sp^1, sp^2 and sp^3) orbitals in molecule complies with the octet rule. This is because regardless of the type of hybridization in an atom involving one *s* and three *p* orbitals will be four orbitals which is enough to accommodate a total of eight electrons in a compound. However the octet rule does not hold in some molecules where the atom may use the d orbital in addition to the *s* and *p* orbitals to form hybrid orbitals.

3.5.4: s, p and d ORBITALS-HYBRIDISATION

Atoms of elements in the second period of the periodic accommodate a maximum of eight electrons in their valence shell and also the s and p orbitals for their hybrid. This explains why they usually obey the octet rule. However, elements of the third period on, with more than eight electrons in their valence shell cannot always form hybrid molecules by using only the s and p orbitals. That is the formation of these hybrids must include the d orbitals.

As an illustration, PF_5 will be considered. Here the central atom is phosphorus (P) and the ground state (i.e. the lowest energy state) electronic configuration of phosphorus is;

$$P = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$$

Phosphorus has to be excited to generate orbitals to accommodate all the five chlorine atoms. Thus if energy is supplied to raise one of the 3s /3p electrons to a higher energy level the excited state electronic configuration of P will be:

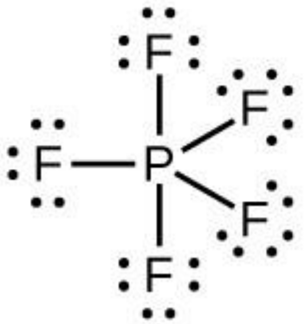
$$P^* = 1s^2\ 2s^2\ 2p^6\ 3s^1\ 3p^3\ 3d^1$$

But more specifically, the excited state valence shell electronic configuration is;

P* =↑↑↑ ↑ ↑

$3s^1$ $3px^1$ $3py^1$ $3pz^1$ 3d 3d 3d 3d 3d

The five fluorine atoms will be accommodated in the 3s, 3px, 3py, 3pz and 3d orbitals created as a result of the excitation. Also, because one s, three p and one d (sp^3d) orbitals were used in the hybridization, the shape of the molecule will be a trigonal bipyramid.



Here, there are ten electrons around the phosphorus atom, which means that the octet rule has been exceeded. Thus the use of the d orbital in addition to the *s* and *p* orbitals to form covalent bonds is an example of valence - shell expansion (expansion to the octet rule).

As another illustration, let's consider SF_6. Here the central atom is sulphur (S) and the ground state (i.e. the lowest energy state) electronic configuration of sulphur is;

$S = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

Sulphur has to be excited to generate orbitals to accommodate all the six fluorine atoms. Thus if energy is supplied to raise one of the $\frac{3s}{3p}$ electrons to a higher energy level the excited state electronic configuration of S will be:

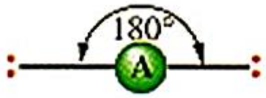
$S^* = 1s^2\ 2s^2\ 2p^6\ 3s^1\ 3p^3\ 3d^2$

But more specifically, the excited state valence shell electronic configuration is;

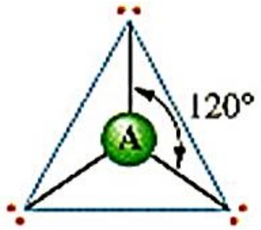
S* = ↑↑ ↑ ↑ ↑ ↑

$3s^1$ $3px^1$ $3py^1$ $3pz^1$ $3dz^2$ $3dx^2 - y^2$ 3dxy 3dyz 3dxy

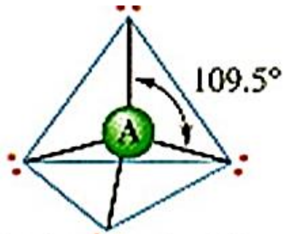
The six fluorine atoms will be accommodated in the 3s, 3px, 3py, 3pz, $3dz^2$ and $3dx^2 - y^2$ orbitals created as a result of the excitation. Also, because one *s*, three *p* and two *d* (sp^3d^2) orbitals were used in the hybridization, the shape of the molecule will be an octahedral. Here also, there are twelve electrons around the sulphur atom; which means that the octet rule has also been exceeded. Thus the use of the d orbital in addition to the s and p orbitals to form covalent bonds is an example of valence – shell expansion (expansion to the octet rule).



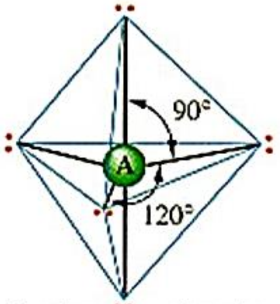
2 charge clouds,
linear



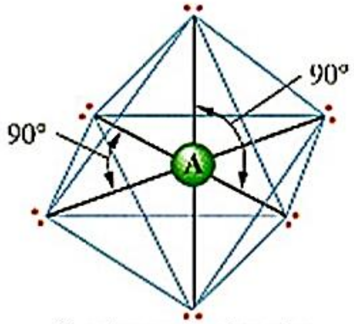
3 charge clouds,
trigonal planar



4 charge clouds,
tetrahedral



5 charge clouds,
trigonal bipyramidal



6 charge clouds,
Octahedral

PRACTICE QUESTIONS

1. (a) How many orbitals are in the following:
    - (i) The 3p orbitals
    - (ii) The 2s orbitals
    - (iii) The third energy level corresponding to $n = 3$.

   (b) Write the maximum number of electrons that each orbital and each energy level can take.

2. Give reasons for the following:
   (i) Electrons will fill the 4s orbital before other electrons will fill in the 3d orbitals.
   (ii) An unpaired electron will enter into an} of the vacant 3p orbital during the filling of orbitals
   (iii) No two (2) electrons have the same four quantum numbers.

3. Write the electronic configuration of the following elements K, S, P, and Ar

4. Deduce the shape of the following molecules.
   (a) PCI_5 (b) PF_3 (c) SP_6 (d) XeF_4 (e) CH_4 (f) NH_3
   (Xe = 54, S = 16, P = 15, C = 6, N = 7, Al = 13, B = 5, Be = 4)

CHAPTER 4

4.0 CHEMICAL SYMBOLS, FORMULAS AND EQUATIONS

4.1 CHEMICALSYMBOLS: Chemical symbols are the chemist abbreviated form of writing or representing the names of elements. The principle applied when representing element was put forward by Berzkelius in 1814. The principle entails the following.

1. The first principle uses the first letter, (written in capital letter) of the name of an element as its symbol. Examples includes; Hydrogen (H), Boron (B), Carbon (C), Nitrogen (N) Oxygen(O) Fluorine (F)Phosphorus (P)
2. When the first letter had already been adopted. The first letter and any other letter in the name of the element is used as the symbol. Here, the first letter is written in capital letter while the second letter is written in small letter. Examples includes ; Helium (He), Lithium (Li) Beryllium (Be), Neon (Ne), Magnesium (Mg), Aluminium (Al)
3. When these two methods have been adopted, the symbol of the elements is then derived from the Latin names of the elements using method one and two above. Example includes; Sodium (Natrium, Na), Potassium (kalium, K), Iron (Ferrum, Fe) and Copper (Caprum, Cu).

As earlier stated, these abbreviations s are written in capital letter when the symbol is only one letter. In cases where it has two letters, only the first letter is written in capital letter, while the other letter is written in small letter.

The symbols of an element represent

1. One atom of the element
2. A definite mass of the element often expressed in grams

4.2 CHEMICAL FORMULA

A chemical formula is an expression involving chemical symbols and numerical. The symbols represents the different types of elements present (i.e. composition) in the compound while the numerical indicates the number of atoms in one molecule of a compound, when it is written as a subscript after the symbol of the element. Example is H_2 which show that it contains two atoms of hydrogen; H_2SO_4 shows that the chemical formula contains two atoms of hydrogen, one atom of sulphur and four atoms of oxygen.

There are basically three types of chemical formulas namely empirical, molecular and structural formulas.

i. **EMPIRICAL FORMULA**: This is the simplest formula of a compound that shows the simplest whole number ratio of atoms of different elements present in a compound. Hence the empirical formula of the compound $C_2H_4O_2$ is CH_2O, where the integer multiplier is 2.

Normally, the results of chemical analysis are expressed as percentage by mass of each constituent element, so to know the identity of the compound the empirical formula will be calculated from the percentage composition. Calculation of the empirical formular of the compound entails first determining the relative number of moles of atoms of each elementpresent in the given mass of the compound. Thereafter, the number of moles of each element is then divided by the smallest number of the mole present.

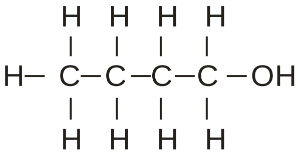
4.2.2 MOLECULAR FORMULA: This is a formula of a compound that shows the exact (actual) number of atoms of different element present in a compound. The molecular formula is given by

Molecular Formula = Empirical formula X integer multiplier

Molecular formula = n (Empirical formula)

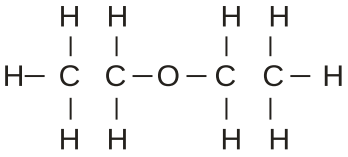
Sometimes, empirical formula and molecular formula can be the same. This is when the molecular formula cannot be reduced further. Examples includes NH_3 (ammonia), $CaCO_3$ (calcium trioxocarbonate (IV), H_2O (water) CO_2 (carbon(IV)oxide) etc.

4.2.3 STRUCTURAL FORMULA: - The structural formula shows the way that atoms are joined together in a molecule. Knowledge of the structural formula of compound is important in the study of chemistry because some compounds may have the same molecular formula and empirical formula and the only thing that will show that the compounds are different is their structural formula. As an illustration, Butanol and ethyl ether have the same empirical and molecular formula as $C_4H_{10}O$. The only thing that differentiates the two and gives both their respective unique set of properties is the structural formula.



$$\begin{array}{cccccccccc} & & H & & H & & H & & H & \\ & & | & & | & & | & & | & \\ H- & & C & - & C & - & C & - & C & -OH \\ & & | & & | & & | & & | & \\ & & H & & H & & H & & H & \end{array}$$

Butanol



$$\begin{array}{ccccccccc} & H & & H & & H & & H & \\ & | & & | & & | & & | & \\ H- & C & & C & -O- & C & & C & -H \\ & | & & | & & | & & | & \\ & H & & H & & H & & H & \end{array}$$

Ethylether

Example 4.1

Find the empirical formula of a compound which contains 80% carbon and 20% hydrogen by mass.

(Relative atomic masses, C = 12, H = 1)

Solution

Step 1: Divide the percentage by mass of each element by the relative atomic mass of the element

For carbon - $\frac{80}{12} = 6.6$

For Hydrogen - $\frac{20}{1} = 20$

Step 2: Divide through by the smallest number since atoms cannot be in fraction

$\frac{6.6}{6.6} = 1,\qquad \frac{20}{6.6} = \quad 20$

Therefore empirical formula is CH_3

Example 4.2

An organic compound contains 72% carbon, 12% hydrogen and 16% oxygen by mass. Calculate the empirical formula of the compound (Relatives atomic masses; H = 1, 0 = 16, C= 12)

Solution

Step1

C $=\frac{72}{12.} = 6$,O $=\frac{16}{16} = 1$,H $=\frac{12}{1} = 12$

Step2: Dividing through by the smallest number

$$\frac{6}{1.} = 6, \frac{1}{1.} = 1, \frac{12}{1.} = 12,$$

: - Empirical formula = $C_6H_{12}O$

Example 4.3: A pure compound contains 40% carbon, 6.7% hydrogen and 53.3% oxygen. Find

(i) The empirical formula

(ii) The molecular formula if a mole weighs 60g (Relative atomic masses; H = 1, C = 12, O = 16)

Solution

$$C = \frac{40}{12.} = 3.33, H = \frac{6.7}{1} = 6.7, O = \frac{53.3}{16.} = 3.33$$

Dividing through by the smallest we get

$$C = \frac{3.33}{3.33.} = 1, H = \frac{6.7}{3.33} = 2, C = \frac{3.33}{3.33} = 1$$

: - Empirical formula is CH_2O

(ii) Molecular formula = n (empirical formula) - - - - - - - - (1)

I mole of molecular formula = n (mole of empirical formula

I mole empirical formula = 12gC + 2gH + 16gO

= 30g

From question, 1 mole molecular formula = 60g

From equation (1)

60 = n (30)

60 = 30n

$$n = \frac{60}{30.} = 2 = integer\ multiplier$$

: - Molecular formula = 2(empirical formula)

= $2(CH_2O)$

= $C_2H_4O_2$

4.3 PREDICTING FORMULAS FROM VALENCIES

Recall that in chapter one we defined vacancy as the number of electrons an atom can lose, gain or share to acquire an octet or duplet electronic configuration. The formulas of compounds can be deduced from the valences of component elements or radicals using the following rules

Rule 1: Write the symbols of the component elements or radicals

Rule 2: Place the valences of each elements or radical below the respective element or radical

Rule 3: Interchange the valences and write them as subscript immediately after the respective symbols of the atoms.

Rule 4**:** Write the formula of the compound by first writing the metals followed by the non-metals.

Note: When the subscript is one, it is disregarded and when all the subscripts can divide through, they are further reduced.

Examples 4.4

Write the formula of the compound formed when iron (III) reacts with oxygen.

Rule 1: Fe O

Rule 2: Fe O

3 2

Rule3:

$$\begin{tikzcd} Fe \arrow[dr] & O \\ 3 \arrow[ur] & 2 \end{tikzcd}$$

Rule 4: Fe_2O_3

Example 4.5

What is the formula of aluminum sulphide

Rule 1: Al S

Rule 2: Al S

3 2

Rule3:

$$\begin{tikzcd} Al & S \\ 3 \arrow[ur] & 2 \arrow[ul] \end{tikzcd}$$

Rule4: Al_2S_3

Example 4.6

Write the formula of sodium oxide

Rule 1: Na O

Rule 2: Na O

1 2

Rule 3:

$$\begin{tikzcd} Na & O \\ 1 \arrow[ur] & 2 \arrow[ul] \end{tikzcd}$$

Rule 4: Na_2O

These rules are the same even when writing the formulas of compounds involving radicals. Radicals are groups of atoms collectively carrying a single charge. The only modification is that the radical is enclosed in a bracket if it has a value above one. Below in table 4.1 are some radicals and their valences.

Table 4.1Examples of some radicals and their valencies

Radical	Formula	**Valency**
Ammonium	NH_4^+	**1**
Hydroxide	OH^-	**1**
Trioxonitrate (V)	NO_3^-	**1**
Trioxocarbonate(IV)	CO_3^{2-}	**2**
Tetraoxosulphate (VI	SO_4^{2-}	**2**
Tetraoxophosphate (V)	PO_4^{3-}	**3**

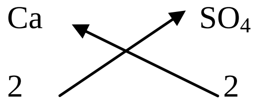
Example: 4. 7
Write the formula of calcium sulphate

Rule 1: Ca SO_4

Rule 2: Ca SO_4

2 2

Rule 3:



Rule 4: $Ca_2(SO_4)_2$.

Since both subscripts can divide through they can be further reduced, leaning our formula as $CaSO_4$

Example 4.8

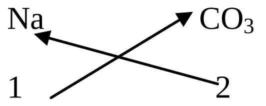
Write the formula of sodium trioxocarbonate(IV)

Rule 1: Na CO_3

Rule 2: Na CO_3

1 2

Rule 3:



Rule 4: Na_2CO_3

In summary, a chemical formula shows how many atoms of each element present in a compound. When a group of atoms is put in a bracket e.g. $Al_2(CO_3)_3$, the subscript that follows the bracket applies to all the atoms inside the bracket only. As an illustration, the formula of aluminum trioxocarbonate(V) implies that for each formula unit of aluminum troxocarbonate(V)

(1) There are two aluminum ions

(2) There are 3 trioxocarbonate ions

(3) In each trioxocarbonate ion there is one carbon atom and three oxygen atoms.

$Al_2\ (CO_3)_3$

2 aluminim ion 3 trioxo carbonate ion

4.4. CHEMICAL EQUATIONS

A chemical equitation is a compressed statement about a chemical reaction, using symbols and formulas. A reaction can be written in words for example oxygen reacting with hydrogen to produce water

$$\text{Oxygen} + \text{Hydrogen} \longrightarrow \text{water.}$$

This type of equation is of little importance to the chemist as it does not indicate the quantities of each reactant taking part in the reaction and the quantities of the product formed in cause of the chemical reaction. It does not even specify the state of the reactant and product.

For a chemical equation to be useful to chemist, the actual quantities of the reactants and products must be specified. This is where the law of conservation of matter comes into place. According to the law, the total quantity of the reactant must equal to the total quantity of the product formed. A chemical equation that has this quality is said to be a balanced chemical equation.

4.5. BALANCING CHEMICAL EQUATIONS

A balanced chemical equation is an exact symbolized expression of a chemical reaction, where all the atoms of the different elements in the reactants are equal to all the atoms of different elements in the products.

In balancing a chemical equation, the following steps should be taken:

Step 1: Write a word equation for the reaction.

Step 2: Write the correct formula of all the reactants and products

Step 3: Select coefficients that will make the equation balanced Note, do not change the subscript in the formulas of the compound while balancing

Example 4.10

Write a balanced chemical equation for the reaction between chlorine and sodium bromide to produce sodium chroride and bromine

Solution

Step 1:

Chlorine + sodium bromide ⟶ sodium chloride + Bromine

Step 2:

Determine the formulas of sodium bromide and sodium chloride using methods for predicting formulas, discussed earlier

$$Cl_2 + NaBr \longrightarrow NaCl + Br_2$$

Step 3: Coefficient are selected in order to balance the equation. The subscript must not be changed. Coefficients are whole numbers written before the formula of a compound, element, ion, molecule, indicating the relative number of unit reacting in the chemical reaction.

$$Cl_2 + 2NaBr \longrightarrow 2NaCl + Br_2.$$

Example 3.11

Write a balanced chemical equation for the reaction between hydrochloric acid and calcium trioxocarbonate (IV) to produce calcium chloride, water and carbon(IV) oxide

Solution

Step 1:

Hydrochloric acid + calcium trioxocarbonate (IV) → Calcium chloride + water + carbon(IV)oxide

Step 2:

Using the steps for predicting formulas, predict the formulas for calcium trioxocarbonate(IV), calcium chloride, carbon(iv)oxide, hydrochloric acid, and water.

$$HCl + CaCO_3 \longrightarrow CaCl_2 + H_2O + CO_2$$

Step 3: Select coefficient on either sides of equation's formulas that will balance the equation.

$$2HCl + CaCO_3 \longrightarrow CaCl_2 + H_2O + CO_2$$

Example 4.12

Write the balanced equation for the reaction between aluminum sulphate and calcium chloride to produce aluminum chloride and a white precipitate of calcium sulphate solution.

Step 1:

Aluminium sulphate + calcium chloride $\longrightarrow$ Aluminum chloride + calcium sulphate

Step 2:

$Al_2(SO_4)_3 + CaCl_2 \longrightarrow AlCl_3 + CaSO_4$

Step 3:

$Al_2(SO_4)_3 + 3CaCl_2 \longrightarrow 2AlCl_3 + 3CaSO_4$

N.B

The oxidation states of elements or radicals with variable oxidation state are always stated e.g. carbon (II) oxide implies that the carbon has the oxidation state of + 2. Iron (III) implies oxidation state of +3.

CHAPTER 5

5.0 STOICHIOMETRY

This is the aspect of chemistry that deals with quantities of substances. These quantities can be expressed in terms of number of moles, mass, volume and Avogadro's number. And these are based on;

i. Conservation of mass
ii. Relative masses of atoms
iii. The mole concept

This concept is used in all areas of chemistry which include;

i. predicting the quantities of reactants and products
ii. interpreting analytical results in chemistry
iii. preparation of standard solutions
iv. ascertaining the cost effectiveness of large scale chemical reactions

5.1 THE MOLE CONCEPT

The mole concept is the expression of quantities (i.e. amount of solute in solution or solvent) in terms of number of moles, mass, volume and Avogadro's number.

5.1.1 THE MOLE AND THE ADVOGADRO'S NUMBER

The ***mole*** is the chemist way of measuring the amount of a substance. One mole of a chemical species contains exactly one gram atomic mass, molecular mass or formula mass of the species. For example:

1 mole = One atomic mass

Fluorine = 19g

Calcium = 40g

A mole of specie also contains a constant number of the elemental particles, atoms, ions molecules etc. The number is 6.02×10^{23} and it is called the Avogadro's number. One mole ofspecie will contain one atomic mass of that specie and will also contain the Avogadro's number of particles.

Table 5.1 Relationship between atomic mass and the Avogadro's number

ONE MOLE	ONE ATOMIC MASS	ONE AVOGADROS NUMBER
Hydrogen	1g	6.02×10^{23} atoms
Boron	11g	6.02×10^{23} atoms
Fluorine	19g	6.02×10^{23} atoms

There is a relationship between one mole, one gram atomic mass (gram atomic weight) and the number of particles (Avogadro's number) of a chemical species. Their values are inter - changeable. It is also important to note that when one is converting from any of these three quantities to another, one mole, one atomic mass and one Avogadro number is used as the conversion factor.

Example 5.1
Express as mole (a) 24g of carbon (b) 10g of Neon (c) 120g of calcium

Solution

Since we are expected to convert from mass to mole, then our conversion factor will be 1 mole = 1 gram atomic mass

(a)
1 mole = 12g
$\underline{x}$ mole = 24
Note that like terms are always on the same side of the equation. Cross multiply and make x subject

24g x 1 mole = 12g X $\underline{x}$mole

$$\frac{24g\ x\ 1\ mole}{12g} = x\,mole = 2\,moles$$

: - 24g of carbon is 2 moles

(b) 1 mole of Neon = 20g

$\underline{x}$ mole of Neon = 10g

$$x\,mol = \frac{10g\ x 1 mol}{20} = 0.5$$

:- 10g of Neon is 0.5 mol

(c) 1 mole of calcium = 40g

X mole of calcium = 12g

$$x\,mol = \frac{120g\ x 1mol}{40} = 3$$

12g of calcium is 3 moles

Example 5.2

What is the mass of 0.3mol of phosphorus and how many atoms does it have?

Solution

For the first part of the question, we are expected to covert from mole to mass. Therefore, our conversion factor is:

1 mole = 1 gram atomic mass

1 mole phosphorus = 31g

0.3 mole phosphorus = x g

Note that like terms are always on the same side of the equation. Cross multiply and make *x* subject

1 mole x xg = 31g x 0.3mol

$$xg = \frac{31g\ x 0.3mol}{1mol} = 9.3g$$

: - 0.3mol of phosphorus has mass of 9.3g.

In the second part of the question, you are expected to calculate the number of atoms (Avogadro's number) in 0.3moles or 9.3 gram phosphorus. Depending on how we want to solve this problem, ourconversion factor can either be

i) 1 mole = 1 Avogadro number (6.02 x 10^{23}) OR

ii) 1 gram atomic mass = 1 Avogadro number (6.02 x 10^{23})

But whichever path we take, we will still arrive at the same answer.

Solving from the first path, we have,

1 mol = 6.02 x 10^{23}

0.3mol = x

xx 1mol = 0.3mol x 6.02 x 10^{23}

$$x = \frac{0.3mol\ x 6.02 x 10^{23}}{1mol}$$

x= 1.806 X 10^{23} atoms in 0.3mole phosphorus

Try and solve the question, using the second path way.

5.1.2 THE MOLE AND THE GRAM FORMULA MASS

The ***gram formula mass*** is the quantity of a chemical specie whose mass in gram is numerically equal to the sum of all the atomic masses of its constituent elements. When the formula is for an element, e.g. B, F, O, Zn, N, etc we use the atomic mass. Also when the formula is that of a molecule (e.g. H_2O, CH_4, $CaCO_3$etc.) the term gram molecular mass is used in place of gram formula mass. The term gram formula mass is still retained for ionic compounds since it also represent a mole and one Avogadro number.

Example 5.3

Determine the gram formula mass of $CaCO_3$

Solution

The atomic masses of the constituent elements are

Element	Gram Atomic mass
Ca	40
C	12
O	(16 x 3) = 48

Gram molecular mass = 40+12+48=100g

The gram atomic mass of oxygen is multiplied by three because there are three atoms of oxygen in the compound's formula. Therefore, the sum in gram of the masses of all the atoms in the formula $CaCO_3$ is 100g.

This, implies that one mole of $CaCO_3$ is equivalent to 100g and has 6.02×10^{23} number of $CaCO_3$ molecules.

5.1.3 MOLE, MASS AND VOLUME RELATIONSHIP

At standard temperature, ($0^{O}C$ or 273k) and standard pressure (760mmHg or 101.3×10^3 pa), the volume occupied by one mole of any gas is a constant value. That value is called the molar volume and it is numerically equal to $22.4dm^3$• For example, the gram molecule mass of one mole of carbondioxide (CO_2) is

Element	Gram Atomic Mass
C	12
O	16 x 2 = $\underline{32}$
	$\underline{449}$

This one mole, contains 6.02×10^{23} molecules and occupies a volume of $22.4dm^3$ at stp

In summary,

1 mole = one gram formula mass
1 mole = 6.02×10^{23} atoms, molecules, formulas, species etc.
1 mole = $22.4dm^3$ for any gas at s.t.p

Examples 5.4

Calculate the (a) volume at s.t.p of ammonia in 8.50g of ammonia gas.

(b) How many molecules of ammonia will there be in the sample

(c) Express the volume at s.t.p in moles (one gram atomic mass of NH_3 = 17g, one Avogadro number = 6.02×10^{23})

Solution

(a) 17g = 22.4 dm^3 (conversion factor) 8.59 = $\underline{x}$

$$\underline{x} = \frac{8.5gx22.4dm^3}{17g} = 11.2dm^3$$

(b) 179 = 6.02×10^{23} molecules (conversion factor)

8.5g = $\underline{x}$

$$\underline{X} = \frac{8.5gx6.02x10^{23}}{17g} =$$

(c) 1 mole = 22.4dm^3 (conversion factor)

$\underline{x}$ = 11.2dm^3

$$\underline{x} = \frac{11.2\text{dm}^3 \text{ x } 1\,\text{mole}}{22.4\text{dm}^3} = 0.5mile$$

5.1.4. MOLE RATIO, MASS AND VOLUME RELATIONSHIP IN CHEMICAL EQUATION

The whole number in front of the reactant and product formula in a chemical reaction represents the number of moles of reactants, reacting to give the number of moles of product. These whole numbers are the mole ratio of the reactants and products in a chemical reaction. When no whole number is written in front of a formula in a chemical equation, it implies that the mole ratio is one. Example

Equation	$2H_2$+	O_2	$\longrightarrow$	$2H_2O$
Mole ratio	2	1		2
Reacting mass	(2x2)	(16x2)		(18x2)
Reacting mass	4g	32g		36g

From the above example, it is clear that the mass that reacted is simply the product of the number of moles and the gram formula mass.

: - Reacting mass = Number of moles x gram formula mass Rearranging, we get

$$\text{Number of moles} = \frac{\text{Re acting mass gram}}{\text{Gram formula mass}}$$

Example 5.5

A sample of CO_2 has a mass of 11.0 grams

(a) Calculate the number of moles of CO_2 in the sample

(b) What volume will the sample occupy at s.t.p. (C = 12 0 =16)

Solution

(a) Reacting mass= 11.0g
Formula mass= 44g
No. of mole = x

Reacting mass = formula mass x number of moles

$$number of\ moles = \frac{\text{Re}\,acting\,mass}{formula mass}$$

$$\frac{11.0g}{44g} = 0.25mol$$

(b) At Stp 1 mole = 22.4dm^3
0.25mole = x dm^3

$$X = \frac{0.25mol\,x\,22.4dm^3}{1} = 5.6dm^3$$

Example 5.6

Calculate the mass of carbon (iv) oxide CO_2 produced on burning a mass of 104g ethyne C_2H_2 (C=12, O=16, H=l)

Solution

$$2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O$$

Mole ratio	2	5	4	2
Gram formula	2 x 26,	32 x 5,	44 x 4	18 x 2
Mass	52g	160g	176g	36g

From the equation, 176g of CO_2 is produced on burning 52g of C_2H_2. What mass of CO_2 will be produced on burning 104g of C_2H_2?

As usual, arrange like terms on the same side of the two equations, cross multiply and make the unknown the subject

52g C_2H_2 produced 176g of CO_2

104g C_2H_2 producedxg of CO_2

$$x = \frac{104x176}{52} = 352$$

Example 5.7

What mass of zinc tetraoxosulphate (VI) is obtained from reacting 10g of zinc with excess dilute tetraoxosulphate (VI) acid. (Zn = 65, S =32, O=16)

$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

Solution

Question summary

What mass of $ZnSO_4$ is obtained from 10g of Zn?

From the equation, the conversion factor is 161g $ZnSO_4$ is obtained from 65g Zn

i.e. 161g$ZnSO_4$ = 65g Zn

X g$ZnSO_4$ = 10g Zn

$X = \frac{161\ X\ 10}{65} = 24.8g\ ZnSO4$

5.2.STIOCHIOMETRIC CALCULATIONS INVOLVING A LIMITING REAGENT

So far, we have been dealing with reaction were reactants are mixed in stoichiometric quantities. That is reactants reacts at exactly the correct amount and are completely used up in the reaction.

There are some other instances where some reactants are not enough to completely react with the others, or when one reactant is in excess of what would exactly and completely react with the other reactant. In this case, the insufficient reactant will be consumed before the reactants in excess are used up. And as such the quantity of the product is determined by the insufficient reagent, which when used up no more products can be formed. The insufficient reagents limit the amount of the product that can be formed and therefore called the **limiting reactant or reagent.**

Example 5.8

What mass of zinc is required to completely react with 73.9g of tetraoxosulphate (VI) acid? (Zn = 65, S =32, O=16)

$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

Solution

Question summary

The question is asking what quantity of zinc will completely use up 73.9g of tetraoxosulphate (VI) acid.

From the equation, one mole of zinc will react completely with one mole of tetraoxosulphate (VI) acid and we were giving the reacting mass of H_2SO_4. We can then use this value to calculate the number of mole of H_2SO_4 that reacted.

Reacting mass (H_2SO_4) = molecular mass x number of moles

Therefore, $\frac{Reacting\ mass}{molecular\ mass} = number\ of\ moles\ of$ H2SO4

Number of moles of $H_2SO_4 = \frac{73.9g}{98g/mol} = 0.754 mol\ of\ H2SO4$

Recall from the equation that one mole of zinc will completely react with one mole of H_2SO_4. Therefore since the number of moles of H_2SO_4 that reacted is 0.754mol, then it will react with 0.754mol of Zn.

Now to get the mass of zinc that reacted we use the same formula

Reacting mass (Zn) = molecular mass x number of moles

Reacting mass (Zn) = 65g/mol x 0.754 moles
Reacting mass (Zn) = 49.01g

This question can also be solved using a direct and quick method thus;

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

Mole ratio: 1 1 1 1
Gram formula: 1 x 65, 1 x 98 1x 161 1 x 2

Mass: 65g 98g 161g 2g

From the equation, 1mol of Zn react with 1mol of H_2SO_4

i.e. 65g Zn98g ——— H_2SO_4
Xg ——— 73.9g
Cross multiply and make Xg subject
$Xg = \frac{65g/mol\ x73.9g}{98g/mol} = 49.01g$

The result obtained from the last example tells us that 49.01g of zinc mixed completely with 73.9g of H_2SO_4.However, if any of this reactant is reduced for example Zn to 35.0g, it will limit the amount of product that will be formed. In any stoichiometric problem, it is also important to determine which reactant is limiting in order to accurately determine the amount of product that will be formed.

Example 5.9
What mass of zinc tetraoxosulphate (VI) can be produced when 35.0g of zinc is allowed

tocompletely react with 73.9g of tetraoxosulphate (VI) acid? (Zn = 65, S =32, O=16)

$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

Solution

Question summary

The question is asking what quantity of zinctetraoxosulphate (VI) will be produced by completely reacting 35.0g zinc with 73.9g of tetraoxosulphate (VI) acid.

From the equation, one mole of zinc will react completely with one mole of tetraoxosulphate (VI) acid and we were giving the reacting mass of both Zn and H_2SO_4. We can then use these values to calculate the number of mole of the reactants.

Number of moles of $H_2SO_4 = \frac{73.9g}{98g/mol} = 0.754mol\ of\ H2SO4$

Number of moles of $Zn = \frac{35.g}{65g/mol} = 0.54mol\ of\ Zn$

From the equation one mole of each reactant will completely react with the other. It becomes obvious that zinc is the limiting reagent. Also, since one mole of zinc will produce one mole of zinc tetraoxosulphate (VI), than the mole of zinc should be used to calculate quantity of zinctetraoxosulphate (VI) that will be produced.

Mass ($ZnSO_4$) = molecular mass x number of moles

Mass ($ZnSO_4$) = 98g/mol x 0.54 moles

Mass ($ZnSO_4$) = 52.78g

5.3OTHER METHODS OF EXPRESSING CONCENTRATION OF SOLUTIONS

There are other methods of expressing the concentration of solutions or solventswhich are not commonly used. Some of them are tabulated here in Table 5.1.

Table 5.1 summary of Concentration Expression

Unit	Symbol	Definition	Relationship
Molarity	M	Number of moles of solute per litre of solution	$M = \frac{n}{\text{Litre (L) of solution}}$
Molality	M	Number of moles of solute per kilogram of solution	$m = \frac{n}{\text{Kg solvent}}$
Mole Fraction	X	Ratio of the moles of solute to the total	$X = \frac{n2}{n1+n2}$

		moles of solute plus solvent	
Normality	N	Number of equivalent of solute per litre of solution	**N=** $\frac{equivalent}{\text{litre of solvent}}$
Percent by weight	Wt %	Parts by weight of solute per 100 parts by weight of solution.	Wt %= $\frac{g2}{g1+g2}\ X\ 100$
Percent by Volume	Vol%	Parts by weight of solute per 100 parts by volume of solution	Vol%= $\frac{V2}{V1+V2}\ X\ 100$

PRACTICE QUESTIONS

1. What volume will the following gases occupy at STP
   - i) 42g of N_2
   - ii) 16g of O_2
   - iii) 0.2mol of CO_2
   - iv) 3.02×10^{23} molecules of CO
   - v) 1.20×10^{23} molecules of CH_4

2. (a) How many moles are present in 1g of sodium hydroxide?
   (b) What is the mass of 1.0mol of oxygen atoms?

3. Using 12g of copper, what mass of Copper (ii) trioxonitrate (v) will be formed in the reaction
   $3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$
   Cu = 63.5, O = 16, N = 14, H= 1)

4. How many moles are contained in 47g of magnesium trioxonitrate (v) $Mg(N0_3)_2$
   (a) How many molecules of $Mg(NO_3)_2$ are in the sample
   (b) How many moles are there in:
   (i) 6g of magnesium
   (ii) 6g of oxygen gas

CHAPTER 6

STATE OF MATTER AND THE GAS LAWS

Matter is defined as anything that has mass and occupies space. Matter is everything on earth including the universe itself. They include.

1. Things too small to be seen with our naked eyes e.g. atoms, protons, electrons, ions, amoeba, etc
2. Things we cannot even see at all but can be detected by other means e.g. rays, gas, air, etc.

Experimental results have proved that matter contains positive and negative charges. Since matter appear to be uncharged, it then means that matter contain equal numbers of positive and negative charges.

6.1 STATE OF MATTER

The three physical states of matter are

1. SolidState: Here the particles are held in position by strong inter-particular (cohesion) force. Hence solid state matter

i. Have a fixed position
ii, Have a definite volume and shape
iii. Have only enough kinetic energy to vibrate
v. Not compressible.
vi.

2. LiquidState: Here the particles inter-particular (cohesion) forces are not as strong as in the solid state. Hence the liquid state matter

i. does not have a fixed position
ii. Have a definite volume but not a definite shape.
iii. Have enough kinetic energy to vibrate and translate.
iv. Not compressible.

3. Gaseous State: Here the particles are far apart and the forces of attraction between them are very weak. Therefore, the gaseous state matter:

I. Does not have a fixed position
II. Does not have a definite volume nor shape
III. Have enough kinetic energy to vibrate and translate
IV. Compressible.

It should be noted that when the heat content in matter is altered, matter changes from one state to another. Also, some matters changes from solid to gaseous state directly and vice versa without passing through the liquid state. Such matters are said to *sublime*.

6.2 THE GAS LAWS

The Gas Laws provides the description of the ideal gas behaviour based on experimental works by notable scientists like Boyle, Charles, Dalton and Graham.

6.2.1 THE KINETIC THEORY OF GASES

The Kinetic theory of gases states that:

i. Gaseous particles are very tiny.

ii. Gases have negligible force of attractions because their molecules are far apart.

iii. Gases also have negligible volume because their molecules arc so tiny, far apart, and with empty spaces between them, making their actual volume very little compared to their containing vessels.

iv. The gas molecules are always in a state of random motion hence the total kinetic energy of the entire gas molecule in a container at constant temperature and pressure is constant.

v. The pressure exerted by a gas depends on the contact collision of the gas molecules with themselves and with the walls of the containing vessels.

6.2.2 BOYLE'S LAW

Boyle's law was put forward by an Irish scientist Robert Boyle in the 1600s. It states that the volume of a given mass of gas is inversely proportional to its pressure provided temperature remains the same (constant). That is, as volume is increasing, the pressure will be decreasing at the rate in which the volume is increasing and vice versa. This means if the volume is doubled, the pressure will be halved. And the product of the two variables (i.e. volume and pressure) will always remain the same (i.e. constant).

The law can be expressed mathematically as $V \propto \frac{1}{P}$

$\therefore -V = \frac{K}{P}$

$K = VP$

Where

V = Volume of the gas sample

P = Pressure exerted by tile gas sample.

K = Constant

This law can be shown to be true by confining a known volume of air in cylinder with a movable piston.As the volume of the gas is varied, the resultant change in pressure is read and recorded.

From the results, it will be observed that as volume is halved, pressure is doubled and vice versa. And the product of pressure and volume is always the same.

$V_1 P_1 = V_2 P_2 = V_3 P_3$

Table 6.1: **Experimental Data Illustrating Boyle's Law**

e	Volume	Pressure	Volume x Pressure
1	100.0cm^3	10.0 atm	1000 atm cm^{-3}
2	500.0cm^3	2.00 atm	1000 atm cm^{-3}
3	250.0cm^3	4.00 atm	1000 atm cm^{-3}
4	125.0cm^3	8.00 atm	1000 atm cm^{-3}
5	62.5cm^3	16.00 atm	1000 atm cm^{-3}

Figure 6.1: Graph illustrating Boyle's law (Gas pressure – Volume relationship). A plot of Volume versus Pressure

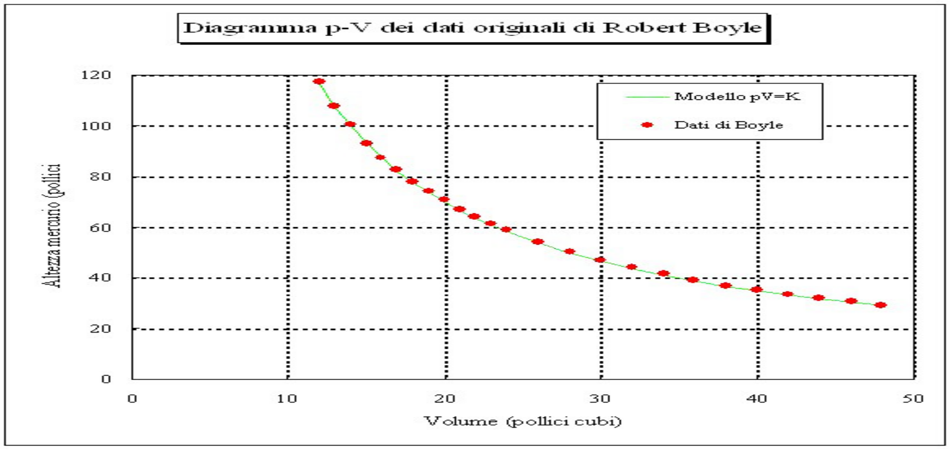
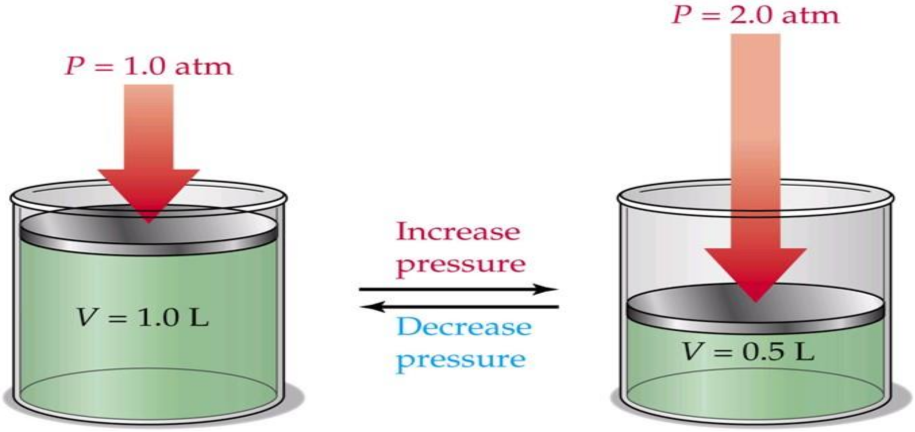


Figure 6.2: Boyle's law experiment (a) The volume at 1 atm pressure is 1.0L (1000cm^3) (b) When pressure is doubled to 2 atm, the volume will be halved (0.5L or 500cm^3). Tripling the pressure will reduce the volume to one-third of the original volume



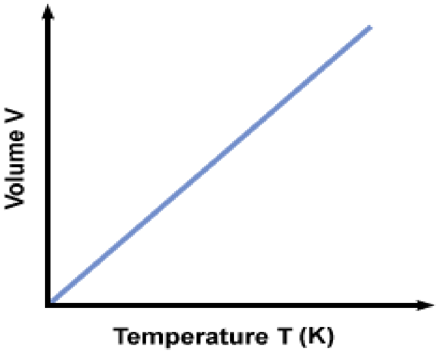
6.2.3 CHARLES LAW

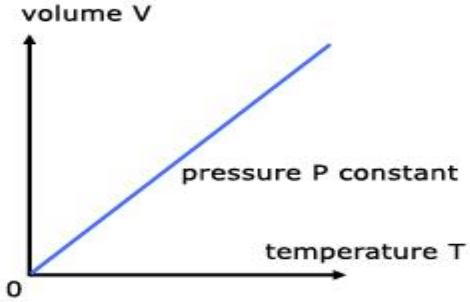
The relationship between gas volumes and temperature at constant pressure was put forward by a French scientist Jacques Charles in the l700s. The law states that: The volume of a given mass of gas is directly proportional to its absolute (Kelvin) temperature if the pressure remains the same (constant). That is as the volume is increasing, the temperature will equally increase and vice versa. And in every case, the value obtained by dividing the volume by the Kelvin temperature is always the same.

The law can be expressed mathematically as $V \alpha T$
$\therefore V = KT$

Rearranging, we get
$\frac{V}{T} = K$ (At a constant pressure)

Where
V = Volume of the gas sample
T = Kelvin temperature of the gas sample
K = the constant





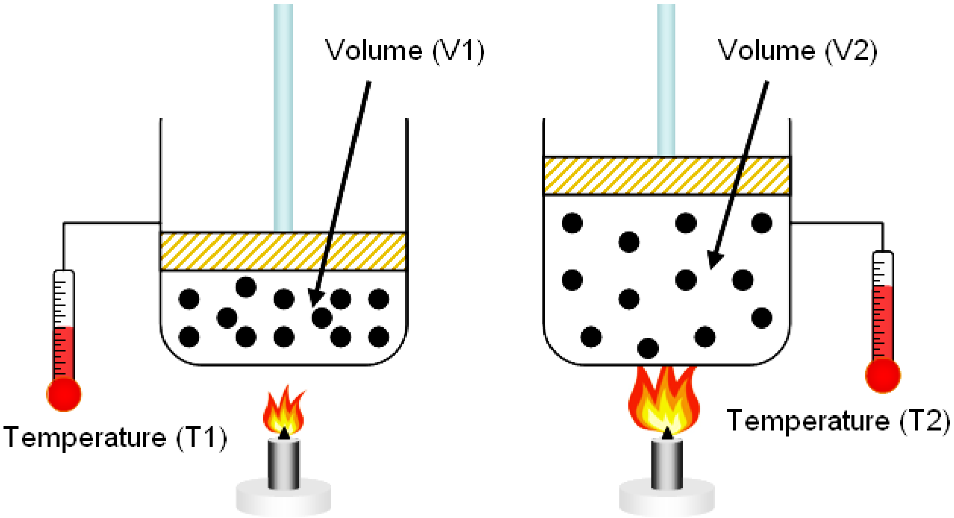
Charle's law 0 Kelvin (absolute zero)

The relationship between the gas volumes and temperature can be demonstrated by confining a gas in a cylinder with a weighted piston. Here, the pressure exerted by the gas is equal to the pressure exerted on the gas by the weighted piston which is not moving.

As the temperature is increased by heating, the gas will expand, forcing the weighted piston upward so as to give the gas an increased volume. Also, when the temperature of the cylinder is reduced by cooling, the gas will contract, forcing the weighted piston downward to assume a reduced gas volume

Figure 6.3

Charles experiment: At constant pressure, if temperature is doubled, the volume will be increased to two times the original volume.



From the results of the experiment, it is observed that at every change in temperature, the volume changed, in the same direction. That is, increased temperature gave increased volume and vice versa. And for every trial, the value obtained by dividing volume by Kelvin temperature was always, the same:

i.e. $\frac{V^1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3}$

6.2.4 GENERAL GAS EQUATION

This is a mathematical statement, which combines Boyle's law and Charles law. This equation is used by chemist to investigate what the volume of gases will be when both their temperature and pressure are changed. It is used to solve problems in which all the three variables volume, pressure and temperature change.

From Boyle’s law:

$V \alpha \frac{1}{P}$

Combining both laws we get:

$V \alpha \frac{T}{P}$

$\therefore$ -V = K $\frac{T}{P}$ re-arranging we get:

$\frac{VP}{T} = K$

$\therefore \frac{V_1P_1}{T_1} = \frac{V_2P_2}{T_2} = \frac{V_3P_3}{T_3}$

6.2.5 STANDARD TEMPERATURE AND PRESSURE (STP)

As the volume of a sample of gas depends on the temperature and pressure, therefore for comparing volumes of gases, a standard temperature and pressure are used. The standard temperature is 0°C (273K) while the standard pressure is 760 mmHg (101.3 x 10^3pa). The standard temperature and pressure can also be called STP

Example 6.1

A certain mass of gas occupies $100cm^3$ at 255mmHg. What will be its volume at 390mmHg, assuming no change in temperature.

Solution

The question involves only the gas volume and pressure. Therefore, Boyle's law mathematical expression will be used in solving the problem.

$V_1P_1 = V_2P_2$
Initial gas volume $V_1 = 100cm_3$
Initial gas pressure $P_2 = 255mmHg$
Final gas volume V_2 = unknown
Final gas pressure $P_2 = 390mmHg$

Make the unknown value subject of the formula

$$\frac{V_1P_1}{P_2} = V_2$$

$$\therefore V_2 = \frac{100cm^3 \text{ x } 255mmHg}{390mmHg}$$

$$V_2 = \frac{10200cm^3}{780} \qquad = 130.77cm^3$$

6.2.7 DALTON'S LAW OF PARTIAL PRESSURES

Dalton's law of partial pressures states that the total pressure of a mixture(non-reacting gases) of ideal gases is the sum of all the individual pressures of the gases only when they occupy the same volume:

$$P = P_A + P_B + P_C$$

Note that a mixture of gases contains two or more gases which do not: react chemically together. Also, the partial pressure is the pressure exerted by each of the gases in the mixture.

That is, the total pressure of a mixture of $1dm^3$ of oxygen at 100mmHg and $1dm^3$ of nitrogen at 200mmHg will be 300mmHg.

6.2.8 GRAHAM'S LAW OF DIFFUSION

Graham's law of diffusion state that at constant temperature and pressure, the rate of diffusion of a gas is inversely proportional to the square root of its density. Molecular masses can also be used in terms of the density. Graham's law mathematical expression is:

$R_1 = \frac{K}{\sqrt{d_1}}$

$\frac{R_1}{R_2} = \sqrt{\frac{d_2}{d_1}}$ OR $\frac{R_1}{R_2} = \sqrt{\frac{m_2}{m_1}}$

R_1 and R_2: Initial and final rate of diffusion
d_1 and d_2: Initial and final densities of gases
m_1 and m_2: Initial and final molecular mass of gases

Example 6.2

What is the total pressure exerted by the mixture of l dm^3 of oxygen at 320mmHg. $1dm^3$ of nitrogen gas at 230mmHg

Solution

According to Dalton‘s law of partial pressure, the total pressure will be the sum of all the individual partial pressures since they occupy the same volume.
$P = P_{oxygen} + P_{nitrogen}$
P = (320 + 230) mmHg = 530mmHg

Example 6.3

A volume of $3dm^3$ of nitrogen is mixed with a volume of $2dm^3$ of oxygen, with both at the same pressure of l01.3mmHg. What is the partial pressure of each gas in the mixture?

Solution

Gas A (nitrogen)

$V_1 = 3dm^3$ $P_1 = 101.3$
$V_2 = 5dm^3$ $P_2 = x$

$P_2 = \frac{P_1V_1}{V_2}$

$P_2 = \frac{101.3 \text{ x } 3}{5}$= 60.78mmHg

Gas A (Oxygem)

$V_1 = 2dm^3$ $P_1 = 101.3$

$V_2 = 5dm^3$ $P_2 = x$

$P_2 = \frac{P_1V_1}{V_2}$

$P_2 = \frac{101.3 \text{ x}2}{5} = 41.32mmHg$

Example 6.4

A volume of nitrogen gas at 300 mmHg is 450cm^3. The gas is connected to oxygen at 400mmHgwith a volume of 550cm^3. What is the pressure of the mixture, assuming temperature is constant?

Gas A (nitrogen)

$V_1 = 450cm^3$ $P_1 = 300mmHg$
$V_2 = 1000cm^3$ $P_2 = x$

$P_2 = \frac{P_1V_1}{V_2}$

$P_2 = \frac{450cm3 \text{ X } 300mmHg}{1000} = 135mmHg$

Gas A (Oxygen)

$V_1 = 550cm^3$ $P_1 = 400mmHg$
$V_2 = 1000cm^3$ $P_2 = x$

$P_2 = \frac{P_1V_1}{V_2}$

$P_2 = \frac{550cm3 \text{ x } 400mmHg}{1000} = 220mmHg$

$P_T = P_{N2} + P_{O2}$
$P_T = 135mmHg + 220mmHg$
$= 355mmHg$

Examples 6.5

Calculate the rate of diffusion of methane (CH_4) and sulphur dioxide (SO_2).

Solution

The gases densities is not reflected in the question and in solving this problem the expression of Graham law that contains molecules masses showed be used because molecular' masses are easily determined from atomic masses.

$$\frac{R_1}{R_2} = \sqrt{\frac{m_2}{m_1}}$$

R_1 = Rate of diffusion of CH_4
R_2 = Rate of diffusion of SO_2
M_1 = Molecular mass of CH_4 = 16
M_2 = Molecular mass of SO_2 = 64

$$\frac{R_1}{R_2} = \sqrt{\frac{64}{16}}$$

$$\frac{R_1}{R_2} = \sqrt{4}$$

From the results, it shows that the rate of diffusion of methane CH_4 is twice that of sulphur dioxide.

PRACTICE QUESTIONS

1. What conditions are called the standard temperature and pressure (s.t.p) for measuring gases? (b) What is the molar volume of gases at s.t.p.?

2. The volume of a given mass of gas is 804cm^3 at temperature of 127°C. Calculate the temperature of the gas when its volume is reduced to 603cm^3 while the pressure remains constant.

3. A gas sample has a volume of 210dm^3 at 37°C and 106.6mmHg. What would its final temperature be if the volume is reduced to 170dm^3 and at a pressure of 76.4mmHg ;

4. A gas has a volume of 120dm^3 at a pressure of 73.6mmHg and a temperature of 30°C. At what: pressure will the gas be when its volume is halved and at a constant temperature.

5. The maximum capacity of a container is 200cm^3. If the container has a volume of 145cm^3 at 20^{o}C, will an increase of temperature to 45°C increase the volume of the container to its maximum capacity assuming the pressure of the container is constant.

6. 600cm^3 of nitrogen gas at 300mmHg is mixed with 400cm^3 of oxygen at 500mmHg. Find the partial pressures of each gas and total pressure of the mixture when the temperature is kept constant·

7. (a) What gas law combines Boyle's Law and Charles Law?
   (b) Show its mathematical derivation.

CHAPTER 7

CHEMISTRY OF THE GROUP 1, 2 AND 3 ELEMENTS

S – BLOCK ELEMENTS

The alkali and alkaline earth metals are the s-block elements because their outermost electrons are found in the s-subshells. The alkali metals are in the group one and they have one electron in their outermost s-subshell while the alkaline earth metal have two electrons and are in group two.

7.1 GENERAL OBSERVATIONS ABOUT THE MAIN – GROUP ELEMENTS

In studying the chemistry of the main group elements, there are some general trends observed. These periodic trends are discussed below:
Elements of the left side of the periodic table are mainly metals, while those on the right side of the periodic table are non-metals. Ionization energies and electronegativities are low for metal as compared to nonmetals. So the metal tend to lose their valence electrons to form cations (e.g. Na^+, Ca^{2+}, Al^{3+}) in compounds or in aqueous solution. On the other hand, nonmetals react by gain of electrons to form monoatomic anions (O^{2-}, Cl^-) and Oxoanions (NO_3^-,SO_4^{2-}).

Also, oxides of metals are basic; they dissolve in water to give basic solution.

$$Na_2O_{(s)} + H_2O_{(i)} \rightarrow 2NaOH_{(aq)}$$

It should be noted however that oxides of metal in high oxidation states e.g. in some transition metals, can be acidic; chromium (IV) oxide, CrO_3 is an acidic oxide. Oxides of nonmetals are acidic they dissolve in water to give an acidic solution

$$SO_{3(g)} + H_2O_{(i)} \rightarrow H_2SO_{4(aq)}$$

Generally, metals have oxidations states equal to the group number, which corresponds to a loss of the valence electrons in forming compounds. Some metallic elements in the fifth and sixth periods also have oxidation states equal to the group number minus two (e.g. Pb^{2+}). On the other hand, non-metals (apart from fluorine and oxygen which are highly electronegative) have variable oxidation states, stretching from the group number (the most positive value) to the group number minus eight (the most negative value). As an illustration, Chlorine (a Group VII element) has the following oxidations states in compounds; +7, +5, +3, +1, and -1.

The metallic and nonmetallic character of elements changes gradually, in definite ways from left to right across the period and down the group. Generally, metallic character decreases from left to right across the period. While the metallic character increases down the group. This trend is more obvious with the Group III A – VA elements. For examples, in group VA, Carbon is a nonmetal, silicon and Gallium are metalloids, while tin and lead are metals. Reactivity increases down the metallic group. For example, in the Group IA elements; lithium is much less reactive than sodium and potassium. For nonmetals, reactivity decreases down the nonmetallic group, for example fluorine is far more reactive than bromine and iodine.

A second-period element is often rather different from the other elements in its group. The reason for this is that the second period elements generally have small atoms that tend to hold electrons strongly, resulting to high electronegativity. For example while the electronegativity of nitrogen is 3.1, the other member of the group VA have electronegativities values within 1.9 – 2.1.

Another reason why the second – period elements behave differently from the remaining members of their group is that the second period elements involves only the s-and p orbital's in bond formation, which places a limit on the types of compounds they form. The remaining elements in the group involve the use of the s, p and d-orbital indicating that more types of compounds can be formed by these elements. For example, Nitrogen as a second-period element forms only the trihalides (e.g. NCl_3) while phosphorus has both the trihalides (PCl_3) and pentahalides (PCl_5) which it forms using the 3d orbital.

7.2 GROUP 1 – THE ALKALI METALS

The alkali metals are member of the group 1 elements. They have valence shell electronic configuration as ns^1

The alkali metals are chemically the most reactive metal and their reactivity increases as the group decend. This is because the single outer electron is increasingly screened from the positive charge of the nucleus by successive electron shells and so is lost more and more readily. Because the metal is very reactive, it occurs in nature combined with other elements.

The alkali metals are soft and white with a characteristic luster or sheen when freshly cut, this surface tarnishes very rapidly with the formation of a thin layer of the oxide. Table 7.1 shows members of the alkali metals and their electronic configuration.

Table 7.1Group 1 elements and their electronic configuration

ELEMENTS	ELECTRONIC CONFIGURATION
Lithium Li	**3 -** $1S^2\ 2S^1$
Sodium Na	11 – $1S^2\ 2S^2\ 2P^6\ 3S^1$
Potassium K	**19 -** $1S^2\ 2S^2\ 2P^6\ 3S^2 3p^6 4s^1$
Rubidium Rb	**37 -** (Kr) $5s^1$
Caesium Cs	**55 -** (Xe) $6s^1$
Francium	**87 -** (Rn) $7s^1$

The atoms of the elements get larger down the group as more shells of electrons are added, screening the outer electrons from the increasing nuclear charge. Atoms of elements down the group are more likely to have electrons densities transferred away from them in a chemical reaction than atoms of element up the group. This is reflected in the decreasing electrongegativity of the elements down the group.

Atoms of the elements down the group are held together less strongly than those higher up, leading to lower melting points and alsoreducing the strength of the metallic bond. Table 7.2 shows the physical properties of the group 1 elements.

Table 7.2The physical properties of the group 1 elements

Element	Li	Na	K	Rb	Cs
Metallic radius/nm	0.16	0.19	0.24	0.25	0.27
Ionic radius/nm	0.074	0.102	0.138	0.149	0.170
Electrongativity	1.0	0.9	0.8	0.8	0.7
1st Ionization energy/kj mol	520	496	419	403	376
2nd Ionization energy	7298	4563	3051	2632	2420
Melling points/^{0}c	181	98	63	39	29
Boling points/^{0}c	1342	883	760	686	669
Density/gcm^{-3}	0.53	0.97	0.86	1.53	1.88

The group 1 elements have similar electronic configuration in which each has a single electron outside a full shell of inner electrons. This similarity in their electronic configuration directly influences their chemical properties since it determines the way in which they form chemical bond. The similarities in chemical behaviour on them includes

(a) **Reactivity**: - They are chemically the most reactive metals. They are so reactive that they are generally found in nature combined with other elements and the pure metals are usually stored in an inert liquid out of contact with air or water.

The alkali metals react with cold water, displacing hydrogen and forming an alkaline hydroxide solution

$$2M_{(s)} + 2H_2O_{(l)} \longrightarrow H_{2(g)} + 2MOH_{(aq)}$$

$$2Na_{(s)} + 2H_2O_{(l)} \longrightarrow H_2 + NaOH_{(aq)}$$

(b) **Univalence**:- They all have a single electron in their outer s-subshell which is readily lost to form ions with a noble gas configuration and a single positive charge e.g. Na^+, Li^+ etc. The alkali metals thus have only one oxidation state, +1

(c) **Formation of ionic Compound**: - Evidence from the ionization energies of elements suggests that there is a particular stability associated with the electronic configuration of the noble gases. In order for the group 1 elements to achieve this full shell configuration, they give away the single electron in their sub-shell to become M^+ ion. This involves the complete transfer of electron from the atom of the group one element to another atom of another group of element. This relationship is called ionic or electrovalent bond and the compound formed is called ionic compound.

(d) **Strong Reducing Agent**: - As a reducing agent, they are oxidize in the cause of a chemical reaction by

(i) Loss of electron

(ii) Increase in oxidation number

(iii) Addition of oxygen

$$4Na_{(s)} + O_{2(g)} \longrightarrow 2Na_2O_{(s)}$$

From the equation, electrons are removed from sodium and transferred to oxygen. Also oxygen is added to sodium. Therefore we say that sodium is oxidized while oxygen is reduced.

(d) **Low Ionization Energy**: - Ionization energy is the energy needed to remove one mole of electron from one mole of a gaseous atom or gaseous cation. Ionization energy increases across the period, as it becomes harder to remove an electron due to the increasing positive charge across the period without the additional electron shells to screen the outer electrons. The atomic radius gets smaller and electrons are held more firmly.

(e) They all burn in air in strongly exothermic reaction producing typical flame colours.

7.3 CHEMICAL PROPERTIES OF THE ALKALI METALS

1. They tarnish in damp air to form their oxides when these oxides react with water; it forms the corresponding hydroxides, which slowly absorb atmospheric carbondioxide to form crystals of hydrated trioxocarbonate(iv) salt of the corresponding metal.

$$4M + O_2 \longrightarrow 2M_2O$$

$$M_2O + H_2O \longrightarrow 2MOH$$

$\longrightarrow$

$$2MOH + CO_2 \longrightarrow M_2CO_3 + H_2$$

(M = alkali metal)

2. They react with water, liberating hydrogen and forming the corresponding hydroxide solutions which are very basic.

$$2M + 2\ H_2O \longrightarrow H_2 + 2\ MOH$$

The vigour of this reaction increases down the group. While lithium reacts slowly with water, sodium react vigorously, potassium reacts violently with water that the hydrogen formed catches fire. Rubidium and caesuim reacts explosively.

3. They react with dilute acids vigorously liberating hydrogen gas and forming the corresponding salt.

$$2M + 2HCl \longrightarrow H_2 + 2MCl$$

4. When heated, they react with hydrogen to form the corresponding, hydrides.

$$2M + H_2 \longrightarrow 2M^+H.$$

5. They react violently with halogens forming the corresponding halides

$$2M + Cl_2 \longrightarrow 2MCI$$

6. They dissolve in mercury forming the corresponding amalgams which are used as reducing agent

$$M + Hg \longrightarrow M/Hg$$

7. They dissolve in liquid ammonia and some amines to form a blue solution. At higher concentration, the solutions are copper, coloured

$$M + NH_3 \longrightarrow M^+NH_2^- + \tfrac{1}{2}H_2$$

7.4 THE GROUP II ELEMENTS: – THE ALKALINE EARTH METALS

The group II elements are also very reactive metals in which the electropositive character increases down the metallic group. The element in this group has two electrons in their outer shell hence less reactive and harder than the group I elements, as they need more energy to lose the outer two electrons to achieve a noble gas configuration. They all burn in air in strongly exothermic reaction. Some of them produce typical flame colours. Apart from beryllium, which differs from the other alkaline earth metals in its lack of reactivity, alkaline earth metals react with cold water, displacing hydrogen and forming an alkaline hydroxide. Also, apart from beryllium, the alkaline earth metals are white, relatively soft metals, which are good conductors of heat and electricity. Table 7.3 shows the members of the group and their electronic configuration.

Table 7.3 The group II element and their electronic configuration.

ELEMENT	ELECTRONIC CONFIGURATION
Beryllium Be	4 – $1s^2\ 2s^2$
Magnesium Mg	12 – $1s^2\ 2s^2\ 2p^6 3s^2$
Calcium Ca	20 – $1s^2\ 2s^2\ 2p^2\ 3s^2\ 3p^2\ 4s^2$
Strontium Sr	38 –(Kr) $5s^2$
Barium Ba	56 – (Xe)$6s^2$
Radium Ra	88 – (Rn) $7s^2$

They form basic oxides and hydroxides with general formula MO and $M(OH)_2$. Their oxides and hydroxides are either sparingly soluble or insoluble.

The freshly cut surfaces are shiny, but they quickly oxidize and the oxide film protects the metal from further reaction.

The group II element ionizes with the loss of two electrons to form ions with oxidation number of +2 e.g. Ca^{2+}, Mg^{2+} etc.

Like the alkali metal, the ionization energy and the electronegativity of the alkaline earth metals decrease down the group-as the number of shell increases, the attractive pull of the nucleus to the outer electrons decreases, as the electron are screened more effectively from the positive charge of the nucleus.

Like he alkali metals, metals down the group are held together less strongly than those higher up, leading to lower melting point. The strength of the metallic bond also decreases down the group as the density of the positive ions in the metal lattice decreases as the ion get larger. Also reactivity increase down the group as the element at the bottom of the group are more reactive and softer than those on top.. For example, Barium in the six period react with water much like the alkali metals. It is also a soft metal much like the alkali metals. Magnesium in the third period is a less reactive and harder metal.

7.5 SIMILARITIES BETWEEN ALKALI AND ALKALINE EARTH METALS.

1. They are both high up in the electrochemical series hence good reducing agent.
2. They both react with water, reducing it to hydrogen and the metal hydroxide.

   Group (1) $2M + 2H_2O \xrightarrow{\quad} 2MOH + H_2$

   Group (2) $M + 2H_2O \xrightarrow{\quad} M(OH)_2 + H_2$
3. They both have their valence shell electrons in the s-subshell.

4. They both show one oxidation state.

5. The nitrates of all the s-book elements decompose on heating with a bunsen flame.

6. The s-block elements are so reactive that they are not found free in nature. And they are extracted from there ore by electrolysis.

7. Their hydroxides decompose to form the corresponding oxide and water.

Group (1) $2MOH \longrightarrow M_2O + H_2O$

Group (2) $M(OH)_2 \longrightarrow MO + H_2O$

8. They are soft and easily cut with a knife

9. They both have low melting and boiling points

10. They have low densities (Li, Na, K,) are less dense than water
11. They have low standard enthalpies (heats) of melting and varpourisation
12. They show typical flame colours; Li – red, Na – yellow, K, - lilac, Rb – , Cs, - blue, Be – colourless, Mg, - Brilliant white, Ca – Brick red, Sr – crimson

7.6 DIFFERENCE BETWEEN ALKALI AND ALKALINE EARTH METALS.

1. The alkali metals are more electropositive than the alkaline earth metals.
2. The alkali metals have one electron in their outer shell while the alkaline earth metals have two.
3. The group II elements show stronger metallic bonding than the group I. This is reflected in their properties
4. All common group I metal salts are soluble in water. All group II salts where the anions have a charge of – 1 are soluble, with the exception of hydroxides. All group II salts where the anion has a charge of – 2 are insoluble with the exception of a few magnesium and calcium salts.
5. Group I nitrates except Lithium decompose on heating to give stable nitrite while group II nitrates give oxide

Group (I) $2NaNO_{3(s)} \longrightarrow 2NaNO_{2(s)} + O_{2(g)}$

Group (II) and Lithium

$4LiNO_{3(s)} \longrightarrow 2Li_2O_{(s)} + 4NO_{2(g)} + O_{2(g)}$

$Mg(NO_3)_{2(s)} \longrightarrow 2MgO_{(s)} + 4NO_{2(g)} + O_{2(g)}$

6. The compounds of Group I metals are thermally more stable than those of group II metals. The carbonates and hydroxides of Group 1 metals (except Li_2CO_3 and LiOH) do

not decompose at 1000°C, but those of group II metals decompose to their oxides on heating.

$Li_2CO_3 \longrightarrow Li_2O + CO_2$
$CaCO_3 \longrightarrow CaO + CO_2$

$2LiOH \longrightarrow Li_2O + H_2O$
$Ca(OH)_2 \longrightarrow CaO + H_2O$

As stated earlier (section7.1),a second period element show properties that aredifferent from its group. These differences are more obvious in the right side of the periodic table. For example:

Lithium though in group I resembles group II because it shows similar properties with the group II elements.

1. When heated in an ordinary Bunsen flame the group I carbonates are stable with the exception of lithium carbonate, Li_2CO_3. The group II carbonates together with lithium carbonate decomposes to form stable oxides, with the liberation of carbon dioxide gas

$$Ca\,CO_{3(s)} \longrightarrow CaO_{(s)} + CO_2(g)$$

$$Li_2\,CO_{3(s)} \longrightarrow Li_2O_{(s)} + CO_{2(g)}$$

2. Group I nitrates, with the exception of lithium nitrate $LiNO_3$ decompose on heating on a Bunsen flame to give their corresponding nitrite and these($NaNO_2$) are stable to heat.

$$2Na\,NO_{3(s)} \longrightarrow 2\,NaNO_{2(s)} + O_{2(g)}$$

In contrast, lithium nitrate and all the group II nitrates decompose on heating to form the corresponding oxide.

$$4\,LiNO_{3(s)} \longrightarrow 2Li_2O_{(s)} + 4NO_2 + O_{2(g)}$$

$$2Mg\,(NO_3)_{2(s)} \longrightarrow 2MgO + 4NO_2 + O_{2(g)}$$

3. Li_2CO_3 is only slightly soluble in water at room temperature, whereas sodium carbonate and other group I elements carbonate are soluble

Also, beryllium differs from the other members of its group by its lack of reactivity. Furthermore, while the hydroxides of magnesium and barium are basic, beryllium hydroxide is amphoteric, reacting with both acids and bases.

7.7 THE GROUP III ELEMENTS

The group III elements mark the beginning of the p-block elements. These elements have three electrons in their outer shell, two in the s-subshell and one p-subshell. Their valence shell electronic configuration is represented as $ns^2\ np^1$. The principal oxidation state of the Group III elements is +3. Table 7.4 below shows the members of the group and their electronic configuration.

Table 7.4 The Group III elements and their electronic configurations.

Elements	Symbol	Electronic Configuration
Boron	B	$5 – 1s^2 2s^2 2p^1$
Aluminium	Al	$13 – 1s^2\ 2p^6\ 3s^2 3p^1$
Gallium	Ga	$31 – (Ar)\ 3d^{10}\ 4s^2\ 4p^1$
Indium	In	$49 -\ (Kr)\ 4d^{10}\ 5s^2\ 5p^1$
Thalium	Ti	$81 – (Xe)\ 5d^{10}\ 6s^2\ 6p^1$

There is a gradation in the properties of these elements as we go down the group. This gradation of properties can be explained in terms of:

7.7.1. METALLIC CHARACTERISTICS: - Metallic character increases down the group, from Boron which shows clearly non-metallic properties, through aluminium which shows amphoteric properties to the rest of the elements (gallium, indium and thallium) which are metals and also show metallic character.

In common with other reactive metals, aluminium will give off hydrogen gas with hydrochloric or sulphuric acids. But it does not react with nitric acid because the acid render's the aluminum surface passive. Boron does not give of hydrogen with sulphuric and nitric acid instead the boron reduces the acid

$$2B + HNO_3 \longrightarrow 2H_3BO_{2(aq)} + 6NO_{2(g)}$$

Boron, aluminium and gallium all show an oxidation state of +3 in their compounds whileindium and especially thalium prefers an oxidation number of +1. These properties of the group shows clearly that metallic property of the elements increases as one go down the group.

7.7.2 NATURE OF THEIR BOND

Bonding in boron is covalent. The atom shares its $2s^2\ 2p^1$ valence electrons to attain a full valence shell configuration, with oxidation state of +3. Aluminium also form many covalent compounds (e.g. $AlCl_3$) as well as ionic ones e.g. AlF_3 with +3 oxidation state. But gallium, indium and thallium form predominantly ionic compounds with oxidation states of +1.

The elements in this group all form halides with the general formular MX_3 e.g. BCl_3, $AlCl_3$, $GaCl_3$. Some of these chlorides dimerise e.g. aluminium trichloride gives Al_2Cl_6 with a mixture of both covalent and coordinate bonding. Boron chloride (BCl_3) and aluminium chloride ($AlCl_3$) are covalent, hence they show nonmetallic character. Indium and especially thallium which prefer an oxidation state of +1 will prefer an ionic bond.

7.7.3. RELATIVE STABILITY OF THEIR OXIDATION STATES:-

The metallic behavior of an element deceases as the positive oxidation number of its elements in compound increases. Thus as the +1 oxidation state becomes more stable down the group so is the increase in their metallic properties.

The +1 oxidation state increases down the group because increase in electronic shell screens the valence shell electrons from the attractive nuclear pull. Therefore, covalent bonding does not form between large atoms. Here, the s-electrons remain inert and do not take part in bonding, while the p-electron becomes easily lost to form ionic bond. So the +1 oxidation state becomes more stable than the +3 oxidation state down the group.

7.7.4 ACIDIC / BASIC NATURE OF THEIR OXIDES: - All the elements give oxides with general formula E_2O_3

Boron burns in oxygen at 700°C to form boric oxide B_2O_3 which dissolves in hot water to form boric acid. $B_2O_3 + 3H_2O \longrightarrow 2H_2BO_3$

Boric acid and boric oxide reacts with metal oxide or hydroxide to form borates (borates are salts of oxyacide of boron). This clearly shows that boron exhibits nonmetallic properties

Aluminum reacts with oxygen to form aluminium oxide (alumina)

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

Aluminum oxide shows amphoteric properties as it reacts with both acids and bases. It forms simple aluminuim salts with acids.

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

While it reacts with bases to form the corresponding metal aluminates.

$$Al_2O_3 + 2NaoH + H_2O \longrightarrow 2NaAl(OH)_4$$

PRACTICE QUESTIONS

1. (a) Give an account of how lithium, though in Group 1 behave like the Group II elements.
2. (a) Write balanced chemical equation for the following reactions:

(i) $K + H_2O \longrightarrow$
(ii) $Mg(NO_3)_{2(s)} \xrightarrow{heat}$
(iii) $Mg + Cl_2 \longrightarrow$
(iv) $LiNO_{3(s)} \xrightarrow{heat}$
(v) $CaCO_{3(s)} \xrightarrow{heat}$
(vi) $LiCO_{3(s)} \xrightarrow{heat}$

3. Explain why and how beryllium though a group II element does not behave like the other members of its group

Explain why the ionization $M^+ + e^-$ takes place more readily as you pass down the group I elements.

CHAPTER 8
ELECTROCHEMISTRY

Electrochemistry

Electrochemistry is best defined as *the study of the interchange of chemical and electrical energy*. It is primarily concerned with two processes that involve oxidation–reduction reactions: the generation of an electric current from a spontaneous chemical reaction and the opposite process, the use of a current to produce chemical change.

Terms Associated with Electrochemistry

Cell Notation

An electrochemical cell consists of two half-cells, which can be represented by cell notation. An example of electrochemical cell is the Daniel Cell. The Daniel cell is composed of two half cells. It is represented by the cell notation:

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

The anodic half is written first on the left hand side.
The single line denotes the boundary between a metal and its ions in solution.
The double line represents the porous partition or salt bridge.

Standard Electrode Potentials (Reduction Potentials)

The standard electrode potential of a cell is the potential difference or voltage of the cell at equilibrium under standard conditions. Under such standard condition, the anode is a standard hydrogen electrode, where hydrogen is oxidized:

$$\tfrac{1}{2} H_{2(g)} \rightarrow H^{+}{}_{(aq)} + e^{-}$$

The cathode reaction is the half reaction that is been considered.

The electrode potential is also known as the reduction potential $E^0_{red.}$ The reduction potential expresses the tendency of the oxidizing agent to be reduced (i.e the ease with which an oxidizing agent gains electron and become reduced).

Hydrogen is assigned a value of zero. Oxidizing agents stronger than H^+ (i.e lower than hydrogen in the electrochemical series) have positive values e.g (F_2 = +2.866 V) and negative for oxidizing agents that are weaker than H^+ (e.g., −0.763 V for Zn^{2+}).

Mathematically, the potential difference of a cell in a redox reaction is given as

$E^0_{cell} = E^0_{cathode} – E^0_{anode}$

E° cell = E° reduced - E° oxidised

= E° right - E° left

Question 1

What is the EMF of the Daniel Cell represented by the notation:

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

Given that:

$Zn^{2+} + 2e^- \rightarrow Zn_{(s)}$; $E^\circ = -0.76V$

$Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$; $E^\circ = +0.34V$

Solution: $E^\circ = E^\circ$ cathode – E° anode

= 0.34 – (-0.76)

= 0.34 + 0.76 = 1.10V

Electrochemical Cells

A device for producing an electrical current from a chemical reaction (redox reaction) is called an **electrochemical cell.**

Voltaic Cells

A Voltaic cell, also known as a galvanic cell is one in which electrical current is generated by a spontaneous redox reaction. A simple voltaic cell is shown below. Here the spontaneous reaction of zinc metal with an aqueous solution of copper sulphate is used.

$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

A bar of zinc metal (anode) is placed in zinc sulphate solution in the left container. A bar of copper (cathode) is immersed in copper sulphate solution in the right container. The zinc and copper electrodes are joined by a copper wire. A salt bridge containing potassium sulphate solution interconnects the solutions in the anode compartment and the cathode compartment.

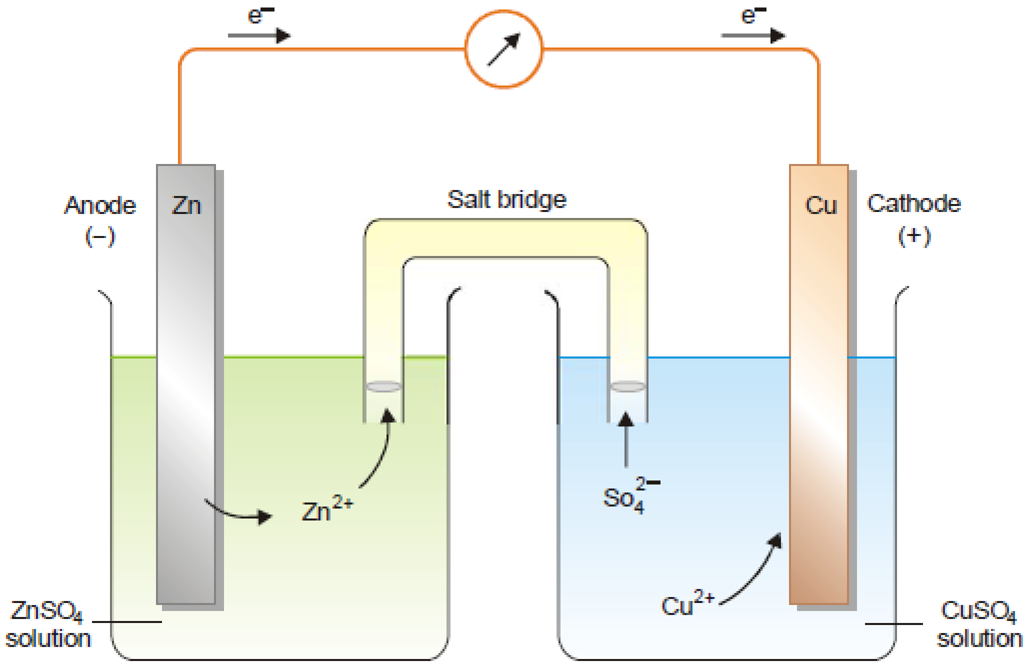
The oxidation half-reaction occurs in the anode compartment.

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

The reduction half-reaction takes place in the cathode compartment.

$Cu^{2+} + 2e^- \longrightarrow Cu$

Anode

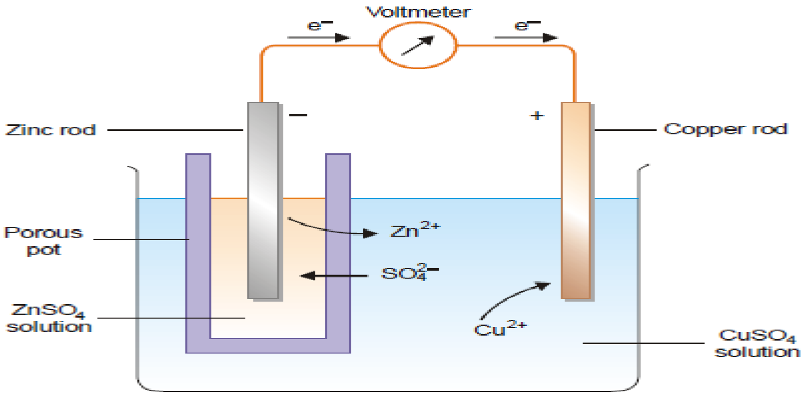


When the cell is set up, electrons flow from zinc electrode through the wire to the copper cathode. As a result, zinc dissolves in the anode solution to form Zn^{2+} ions. The Cu^{2+} ions in the cathode half-cell pick up electrons and are converted to Cu atoms on the cathode. At the same time,

SO_4^{2-} ions from the cathode half-cell migrate to the anode half-cell through the salt bridge. Likewise, Zn^{2+} ions from the anode half-cell move into the cathode half-cell. This flow of ions from one half-cell to the other completes the electrical circuit which ensures continuous supply of current. The cell will operate till either the zinc metal or copper ion is completely used up.

Daniel Cell

It is a typical voltaic cell. It was named after the British chemist John Daniel. It is a simple zinc copper cell like the one described above.



In this cell the salt-bridge has been replaced by a porous pot. Daniel cell resembles the above voltaic cell in all details except that Zn^{2+} ions and SO_4^{2-} ions flow to the cathode and the anode respectively through the porous pot instead of through the salt-bridge. Inspite of this difference, the cell diagram remains the same.

Cell reaction

The flow of electrons from one electrode to the other in an electrochemical cell is caused by the half-reactions taking place in the anode and cathode compartments. The net chemical change obtained by adding the two half-reactions is called the **cell reaction.** Thus, for a simple voltaic cell described above, we have

(*a*) Half-reactions:

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

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

(*b*) Cell reaction by adding up the half-reactions:

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

Cell potential or EMF

The flow of current through the circuit is determined by the 'push', of electrons at the anode and 'attraction' of electrons at the cathode. These two forces constitute the 'driving force' or 'electrical pressure' that sends electrons through the circuit.

This driving force is called the **electromotive force** (abbreviated **emf**) or **cell potential.** The emf of cell potential is measured in units of volts (V) and is also referred to as **cell voltage.**

Cell diagram or Representation of a Cell

A cell diagram is an abbreviated symbolic depiction of an electrochemical cell.

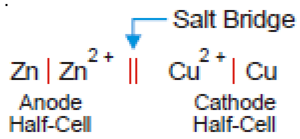
IUPAC Conventions. In 1953 IUPAC recommended the following conventions for writing cell diagrams. We will illustrate these with reference to Zinc-Copper cell. It may be noted that the metal electrode **in anode** half-cell is on the left, while **in cathode** half-cell

(1) a **single vertical line** (|) represents a phase boundary between metal electrode and ion solution (electrolyte). It is on the right of the metal ion.

(2) A **double vertical line** (||) represents the salt bridge, porous partition or any other **means** of permitting ion flow while preventing the electrolyte from mixing.

(3) **Anode half-cell is written on the left** and **cathode half-cell on the right.**

(4) In the **complete cell diagram, the two half-cells are separated by a double vertical line (salt bridge) in between.** The zinc-copper cell can now be written as



(5) The symbol for an **inert electrode,** like the platinum electrode is often enclosed in a bracket.

For example,

Mg /Mg^{2+}/H^+/H_2 (Pt)

(6) The value of emf of a cell is written on the right of the cell diagram. Thus a zinc-copper cell has emf 1.1V and is represented as

Zn /ZnSO4// CuSO4/ Cu E = + 1.1 V

Convention regarding sign of emf value

Thus the emf of the cell is given the **+ve sign.** If the emf acts in the opposite direction through the cell circuit, it is quoted as **–ve value.** For example, Daniel cell has an emf of 1.1V and the copper electrode is positive. This can be expressed in two ways :

$$\mathrm{Zn} \mid \mathrm{ZnSO_4} \parallel \mathrm{CuSO_4} \mid \mathrm{Cu} \qquad E = +\,1.1\ \mathrm{V}$$

$$\mathrm{Cu} \mid \mathrm{CuSO_4} \parallel \mathrm{ZnSO_4} \mid \mathrm{Zn} \qquad E = -\,1.1\ \mathrm{V}$$

The negative sign indicates that the cell is not feasible in the given direction. The reaction will take place in the reverse direction.

Calculating the emf of a cell

The emf of a cell can be calculated from the half-cell potentials of the two cells (anode and cathode) by using the following formula

Ecell = Ecathode – Eanode

$= E_R – E_L$

where ER and EL are the reduction potentials of the right-hand and left-hand electrodes respectively.

It may be noted that absolute values of these reduction potentials cannot be determined. These are found by connecting the half-cell with a standard hydrogen electrode whose reduction potential has been arbitrarily fixed as zero.

Some important points concerning the Table of Standard Reduction Potentials

(1) The more positive the value of E°, the better the oxidising ability (the greater the tendency to be reduced) of the ion or compound, on moving upward in the Table.

(2) The more negative the value of E° the better the reducing ability of the ions, elements or compounds on moving downward in the Table.

(2) Under standard conditions, any substance in this Table will spontaneously oxidise any other substance lower than it in the Table.

USES OF ELECTRODE POTENTIAL

1. **Predicting Feasibility of Reaction**

The feasibility of a redox reaction can be predicted with the help of the electrochemical series.

The net emf of the reaction, Ecell, can be calculated from the expression

E°cell = E°cathode – E°anode
In general, if E°cell = + ve, the reaction is feasible
E°cell = – ve, the reaction is not feasible

Practice:

1. Predict whether the reaction

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

is feasible or not. Consult the table for the E° values.

Given :

Ag/Ag+ $E^{o} = 0.80V$

$Zn^{2+}/Zn\ \ E^{o} = -0.763$

solution

The cell half reactions are

Anode : $2Ag_{(s)} \longrightarrow 2Ag^{+}(aq) + 2e^{-}\ E° = 0.80\ V$

Cathode : $Zn^{2+}_{(aq)} + 2e^{-} \longrightarrow Zn_{(s)}\ E° = -0.763\ V$

E°cell = E°cathode – E°anode

∴ E°cell = – 0.763 V – 0.80

= – 1.563

Since E°cell is negative, the given reaction is not feasible

2. Determine the feasibility of the reaction

$2Al_{(s)} + 2Sn^{4+}_{(aq)} \longrightarrow 2Al^{3+} + 3Sn^{2+}_{(aq)}$

Given

Al/Al^{3+} $E^{o} = -1.66V$

Sn^{4+}/Sn^{2+} $E^{o} = +0.15V$

Solution

The given reaction consists of the following half reactions

Anode : $2Al(s) \longrightarrow 2Al^{3+} + 6^{e}–$ $E° = – 1.66$ V

Cathode : $3Sn^{4+} + 6e– \longrightarrow 3Sn^{2+}$ $E° = + 0.15$

E°cell = 0.15 – (– 1.66)

= 1.81 V

Since E°cell is positive, the reaction is feasible.

2.Uses of electrode potential in predicting displacement reactions of aqueous salt solutions

Metals near the bottom of the electrochemical series are strong reducing agents and are themselves oxidised to metal ions. For example,

zinc lying down below the series is oxidised to Zn^{2+} ion, while copper which is higher up in the series is produced by reduction of Cu^{2+} ion.

$Zn \longrightarrow Zn^{2+} + 2e–$

$Cu^{2+} + 2e^- \longrightarrow Cu\downarrow$

Thus when zinc is placed in $CuSO_4$ solution, Cu metal gets precipitated. In general we can say that a metal lower down the electrochemical series can precipitate the one higher up in the series.

3. **Use of EP in predicting whether a metal will displace hydrogen from a dilute acid solution**

Any metal above hydrogen in the electrochemical series is a weaker reducing agent than hydrogen itself and cannot reduce H^+ to H_2. Any metal lying below hydrogen is a stronger reducing agent than hydrogen and will convert H^+ to H_2. This explains why Zn lying below hydrogen reacts with dil H_2SO_4 to liberate H2, while Cu lying above hydrogen does not react.

$Zn + H^+ \text{ (dil } H_2SO_4) \longrightarrow Zn^{2+} + H_2\uparrow$

$Cu + H^+ \text{ (dil } H_2SO_4) \longrightarrow Cu^{2+} + H_2$

CONCEPT OF ELECTROLYSIS

Electrolysis is the passage of a current (direct current) through an ionic substance that is either molten or dissolved in a suitable solvent, producing chemical reactions at the electrodes and decomposition of the substance.

Terms associated with electrolysis

Electrolyte: this is a substance that contains free ions, which carry electric current in the electrolyte. The ions in a substance must be in a mobile state for electrolysis to occur.

Direct current (DC): this provides the energy necessary to create or discharge the ions in the electrolyte. Electric current is carried by electrons in the external circuit.

Electrodes: they are electrical conductors (e.g metals, graphite) that provide the physical interface between the electrolyte and the electrical circuit that provides the energy.

Faraday's First Law of Electrolysis

The mass of a substance formed at an electrode during electrolysis is directly proportional to the quantity of electricity that passes through the electrolyte.

Mathematically:

$m \alpha Q$

where Q is quantity of electricity in coulomb

since $Q = It$

then $m \alpha It$

$m= EIt$

E is a constant known as the electrochemical equivalent of the substance.

Faraday's Second Law

Faraday's second law states that when the same amount of current is passed through different electrolytes/elements connected in series, the mass of substance deposited at the electrodes is directly proportional to their equivalent weight.

Differences	**Electrolytic cell**	**Electrochemical cell**
i. Electrical Structure	There is supply of electricity (direct current).	No electrical supply.
i. Electrodes	Metals can be the same or different	Both metals must be different
iii.Direction of electron flow	From anode to cathode through external circuit	From the more electropositive metal to the

		less electropositive metal
iv.Energy transformation	Electrical energy to chemical	Chemical energy to electrical energy
v.Reactions at the terminals	Oxidation occurs at the positive terminal while reduction occurs at the negative terminal	Reduction occurs at the positive terminal while oxidation occurs at the negative terminal

CHAPTER9

9.0 REDUCTION OXIDATION REACTION

9.1 FUNDAMENTAL CONCEPT OF OXIDATION AND REDUCTION REACTION

Oxidation and reduction reactions are two processes which usually occur simultaneously. The term ***redox*** is used by chemist as an abbreviation for the reactions and it involves not only the addition and removal of hydrogen and oxygen, but has been extended to include all electron-transfer processes. There definitions can be done under four headings.

9.1.1. IN TERM OF ADDITION AND REMOVAL OF OXYGEN

Oxidation is the addition of oxygen while reduction is the removal of oxygen.

i. $ZnO + C \longrightarrow Zn + CO$

Zinc is reduced while carbon is oxidized

ii. $CuO + CO \longrightarrow Cu + CO_2$

CuO reduced while carbon II oxide is oxidized.

9.1.2. In terms of addition and removal of hydrogen

Oxidation is the removal of hydrogen while reduction is the addition of hydrogen

i. $4HCI + O_2 \longrightarrow 2H_2O + 2CI_2$

Chlorine is oxidized while oxygen is reduced

ii. $H_2S + CI_2 \longrightarrow 2HCI + S$

Sulphur is oxidized while chlorine is reduced

9.1.3. In terms of electron transfer

Oxidation is the loss of electrons while reduction is the gain of electrons.

$2FeCI_2 + CI_2 \longrightarrow 2FeCl_3$

Iron (II) is oxidized while chlorine is reduced. The two half reaction can be written thus:

$2Fe^{2+} - 2e^- \longrightarrow 2Fe^{3+}$ (oxidized)

$CI_2 + 2e^- \longrightarrow 2Cl^-$ (reduced)

9.1.4. In terms of change in oxidation number

Oxidation is the increase in oxidation number while reduction is the decrease in oxidation number. A substance is oxidized if its oxidation number increases from left to right while decrease in the oxidation number of a substance from left to right is reduction.

$2C + 2HNO_3 \longrightarrow 2CO + H_2O + 2NO_2$

Here, the oxidation number of C = 0 on the left and on the right it became C = 2+. Therefore carbon has being oxidized.

In summary, oxidation is:

1. Addition of Oxygen
2. Removal of hydrogen
3. loss of electron
4. increase in oxidation number

While reduction is:

1. Removal of Oxygen
2. Addition of hydrogen
3. gain of electrons
4. decrease in oxidation number

9.2 OXIDISING AND REDUCING AGENTS

An ***oxidizing agent*** is a substance which brings about oxidation and its reduced in the cause of a redox reaction.

Also a ***reducing agent*** is a substance which brings about reduction and it's oxidized in the cause of a redox reaction. Illustration;

(i) $CuO + CO \longrightarrow Cu + CO_2$

Here copper has been reduced; therefore copper is the oxidizing agent while carbon that has been oxidized is the reducing agent.

(ii) $CuSO_4 + Zn \longrightarrow ZnSO_4 + Cu$

Here copper which is reduced is the oxidizing agent while zinc is oxidized hence the reducing agent.

$$CuSO_4 + Zn \longrightarrow ZnSO_4 + Cu$$

$$Cu^{2+} + \overset{0}{Zn} \rightarrow \underset{\substack{reduced \\ (Oxidising\ Agent)}}{\overset{o}{Cu}} + \underset{\substack{Oxidised \\ (Reducing\ Agent)}}{Zn^{2+}}$$

9.3 TESTS FOR OXIDING AGENTS

1. Most oxidizing agent give off iodine from acidified potassium iodide solution, forming a red-brown solution which turns dark-blue upon the addition of starch
2. Bubbling sulphur (IV) oxide through an aqueous solution of the substance will give tetraoxosulphate (VI) ion.

9.4 TESTS FOR REDUCING AGENTS

1. Reducing agents decolorize the deep purple colour of acidified potassium tetraoxomanganate (VII) ($KMnO_4$)
2. Reducing agents produce a green solution upon warming with an orange solution of acidified dipotassiumhepta-oxochromate (VI) ($K_2Cr_2O_7$)

9.5 OXIDATION NUMBER

Oxidation numbers arecharge assigned to element in the free or combined states according to some set rules. Oxidation number can also be known as oxidation state.

9.5.1 RULES FOR DETERMING OXIDATION NUMBER

1. The oxidation number of atoms of elements in an uncombined state is zero.

2. The oxidation number of a monoatomic ion is equal to the charge on the ion.

3. The sum of all the oxidation numbers of atoms in a molecule (or a polyatomic ion) is the charge on the particle.

4. In many compounds of oxygen, the oxidation number of oxygen is -2. But in peroxides it is -1 and when oxygen is combined with fluorine (e.g. OF_2), the oxidation number of oxygen is +2

5. In many compound of Hydrogen, the oxidation number of hydrogen is + 1 except in metal hydride where hydrogen has an oxidation number of -1

6. Halogens have a negative oxidation number but when they combine with oxygen e.g. in oxide, oxoacids and oxoanions, they have a positive oxidation number

Example 9.1

Calculate the oxidation states of chlorine in

(a) HOCI (b) $HClO_3$*(c)* $KClO_3$

Solutions

(a)

Because the molecule is not carrying any charge, then the sum of all its oxidation numbers will be equal to zero:-

$+ 1 - 2 + x = 0$

Making x subject we get

$x = +2 -1$

$x = + 1$: - The oxidation number of chlorine is + 1.

(b) H = 1

Cl = x

0=-6

Because it is triatomic we multiply the oxidation number of one oxygen atom (-2) by 3 to get -6

$+1 + X -6 = 0$

$x = +6 -1$

$x = +5$

(c) K = 1

CI= x, 0=-6

1 + x -6 =

0 x = +6-1

$x = +5$

Example 9.2

Find the oxidation number of chromium atom in potassium heptaoxodicromate (VI) $K_2Cr_2O_7$

K=1 x 2 = 2
Cr = xX 2 = 2x
0 = -2 x7 = -14

2 + 2x - 14 = 0
2x =+ 14-2
2x = +12
x = + $^{12}\!/_{2}$
x = +6
Cr = +6

9.6 BALANCING OF REDOX EQUATION

9.6.1 By ion-electron or half reaction method

This method is a limited method as it is appliedonly in balancing redox reactions taking place in aqueous solution, involving complete transfer of electrons. This method involves the following steps;

i. Identify the oxidizing agent and the reducing agents
ii. Write half equation for the reaction
iii. In acid and neutral solutions, balance first for oxygen and next for hydrogen as follows
  (a) Balance for every excess oxygen on one side, by adding water on the other side and $2H^+$ on the same side.
  (b) In alkaline medium, balance for every excess oxygen on one side by adding $2OH^-$ on the other side. And one H_2O on the same side and vice versa. If both H and O are in excess on the same side, add OH^- to the other side for each pair of excess H and O
iv. Balance each half reaction for charge.
vi. Cross multiply with the number of charges and cancel out as necessary (equalize the electrons).
vii. Add the two half equations, so that the electrons cancel out as well as other terms.
viii. Finally, insert necessary coefficients for the oxidizing and reducing agent according to the law of conservation of mass

Example 9.3

Balance the redox equation

$MnO_4^- + Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+}$

$$\underset{(Oxidizing\ Agent)}{\overset{7+}{MnO4^-}} \rightarrow Mn^{2+}\ (reduced)$$

$$\underset{(\text{Re}ducing\ agent)}{Fe^{2+}} \rightarrow Fe^{3+}\ (oxidized)$$

$MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$

$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$

Cross multiply with the number of charges and cancel out as necessary (equalize the electrons)

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

$5Fe^{2+} \longrightarrow 5Fe^{3+} + 5e^-$

Sum up

$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

Example 9.4

Balance the following equation using the half reaction method.

Reaction in acid medium

$BiO_3^- + Mn^{2+} \longrightarrow Bi^{3+} + MnO_4^-$

$\underset{(OA)}{BiO_3^-} \longrightarrow Bi^{3+}$ (reduced)

$\underset{(RA)}{Mn^{2+}} \longrightarrow \overset{+7}{M}no_4^-$ (*oxidized*)

$\underset{(OA)}{BiO_3^-} + 6H^+ \longrightarrow Bi^{3+} + 3H_2O$

$\underset{(OA)}{BiO_3^-} + 6H^+ + 2e^- \longrightarrow Bi^{3+} + 3H_2O$

$Mn^{2+} + 4H_2O \longrightarrow MnO_4^- + 8H^+$

$Mn^{2+} + 4H_2O \longrightarrow MnO_4^- + 8H^+ + 5e^-$

$5BiO_3^- + 3\overset{16}{O}H^{+} + 10e^- \rightarrow 5Bi^{3+} + \overset{7}{15}H_2O$

$2Mn^{2+} \quad 8H_2O \rightarrow 2MnO_4^- + 16H^+ + 10e^-$

$5BiO_3^- + 2Mn^{2+} + 14H^+ \rightarrow 5Bi^{3+} + 2MnO_4^- + 7H_2O$

Example 9.5

Balance the redox equation using half –reaction method

$MnO_4^- + Fe^{2+} \rightarrow MnO_2 + Fe^{3+}$

Reaction in alkaline Medium

Solution

$$\underset{(OA)}{\overset{+7}{Mn}O_4^-} \rightarrow \overset{+4}{Mn}O_2 \quad (reduced)$$

$$\underset{(RA)}{Fe^{2+}} \rightarrow Fe^{3+} \qquad (oxidized)$$

$$MnO_4^- + 2H_2O \rightarrow MnO_2 + 4OH^-$$

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$

$$Fe^{2+} \rightarrow Fe^{3+} + 3e^-$$

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$

$$3Fe^{2+} \rightarrow 3Fe^{3+} + 3e^-$$

$$MnO_4^- + 3Fe^{3+} + 2H_2O \rightarrow MnO_2 + 3Fe^{3+} + 4OH^-$$

Example 11.11

Balance the redox equation in alkaline medium using the half-reaction method.

$$MnO_4^- + C_2O_4^{2-} \rightarrow Mn^{2+} + CO_2$$

$$MnO_4^- + C_2O_4^{2-} \rightarrow Mn^{2+} + 2CO_2$$

$$\underset{(OA)}{\overset{+7}{Mn}O_4^-} \rightarrow Mn^{2+} \qquad (reduced)$$

$$\overset{+6}{C}_2 O_4^{2-} \rightarrow 2\overset{+8}{C}O_2 \qquad (Oxidation)$$

$$MnO_4^- + 4H_2O \rightarrow Mn^{2+} + 8OH \qquad (BFO)$$

$$MnO_4^- + 4H_2O + 5e^- \rightarrow Mn^{2+} + 8OH^- \qquad (BFC)$$

$$C_2O_4^{2-} - \rightarrow 5CO_2 + 2e^-$$

$$2MnO_4^- + 8H_2O + 10e^- \rightarrow 2Mn^{2+} + 16OH^-$$

$$5C_2O_4^{2-} \rightarrow 10CO_2 + 10e^-$$

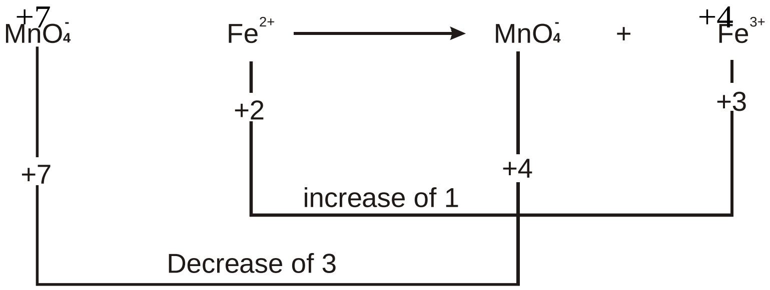
$$2MnO_4^- + 5C_2O_4^{2-} + 8H_2O \rightarrow 2Mn^{2+} + 10CO_2 + 16OH^-$$

9.6.2 OXIDATION NUMBER METHOD

Not all redox reaction occurs in aqueous solution and a complete transfer of electrons is always the casethus, to accommodate for this a wider balancing method is required.

The method is based on the fact that the partial or complete gain of electrons by the oxidizing agent must be equal to the partial or complete loss of electrons by the reducing agent. This method entails the following steps

I. Determine the oxidation number for every element in the equation. Record new oxidation number below affected element. Indicate all increases and decreases in oxidation number. Disregard signs



Ii Cross multiply each half equation by their respective change in oxidation state. To do this, multiply the Mn$^-$ half equations by 1 while the Fe half equation by 3.

$$MnO_4^- + 3Fe^{2+} \rightarrow MnO_2 + 3Fe^{3+}$$

iii. Balance for oxygen by adding water to every side short of oxygen

$$MnO_4^- + 3Fe^{2+} \rightarrow MnO_2 + 3Fe^{3+} + 2H_2O$$

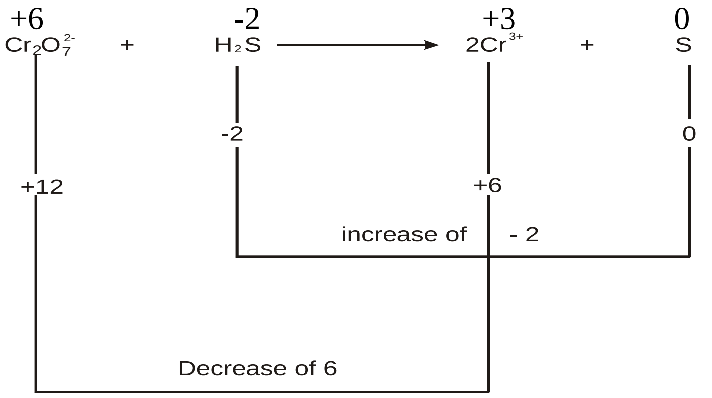
iv. Balance for hydrogen by adding hydrogen ion to any side short of hydrogen.

$$MnO_4^- + 3Fe^{2+} + 4H^+ \rightarrow MnO_2 + 3Fe^{3+} + 2H_2O$$

Example 9.6

Using the change in oxidation number method, balance the redox equation.

$Cr_2O_7^{2-} + H_2S \rightarrow Cr^{3+} + S$



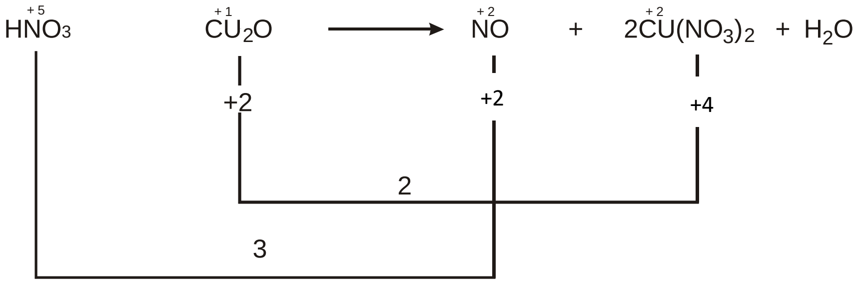
$$2Cr_2O7^{2-} + 6H_2S \rightarrow 4Cr^{3+} + 6S$$
$$2Cr_2O7^{2-} + 6H_2S \rightarrow 4Cr^{3+} + 6S + 14H_2O$$
$$2Cr_2O7^{2-} + 16H^+ + 6H_2S \rightarrow 4Cr^{3} + 6S + 14H_2O$$

Example 9.7

Balance the redox equation using the oxidation number method

Solution:

$$\overset{+1}{H}\overset{+5}{N}\overset{-2}{O}_3 + \overset{+1}{CU}_2O \rightarrow \overset{+2}{CU}(\overset{+5}{N}O_3)_2 + \overset{+2}{N}O + H_2O$$



$$2HNO_3 + 3CU_2O \rightarrow 6CU(NO_3)_2 + 2NO + H_2O$$
$$14HNO_3 + 3CU_2O \rightarrow 6CU(NO_3)_2 + 2NO + H_2O$$
$$14HNO_3 + 3CU_2O \rightarrow 6CU(NO_3)_2 + 2NO + 7H_2O$$

PRACTICE QUESTIONS

1. What is the oxidation number of (a) Aluminium in AI_2O_3 (b) Bromine in NaBr (c) Sulphur in $Na_2S_2O_3$ (d) Hydrogen in NH_3 (e) Magnesium in $KMnO_4$ (f) Chromium in K_2CrO_4
2. Balance the redox equation, using the half-reaction method and assume that the reaction takes places in an acidic medium.

   $Ag + NO_3^- \rightarrow Ag^+ + NO$

3. Iron (iii) chloride reacted with zinc to yield Zinc (ii) chloride and pure iron metal. Balance the redox equation assuming that the reaction occurred in an alkaline medium: $FeCl_3 + Zn \rightarrow ZnCl_2 + Fe$

4. Use the oxidation number method to balance the following redox equation

$(a)\quad Cu + HNO_3 \rightarrow Cu\ (NO_3)_2 + H_2O + NO$

$(b)\quad Ag + NO_3^- \rightarrow Ag^+ + NO$

$(c)\quad MnO_4^- + H_2C_2O_4 \rightarrow Mn_2^+ + CO_2$

8. Balance the redox equation

$Zn + HNO_3 \rightarrow Zn(NO_3)_2 + NO_2 + H_2O$

9. Balance the redox equation using the oxidation number method

$(a)\quad Zn + HNO_3 \rightarrow Zn(NO_3)_2 + NH_4NO_3$

$(b)\quad KMnO_4 + HCl \rightarrow KCl + MnCl_2 + H_2O + Cl_2$

CHAPTER 10

CHEMICAL EQUILIBRIUM

10.1 EQUILIBRIUM

Equilibrium can be defined as a state when two opposing reactions are equal. Equilibrium is a state of a system where there is no observable change in the properties of the system with regards to time. There are two types of equilibrium namely:

10.1.1 STATIC EQUILIBRIUM

In this type of equilibrium, there is a total standstill of the two opposing reactions. An example is when two kids are balanced on a sea-saw. At the point of balance, the kids and the sea-saw are in a point of total stand still

10.1.2 DYNAMIC EQUILIBRIUM

An example of this type of equilibrium is a boy running up an escalator, and the escalator is descending at the same rate at which the boy is ascending. When these two opposing processes (i.e. the boy ascending and the escalator descending) occur at the same time and rate there will be no observable change in the properties of the system.

Generally, dynamic equilibrium involving physical change is called **physical equilibrium** e.g. when liquid water and solid water (ice) exist together. Also, dynamic equilibrium involving chemical change is called the **chemical equilibrium.**

10.2 CHARACTERISTICS OF DYNAMIC EQUILIBRIUM

10.2.1 Constant macroscopic properties: That means that there is no overall large scale change. As the two opposing processes are occurring at the same time and rate, no net change is observed. The system seems to have come to rest to an external observer.

10.2.2 Continuing microscopic process: This means at equilibrium, molecular scale (very small scale) processes continue, although at a balanced rate but cannot be measured by external observer.

10.2.3 Equilibrium is reached only in a closed system: Considering the production of carbon dioxide (CO_2) by the decomposition of calcium trioxocarbonate (IV) ($CaCO_3$). At equilibrium, $CaCO_3$ will be decomposing into CO_2 and calcium (II) oxide (CaO) while the CO_2 and CaO produced will be reacting together again at the same time to form $CaCO_3$.

$$CaCO_{3(S)} \rightleftharpoons CaO_{(S)} + CO_{3(S)}$$

When this reaction takes place in an open system. It is obvious that as the CaCO decomposes to form CaO and CO_2, the CO_2 will be lost into the surrounding and thus there will be no CO_2 to react with the CaO to give the original $CaCO_3$. Therefore, equilibrium will not be reached. But in a closed system, either reaction can take place since there is no escape of any substance.

10.2.4 Equilibrium is attained from either direction: Again considering the above reaction, as $CaCO_3$ decomposes, CaO and CO_2 is formed. Also CaO then combines with CO_2 to produce $CaCO_3$. As the $CaCO_3$ is decomposing, CaO and CO_2 are combining at the same time and rate to form $CaCO_3$. Therefore, equilibrium is reached from the initial reaction and the final reaction.

10.2.5 None of the component in an equilibrium system is ever fully consumed: For the forward and the backward reaction to take place at the same time and rate, the reactants and products must be present in the system at all times.

10.3 EQUILIBRIUM IN REVERSIBLE REACTION

A reversible reaction is one that proceeds in both directions under suitable conditions. The two direction under which a reversible reaction can proceed are called the forward and the backward direction.

A reversible reaction is represented by two half arrows (⇌). The ⇀ arrow represents the forward reaction while ↽ represents the backward reaction.

$$\underset{\text{Reactants}}{A+B} \quad \rightleftharpoons \quad \underset{\text{Products}}{C+D}$$

10.4 EQUILIBRIUM CONSTANT

Equilibrium constant is the constantrelationship that exists between concentrations of reactants and products in a reversible reaction.It is explained by the law of mass action which states that at constant temperatures the rate of a reaction is directly proportional to the active masses of each of the reactants. The concentration of the reactants and products can also be used in place of the active masses.

Considering the reaction;

$$aA + bB \text{ ....} \rightleftharpoons \text{.................} cC + dD$$

Here a(moles) of A reacts with b(moles) of B to produce c(moles) of C and d(moles) of D. r_1 and r_2 represents the rate of forward and backward reaction respectively. At a constant temperature, the expression for the law of mass action is given by:

$r_1 \alpha\ [A]^a\ [B]^b \rightarrow$(Equation 10.1) for the forward reaction

$r_2 \alpha\ [C]^c\ [D]^d \rightarrow$(Equation 10.2) for the backward reaction

$r_1 = K_1\ [A]^a\ [B]^b \rightarrow$ (10.3)

$r_2 = K_2\ [C]^c\ [D]^d \rightarrow$ (10.4)

Where K_1 and K_2 = velocity constant for the forward and backward reactions respectively. At equilibrium, the rate of the forward reaction is equal to the rate of the backward reaction. Therefore equation (10.3) is equal to equation (10.4).

$r_1 = r_2$
$\therefore\ K_1[A]^a\ [B]^b = K_2[C]^c\ [D]^d$

Rearranging so as to bring the constants on the same side, we get: $\frac{K_1}{K_2} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

It should be noted that in the mass action expression, the concentration of the products must appear as the numerator while the concentration of the reactant as the denominator.

$\frac{K_1}{K_2}$ = K = equilibrium constant

Therefore, at constant temperature, the expression of the equilibrium constant is given by:

$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ Equation10.5

The expression is also called the **Equilibrium law**. This law tells us that at constant temperature regardless of the concentration of the reactants and products, the equilibrium constant is the ratio of the rate of the forward reaction to the rate of the reversed reaction. This ratio is a constant for that reaction. An example, is the reversible reaction at equilibrium between hydrogen and iodine to produce hydrogen iodide at a temperature of 458°C

$$I_{2(g)} + H_{2(g)} \longrightarrow 2HI_{(g)}$$

We have:

S/N	**Initial conc. in md/dm^3**			**Equilibrium conc. in mol/dm^3**			**Kc**
	$[H_2]$	$[I_2]$	$[H_1]$	$[H_2]$	$[I_2]$	$[H_1]$	
1.	2.40 x 10^{-2}	1.68 x 10^{-2}	0	0.92 x 10^{-2}	0.21 x 10^{-2}	3.00 x 10^{-2}	46.58
2.	2.44 x 10^{-2}	1.98 x 10^{-2}	0	0.77 x 10^{-2}	0.31 x 10^{-2}	3.34 x 10^{-2}	46.13
3.	2.46 x 10^{-2}	1.76 x 10^{-2}	0	0.92 x 10^{-2}	0.22 x 10^{-2}	3.08 x 10^{-2}	46.87
4.	0	0	3.04 x 10^{-2}	0.35 x 10^{-2}	0.35 x 10^{-2}	2.35 x 10^{-2}	46.40

From this results, it is observed that within the limits of experimental errors, and regardless of what the initial concentrations of hydrogen, iodine or hydrogen iodine were, at equilibrium when their concentration are substituted into the mass action expression, the result will always be constant.

The equilibrium constant Kc gives very useful information about the reaction. It tells how far a reaction proceed before equilibrium is reached.

1. If Kc is large, it indicates that the forward reaction goes almost to completion before equilibrium is reached. And at equilibrium, the product will be greater than the reactant.
2. If Kc = l, it indicates that the concentration of the products and reactants are the same when equilibrium is reached.
3. If Kc is lesser than 1, it indicates that the forward reaction does not go far before equilibrium, is reached. And at equilibrium, the reactant will be greater than the product.

The equilibrium constant is not affected by changes in concentration, pressure and catalyst. But a change in temperature affects the equilibrium constant. At higher temperature, K values increases and the product of that particular reaction. Changes in concentration and pressure will not affect the value of the equilibrium constant because the reaction will automatically adjust itself to attain equilibrium again to give the same Kc value. Also, the presence of a catalyst will not affect the value of the equilibrium constant, it will only lower the activation energy so that the rate of the reaction becomes faster, but still the same K value is obtained.

Equilibrium constant does not have a definite unit. The unit depends on the unit on the numerator and the denominator of the equilibrium law expression. Kc will have no unit when the reaction involves equal number of particles ‘in the products (numerator) and the reactant (denominator) sides, e.g.

$I_{2(g)} + H_{2(g)} \rightleftharpoons 2HI_{(g)}$

$$Kc = \frac{[HI]^2}{[H_2]\,[I_2\,]} \text{ units} \qquad = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})^3}$$

$$= \text{no units}$$

For reactions where the mass-action expression gives unequal particles in the numerator and denominator, K will have a unit e.g.

$$Kc = \frac{[NH]^2}{[N_2]\,[H_2\,]^3} \text{ units} \qquad = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})^3}$$

$$= \frac{1}{(\text{mol dm}^{-3})^2} \qquad = \text{mol}^{-2}\,\text{dm}^{6}$$

10.5 EQUILIBRIUM CONSTANTS INVOLVING GASES

So far we have expressed equilibrium constant with Kc. For reaction involving gases, it is more convenient to express equilibrium constant in terms of the partial pressure of the gases. This is because the partial pressure of gases is proportional to its mole fraction. Therefore, the equilibrium expression of our earlier example;

$H_{2(g)} + H_{2(g)} \quad \rightleftharpoons 2HI_{(g)}$

Becomes: $K_p = \frac{[P_{H1}]^2}{[P_{H2}]\,[P_{I2}]}$

8.6 THE RELATIONSHIP BF TWEEN Kc AND Kp

Using the ideal gas equation:
Pv = Nrt ……………………………….. (Equation 10.6)

Rearranging equation (10.6) we get:
$P = \frac{n}{v} RT$ ……………………………….. (Equation 10.7)
Where:
P = Pressure of the gas in atmosphere

R = Gas Constant
T = Temperature in Kelvin
$\frac{n}{v}$ Number of moles of the gas per volume(is the effective concentration of the gas)
$\therefore \frac{n}{v} = [gas]$
∴Equation (10.7) can be written thus:
P = [gas] RT …………………………… (Equation 10.8)

At constant temperature, the pressure of the gas will be directly proportional to the concentration of the gas. Thus,

$P \; \alpha \; [gas]$

Applying this in an equilibrium expression
$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$
We get
$Kc = \frac{[NO_{2(g)}]^2}{[N_2\,O_{4(g)}]}$ ………………………….. (10.9)

$Kp = \frac{[P_{NO_{2(g)}}]^2}{P_{NO_{4(g)}}]}$ ………………………….. (10.10)

From equation (8.8) P = [gas] RT. Substituting (10.8) in (10.10) we get:

$Kp = \frac{[NO_2]^2 (RT)^2}{[N_2\,O_4\,]RT} \qquad = \frac{[NO_2]^2\,(RT)}{[N_2\,O_4\,]}$ ……………….. (10.11)

Recall that from equation (10.9) that Kc = Kc = $\frac{[NO_{2(g)}]^2}{[N_2\,O_{4(g)}]}$

Therefore substituting (10.9) in (10.11) we get

$K_P = K_c\,RT$ ……………….............. Equation 10.12

Note: This is not always the case.

Let us consider another example:

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

$PV = nRT$ ……………………………….... (10.13)

$P = \frac{n}{v}RT$ ………………………………… (10.14)

$P = [gas]RT$ ……………………………... (10.15)

$Kc \quad = \frac{[NH_{3(g)}]^2}{[N_{2(g)}\,][H_{2(g)}\,]^3}$ …………………. (10.16)

$Kc \quad = Kp \quad = \frac{(PNH_{3(g)})^2}{(PN_{2(g)}\,)(PH_{2(g)})^3}$ ……….. (10.17)

$Kp \quad = \frac{(P_{NH3})^2}{(P_{N2})(P_{H2})^3}$ ……….......... (10.18)

$Kp = \frac{[NH_3]^2(RT)^2}{[N_{2(g)}]RT[H_{2(g)}]^3(RT)^3}$ ………………… (10.19)

$Kp = \frac{[NH_3]^2}{[N_{2(g)}][H_{2(g)}]^3(RT)^2}$ …………………..... (10.20)

Substituting (10.16) in (10.20) we get

$K_P = K_C\,(RT)^2$ ……………………………. (10.21)

The relationship between Kp and Kc can be generalized thus

$K_P = K_C(RT)^{\nabla n}$

Where;

∇n = (No. of moles on product side) – (No. of moles on reactant side)

Note: In this calculation, temperature must be expressed in Kelvin; pressure must be expressed in pascal.

Celsius temperature + 273 = Kelvin temperature 1 atm ≈ 105 Pascal

10.7 HETEROGENEOUS EQUILIBRIA

So far, we have being talking about a single phase equilibria (homogeneous equilibria). An equilibria involving more than one phase is called ***heterogeneous***

equilibria.

An example is $CaCO_{3(S)} \rightleftharpoons CaO_{(S)} + CO_{2(g)}$

Here, $CaCO_3$ and CaO are in a solid phase While CO_2 is in a gaseous phase.

The equilibrium expression for the reaction can be written thus:

$$K_C = \frac{[CO_{(s)}][CO_{2(g)}]}{[CaCO_{3(s)}]}$$

Since the ratio of moles to volume is constant for solid, then their concentration is constant. Therefore the equation can be simplified by writing the equilibrium expression 'in such a way that the concentration of solid and liquid (note, not aqueous) is removed in the equilibrium expression. Therefore, our equation becomes:

$K_C = [CO_{2(g)}]$ OR $K_P = P_{CO(g)}$

Also for $CaO_{(s)} + SO_{2(g)} \rightleftharpoons CaSO_{3(s)}$

We have:

$K_C = \frac{1}{[SO_2]_{(g)}}$ OR

$K_P = \frac{1}{P_{SO_{2(g)}}}$

Examples 10.1:

$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

If the equilibrium concentrations of the PCI_5 and PCl_3; are 0.015 mol/dm3 and 0.78 mol/dm^3 respectively,what is the concentration of Cl_2 if K_{eq} of the system is 35 at a certain temperature?

$$K_{eq} = \frac{[Cl_2][PCl_3]}{PCl_5}$$

$$35 = \frac{[Cl_2]0.78}{0.015}$$

$$\therefore [Cl_2] = \frac{35 \text{ x } 0.015}{0.78} \qquad = 0.67mol/dm^3$$

Example 10.2:

At equilibrium a 1.0L vessel contains 20mol of H_2, 18mol of CO_2, 12.0mol of water (H_2O) and 5.9mol of CO at 427°C. What is the value of K at this temperature?

$CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$

$K_{eq} = \frac{[CO][H_2O]}{[CO_2]\ [H_2]}$

$K_{eq} = \frac{5.9 \text{ x } 12.0}{18 \text{ x } 20} = 0.196 \qquad = 0.2$

Example 10.3:

At equilibrium, the quantities of the substances present in a $20dm^3$ container are: 1.70 mole of $COCl_2$, 0.76mol of CO and 1.50 mole of Cl_2 for the temperature at which equilibrium is reached. What is Keq for the reaction?

$COC1_{2(g)} \rightleftharpoons CO_{(g)} + Cl_{2(g)}$

$[COCl_2] = \frac{1.70}{20} = 0.085$

$[CO] = \frac{0.76}{20} = 0.038$

$[Cl_2] = \frac{1.50}{20} = 0.075$

$Keq = \frac{[CO][Cl_2]}{[COCl_2]} = \frac{0.038}{0.085} \text{ x } 0.075 = 0.0335mol/dm^2$

Example 10.4:

When 1.0mol of N_2O_4 is placed into a $5.0dm^3$ container at 100°C, part of it decomposed to form NO_2. At equilibrium, when the temperature is 100°C. 1.0mol of NO_2 is present. Calculate K for the reaction at 100°C. The balanced equation for the reaction is:

$N_2O_4 \rightleftharpoons 2NO_2$

	N_2O_4	NO_2
At start	1.0mol	0
	$= \frac{1.0}{5} = 0.2mol/dm^3$	
At equilibrium	0.1	1.0mol
	$= \frac{1.0}{5} = 0.2mol/dm^3$	

From the equation, 1 mol N_2O_2 decomposes to give 2mol of NO_2. Therefore 0.1 was decomposed to give 0.2mol NO_2 and so 0.1 N_2O_4 will be left at equilibrium.

$K_{eq} = \frac{(1.0)^2}{0.1} \qquad = \frac{0.04}{0.1} \qquad = 0.40$

Example 10.5:

A 1.00mol sample of $HI_{(g)}$ is heated to 510°C in a sealed flask with a volume of $1.00dm^3$. At equilibrium, 0.14mol of each of the product, $H_{2(g)}$ and $I_{2(g)}$ is present.

(a) Calculate the number of moles of HI that are present at equilibrium.
(b) Write the equilibrium expression for the reaction.
(c) Calculate K_{eq}

$2HI \rightleftharpoons I_2 + H_2$

		HI	I_2	H_2
Moles before reaction		1.0	0	0
Moles at equilibrium	x	0.14	0.14	

From the equation, 2 moles of HI decomposes to give 1 mole of I_2 and H_2. Therefore at equilibrium, 0.28 HI is used up and 0.72 HI will be left at equilibrium.

HI left at equilibrium = l – 0.28 = 0.72 moles

$K_{eq} = \frac{[H_2][I_2]}{[HI]_2}$

$K_{eq} = \frac{[0.14][0.14]}{[0.72]^2}$

$K_{eq} = \frac{0.0196}{0.5184} \qquad = 0.378 \text{ or } 3.73 \times 10^{-2}$

Example 8.6:

Hydrogen and iodine react at 426°C according to:

$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

If 1.00mol of H_2 and 1.00mol, I_2 are placed in a 1.00 litre vessel and allowed to react, what weight of HI will be present at equilibrium. K_{eq}= 55.3

	H_2	I	2HI
At start	1	1	0
At equilibrium	1 – x	1 – x	2x

$K_{eq} = \frac{(2x)^2}{(1-x)^2}$

$55.3 = \frac{(2x)^2}{(1-x)^2}$

$\sqrt{55.3} = \frac{2x}{1-x}$

$7.4\ (1 - x) = \frac{2x}{1-x}$

$7.4\ (1 - x) = 2x$

$7.4 - 74x = 2x$

$7.4 = 2x + 7.4x$

$7.4 = 9.4x$

$X = \frac{7.4}{9.4} = 0.79\text{mol}$

Concentration of HI = 2x

= 2 x 0.79

= 1.6mole

Reacting mass = Molar mass x No. of mole

= 126.9 x 1.6

= 203.04g

10.8 LECHATELIER’S PRINCIPLE

Lechatelier's Principle states that if an external constraint such as change in temperature, pressure or concentration is imposed on a chemical system in equilibrium, the equilibrium position will shift so as to annul the constraint. This principle is used to determine the optimum operating condition for chemical processes in industries.

10.8.1 EFFECT OF TEMPERATURE ON EQUILIBRIUM

The effect of temperature on equilibrium of reversible reaction depends on the value of ΔH (enthalpy change) of the reaction. A positive value for ΔH implies that the reaction is endothermic in the forward reaction i.e. heat is absorbed in the forward reaction and the product tend to be cooler, while the backward is exothermic. A negative value of ΔH implies that the reaction is exothermic in the forward reaction i.e. heat is evolved, or liberated in the forward reaction and the product will tend to be hotter, while the backward is endothermic.

$$\overset{\text{hot}}{A + B} \underset{\text{ExothermicEndothermic}}{\rightleftharpoons} \overset{\text{cold}}{C} \qquad \Delta H = + Ve$$

$$\overset{\text{cold}}{A + B} \underset{\text{EndothermicExothermic}}{\rightleftharpoons} \overset{\text{hot}}{C} \qquad \Delta H = - Ve$$

According to Lechatechier's principle, a change in temperature will cause the equilibrium position to shift so as to annul the effect of the change in temperature. Therefore in an endothermic reaction increase in temperature will shift the equilibrium to the forward reaction. While decrease in temperature, will favour the backward reaction. In the same way, in an exothermic reaction, increase in temperature will shift the equilibrium position to the backward reaction and decrease in temperature will favour the forward reaction.

Examples 10.6

1. $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \Delta H = 90.4kj/mol^{-1}$

This is an endothermic reaction. An increase in the temperature will shift the equilibrium to the forward reaction (right) giving a higher value of K meaning a greater yield of product. While a decrease will favour the backward reaction (left), giving a lower value of K which means a greater yield of reactant.

2. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}\ \Delta H = -395.7kj/mol^{-1}$

This is an exothermic reaction. An increase in temperature will shift the equilibrium to the left (backward reaction), while a decrease in temperature will shift the equilibrium position to the right.

10.8.2 EFFECT OF PRESSURE ON EQUILIBRIUM

For a change in pressure to affect a chemical equilibrium, the following must be in place;

1. At least one of the reactants or products in the reversible reaction must be gaseous.
2. The total moles of gaseous molecules in the forward and reversed reaction must not be the same e.g.

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

Backward reaction has 1 mole N_2 and 3 moles H_2 making a total of 4 moles, while forward reaction has 2 moles NH_3.

According to Lechatechier's principle, if a high pressure is imposed on a system in equilibrium, the equilibrium will shift to the position of low pressure. Also if low pressure is imposed on an equilibrium system, the equilibrium position will shift to the position of higher pressure.

It should be noted however, that the position of high pressure is that with the greater volume or greater number of moles. The position of low pressure is that with less volume or lesser numbers of moles.

In the reaction above, increase in pressure will favour the forward reaction while decrease in pressure will favour the backward reaction. In both cases the equilibrium constant K remains unchanged.

10.8.3 EFFECT OF CONCENTRATION ON EQUILIBRIUM

In an equilibrium mixture, there is a balance between the concentrations of the reactants and the products i.e. these concentrations are in a definite ratio which depends on the condition of the reaction. If more reactants are introduced into the equilibrium system the equilibrium will shift to the right favouring the forward reaction. This results in a proportional increase in the concentration of the products and so the equilibrium constant remains constant. Another way of increasing the amount of products formed is by continually removing the products from the system. Again in order to remove the constraint, the equilibrium will shift to the right, favouring the forward reaction.

Let us consider the reaction below:

$$3Fe_{(S)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(S)} + 4H_{2(g)}$$

If the concentration of a reactant or product is changed, the equilibrium position shifts to annul the change. Increase in the concentration of Iron will shift the equilibrium to the right and a decrease in hydrogen concentration will also favour the forward reaction. But when Fe_3O_4 is increase or H_2O is reduced, the backward reaction is favoured.

10.8.4 EFFECT OF CATALYST ON EQUILIBRIUM

Catalyst does not affect the position of equilibrium. It cannot be used to increase product formation. However, catalyst is very important in chemical industry because they affect the time taken for a reaction to reach equilibrium by lowering the activation energy for a positive catalyst and increasing the activation energy for a negative catalyst.

PRACTICE QUESTION

1. Write down the equilibrium constant for each of the following reaction?
   (a) $CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$
   (b) $C_2H_{4(g)} + H_2O_{(g)} \rightleftharpoons C_2H_5OH_{(g)}$
   (c) $2Mg_{(g)} + O_{2(g)} \rightleftharpoons 2MgO_{(g)}$
   (d) $C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)}$
   (e) $H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$
   (f) $CH_3COOH_{(aq)} \rightleftharpoons CH_3COO_{(aq)} + H^+_{(aq)}$
   (g) $NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$
   (h) $Ce^{4+}_{(aq)} + Fe^{2+}_{(aq)} \rightleftharpoons Ce^{3+}_{(aq)} + Fe^{3+}_{(aq)}$
   Use K or Kc depending on the states of the chemical.
2. At equilibrium at 1.0L vessel contains 20.0mol of H_2, 18.0mol of CO_2 of 12.0mo1 of H_2O and 5.9mol of CO at 427°C. What is the value of K at this temperature? Equation for the reaction is:

   $CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$

3. A reaction between gaseous sulphur dioxide (SO_2) and Oxygen (O_2) gas to produce gaseous sulphur trioxide (SO_3) takes place at 600°C. At that temperature, the concentration of SO_2 is found to be 1.50mol/L, the concentration of O_2 is 1.25mol/L, and the concentration of SO_3, is 3.50mol/L. Using the balanced chemical equation, calculate the equilibrium constant for the system.
4. For the reaction:
   $H_{2(g)} + 1_{2(g)} \rightleftharpoons 2HI_{(g)}$ at 425°C.

   Calculate [HI], given $[H_2 = [I_2] = 4.79 \times 10^{-4}$ mol/L and K = 54.3

5. What is the effect of increase in (i) temperature (ii) pressure and (iii) concentration on the equilibrium reaction?

   $SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}\ \Delta H = -395.7kj/mol^{-1}$

CHAPTER11

INTRODUCTION TO SOLUTION CHEMISTRY

11.1DEFINITION OF SOLUTION

A Solution is a homogeneous mixture of two or more substances in the same or different physical phases, intimately mixed that it behaves like a single substancein many ways. The substances forming the solution are called components of the solution. In solutions that consist of two components,the component which is present in the higheramount is called the solvent while the other component present in a lower amount is known as solute.With respect to the higher and lower amount we mean presence by mass or by moles. Sometimes this becomes confusing when dealing with substances with very close masses or moles. However, we will limit our discussion to binary solutions withvery obvious larger and lower components.

11.2 CLASSIFICATION OF SOLUTIONS

Solution can be classified based on different criteria;

11.2.1PHYSICAL STATE OF SOLUTE AND SOLVENT

Table 10.1 Classified of solution based on physical state of solute and solvent

S/NO	SOLUTE	SOLVENT	EXAMPLES
Solid Solution			
1	Solid	Solid	Alloys
2	Liquid	Solid	Hydrated salts, amalgam of Hg with Na
3	Gas	Solid	Dissolved gases in minerals
Liquid Solution			
4	Solid	Liquid	Salt/sugar in water,
5	Liquid	Liquid	Ethanol in water
6	Gas	Liquid	Carbonated drinks, O_2 in air
Gaseous Solution			
7	Solid	Gas	Iodine vapour in air
8	Liquid	Gas	Water vapour in air
9	Gas	Gas	Air , (O_2+ N_2)

Solutions were water is used as the solvent is called aqueous solution and if not, the solution is called non-aqueous solution.

11.2.2BASED ON THE AMOUNT OF SOLUTE DISSOLVED IN A SOLVENT

a. Unsaturated solution: This is a solution that contains lower solute than the solvent can accommodate at the given temperature. This means at that at a given temperature more solute can be dissolved in the solvent.

b. Saturated solution: This solution has just enough solute that can be dissolved in the solvent at that given temperature such that no solute can be dissolved further. Any further addition will precipitate back the solute

c. Supersaturated solution: This solution contains more solute than can be dissolve in the solvent at that particulartemperature.

One important concept of solutions is in defining how much solute is dissolved in a given amount of solvent. This concept is called concentration. Various words are used to describe the relative amounts of solute in a solution. Dilute describes a solution with very little solute, while concentrateddescribes a solution with a lot of solute. One problem is that these terms are qualitative (they describe only more or less) but not exactly how much.

Several units commonly used to express the concentrations of solution have been discussedin chapter five of this text. Many concentration values varydue to the contraction/expansion of the volume of solution with temperature. For example,Molarity varies with temperature such that concentration of solutions with identical numbers of solute and solvent species can be different at different temperatures. Therefore the more appropriate concentration units used for calculations involving many colligative properties are mole-based whose values are not dependent on temperature. Two such units are mole *fraction* and molality.

The mole fraction,X of a component A is the ratio of its molar amount to the total number of moles of all solution components:

$X_A = \frac{n_A}{n_A + n_B}$= mole fraction of liquid A

Mole fraction has no unit being the ratio of properties with identical units (moles).

Molality is a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms:

$m = \frac{\text{mole}}{KgSolvent}$

Since these units are computed using only masses and molar amounts, they do not vary with temperature and, thus, are better suited for applications requiring temperature-independent concentrations, including several colligative properties, as will be described in this chapter.

11.3 SOLUBILITY

Generally, only a certain maximum amount of solute can be dissolved in a given amount of solvent at a particular temperature. This maximum amount is called the solubility of the solute. It is usually expressed in terms of the amount of solute that can dissolve in 100 g of the solvent at a given temperature. These solubilities vary widely for different solutes. For example NaCl can dissolve up to 31.6 g per 100 g of H_2O, while AgCl can dissolve only 0.00019 g per 100 g of H_2O.The maximum amount of a solute that can be dissolved in a 100g of solvent at a given temperature is termed as its solubility at that temperature. The solubility of a solute in a liquid depends upon the following factors:

(i) Nature of the solute
(ii) Nature of the solvent
(iii) Temperature of the solution
(iv) Pressure (in case of gases)

11.4 RAOULT'S LAW

It states that the partial pressure exerted by any component of an ideal solution is proportional to its mole fraction in the solution.

$P_A \alpha X_A$,$P_A = k X_A$
$P°_A = k$
Therefore,$P_A = P°_A X_A$
$P°_A$, = vapour pressure of pure liquid

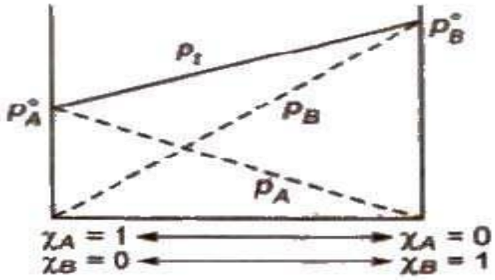
$X_A = \frac{n_A}{n_A + n_B}$= mole fraction of liquid A

In other words, the law can also be stated as; the partial pressure exerted by any component of an ideal solution is equal to the vapor pressure of the pure component multiplied by its mole fraction in the solution.

11.5 IDEAL SOLUTION

An ideal solution is one where the solvent – solvent (A-A) and the solute – solute (B-B) interactions are similar to the solvent – solute (A - B) interactions. An ideal solution obeys Raoult's law. That is the equilibrium partial pressure of the one of the component(say solvent component A) is directly proportional to its mole fraction. That is a plot of P_A against X_A gives a straight line graph.

Figure 10.1 A plot of the equilibrium partial pressure (P_A)against mole fraction (X_A)



$P_A \alpha X_A$,$P_A = k X_A$

$X_A = \frac{n_A}{n_A + n_B}$ = mole fraction of liquid A

The proportionality constant k = P°A, is the vapour pressure of pure liquid, hence
$P_A = P^0 X_A$ Similarly,
$P_B = P^0 X_B$
Therefore, Total pressure of the solution $P_T = P_A + P_B = P^0X_A + P^0 X_B$
Three conditions must be satisfied before a solution can be termed ideal;

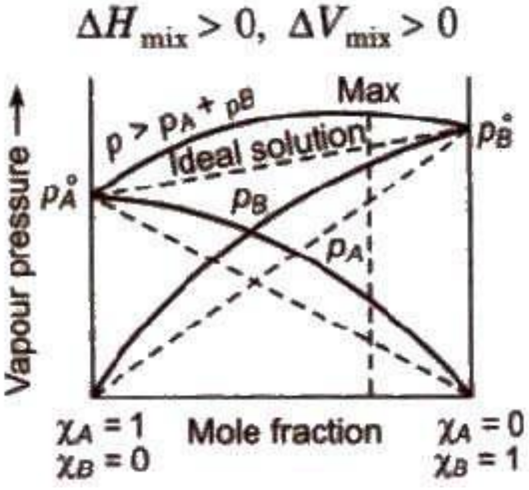
- i. Obeys Raoult's law i.e. $P_A = P^0X_A$, $P_B = P^0 X_B$
- ii. $\Delta H_{mix} = 0$ (ie no energy is evolved or absorbed)
- iii. $\Delta V_{mix} = 0$(ie no expansion is contraction on mixing)

11.6 NON IDEAL SOLUTION (DEVIATION FROM RAOULT'S LAW)

Those solutions which show deviation from Raoult‟s law are called non-ideal solution. There deviation from Raoults law can be positive or negative.
For such solutions,
$\Delta Hmix \neq 0$
$\Delta Vmix \neq 0$

11.6.1 Non-ideal solutions showing positive deviation: In such a case, the A – A or B – B interactions are stronger than A – B interactions and the observed vapour pressure of each component and the total vapour pressure are greater than that predicted by Raoults law. That is the vapour pressure of component A or B is greater than the vapour pressure of the pure solvent multiplied by the mole ratio. The solution will have more vapour than the solution.
$P_A > P^0X_A$
$P_B > P^0 X_B$

Figure 10.2 A Plot showing positive deviation from Raoult's law

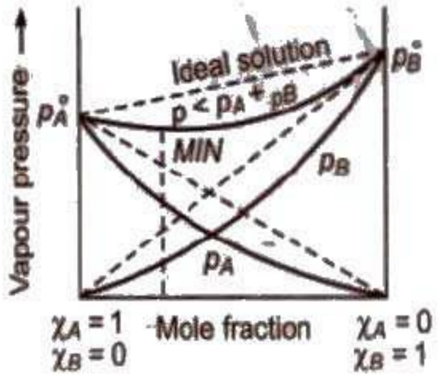


Examples of these type of solutions includes ethanol+ water, carbon disulphide(CS_2) + acetone, ethanol + cyclohexane

11.6.2Non-ideal solution showing negative deviation In this case, the A – A or B – B interactions are weaker than A – B interactions and the observed vapour pressure of each component and the total vapour pressure are lower than that predicted by Raoult‟s law. That is the vapour pressure of component A or B is lower than the vapour pressure of the pure solvent multiplied by the mole ratio. The solution will be lower vapour than the solution.

$P_A < P^0 X_A$
$P_B < P^0 X_B$

Figure 11.3 A Plot showing negative deviation from Raoult's law



Non-ideal solution showing negative deviation

Examples of these type of solutions includes methanol + acetone, acetone + chloroform ($CHCl_3$), H_2O + HCl, H_2O + HNO_3, $CHCl_3$ + CH_3COCH_3

11.8 COLLIGATIVE PROPERTIES

Colligative propertiesare properties that a solution exhibits which depend only on the number of solute particles(or concentration of the solute) that is dissolved in the solvent and not on the chemistry of the solute.These properties are;

i. Lowering of vapour pressure of the solvent
ii. Elevation of boiling point of the solvent
iii. Depression of freezing point of the solvent
iv. Osmotic pressure

Dissolving a solute in a solvent interferes with the activities of the solvent particles such that the solution that is produced has different physical properties compared to the pure solvent alone. This interference result in lowering of the vapour pressure, elevation of the boiling point and depression of the freezing point. Since these properties are associated with the number of solute particles in the solution, one can use them to obtain the molecular weight of the solute.

11.8.1Lowering of vapour pressure of the solvent: When a non- volatile solute such as sugar or common salt is dissolved in a solvent the resultingsolution will have a lower vapour pressure than the pure solvent. The amount of lowering is dependent on the fraction of solute particles in the solution, and the change is usually not much at all as long as the solute itself does not have a significant vapour pressure (nor has a vapor pressure of zero). This colligative property is called vapour pressure depression (or lowering*)*.The vapour pressure of a solvent in a solution is always lower than the vapor pressure of the pure solvent. The vapor pressure lowering is directly proportional to the *mole fraction* of the solute.

$P_{soln} \propto \chi_{solv}$

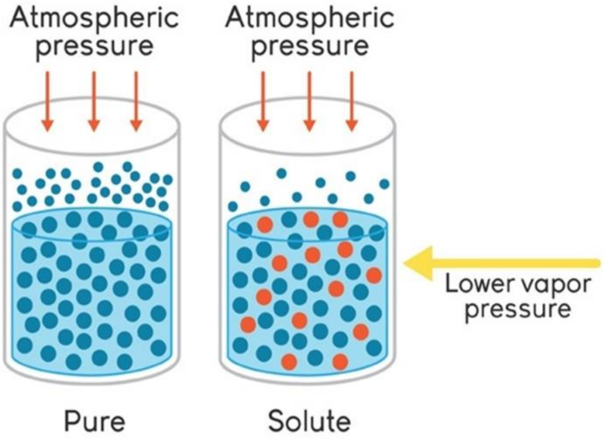
$P_{soln}=\chi_{solv}P^{o}_{solv}$

Where
P_{soln} = the vapour pressure of the solution
χ_{solv} = the mole fraction of the solvent particles
P^{o}_{solv} = the vapour pressure of the pure solvent at that temperature

This equation is also known as Raoult's law. The assumption here is that solute particles take positions at the surface in place of solvent particles, so not as many solvent particles can be evaporated.

$\chi_{solv} + \chi_{solute}=1$
where, χ_{solute} = mole fraction of the solvent or solute.

Figure 11.4 A demonstration oflowering of vapour pressure experiment



The change in vapor pressure (ΔP) can be expressed as

$\Delta P=P_{soln}-P^{o}_{solv}= \chi_{solv} P^{o}_{solv}-P^{o}_{solv}$

or

$\Delta P=(\chi_{solv}-1)P^{o}_{solv}=\chi_{solute}P^{o}_{solv}$

Example 11.1: Calculate the vapor pressure of a solution made by dissolving 47.0 g glucose, $C_6H_{12}O_6$, in 545 g of water. The vapor pressure of pure water is 47.1 torr at 37°C. (Molar masses, water = 18 g/mol , glucose = 180.2 g/mol)

Solution

We will use Raoult's Law, $P_{soln} = \chi_{solv} P^{o}_{solv}$

$\chi_{solv} = \frac{\text{nsolv}}{\text{nsolv} + \text{nsolute}}$

Solvent = 545g water

Solute = 47g glucose

Mole ratio of solvent = $\chi_{solv} = \frac{\text{nsolv}}{\text{nsolv + nsolute}}$

$\chi_{solv} = \frac{\text{nwater}}{\text{nwater+ nglucose}}$

$n_{water} = \frac{\text{reacting mass of water}}{\text{molar mass of water}}$

$$\frac{545g}{18g/mol} = 30.28mol$$

$n_{glucose} = \frac{\text{reacting mass of glucose}}{\text{molar mass of glucose}}$

$$\frac{47g}{180.2g/mol} = 0.261mol$$

$\chi_{solv} = \frac{30.28mol}{30.28mol + 0.261mol} = \frac{30.28mol}{30.54mol} = 0.99$

P_{soln}=0.99×47.1=46.63torrnot much of a change at all.

11.8.2Elevation of boiling point of the solvent: A liquid boils at a temperature when its vapour pressure is equal to the external pressure on the surface of the liquid. Boiling-point elevation describes the process whereby the boiling point of a liquid (a solvent) is increased by the addition of a non-volatile solute, thus the solution has a higher boiling point than its pure solvent.The solute particles interfere with the solvent particles in a manner that solution boil at a higher temperature compared to the pure solvent. Usually, the boiling point of water increases by 0.512^{0}C whenever one mole of any non-electrolyte is dissolved in 1kilogram of water. And the boiling point of the pure solvent is directly proportional to the molal concentration of the solute.

The change in boiling point of dilute solution ΔT_b, from that of the pure solvent is given by the expression.

$\Delta T_b = mK_b$

Here, m = molality of the solution
K_b = molal boiling point elevation constant. This value is a characteristic of the solvent and it varies with different solvent. Some boiling point elevation constants (as well as boiling point temperatures) are listed in Table11.2

Table 11.2 Boiling Points, freezing points, molal boiling point elevation and freezing point depression constants for various solvents (Liquids)

Liquid	**Boiling Point (°C)**	**K_b (°c/m)**	**Freezing Point (°C)**	**K_f (°c/m)**
$HC_2H_3O_2$	117.90	3.07	16.6	3.9
C_6H_6	80.10	2.53	5.48	5.12
CCl_4	76.8	4.95		
H_2O	100.00	0.512	0.00	1.86
Chloroform	61.26	3.63	-63.5	4.68
nitrobenzene	210.9	5.24	5.69	8.1

11.8.3 Depression of freezing point of the solvent: The freezing point of a liquid (i.e. a pure solvent or a solution) is the temperature at which its solid and liquid are at equilibrium so that both have equal vapour pressure. Here the present ofsolute particles interfere with solvent particles such that the ability of the solvent particlesto effectivelyform solid (ice) is hampered and solidification(freezing) then occursat a lower temperature. This is called freezing point depression.This explains why sea water with its large salt content freezes at lower temperatures than pure water.The equation to calculate the change in the freezing point for a solution is similar to the equation for the boiling point elevation:

$\Delta T_f = mK_f$

Where,
m= molality of the solution
K_f = thefreezing point depression constant, which is also a characteristic of the solvent.

Although freezing-point depression is similar to boiling point elevation but the magnitude of the freezing point depression is larger than the boiling point elevation for the same solvent and the same concentration of a solute. Because of these two phenomena, the liquid range of a solvent is increased in the presence of a solute.

Example 11.2: Calculate the boiling point elevation of water when 1.20g of glycerin $C_3H_8O_3$ is dissolved in 47.8g of water (Kb for water = 0.501C/m, Atomic masses, C = 12 g/mol, O = 16 g/mol, H = 1 g/mol)

Solution

Molar concentration of glycerin $M_{\text{glycerin}} = \frac{\text{reacting mass of glycerin}}{\text{molar mass of glycerin}}$

$M_{\text{glycerine}} = \frac{1.20}{92} = 0.011$

Molal concentration of glycerin $m_{\text{glycerin}} = \frac{mole}{\text{Kg Solvent}} = \frac{0{,}011}{0.478} = 0.228\text{m}$

$\Delta T_b = mK_b$

$\Delta T\text{b} = 0.228m\ x\ 0.501^0\text{C}/m = 0.117^0\text{C}$

Example 11.3: Calculate the boiling and freezing point of a 0.8m aqueous solution of glucose ($\text{Kb} = 0.51^0\text{C}/\ m$, $K_f = 1.86^0\text{C}/m$)

Solution

$$\Delta T\text{b} = mKb$$

$\Delta T\text{b} = 0.8m\ x\ 0.501^0\text{C}/m$

$\Delta T\text{b} = 0.41^0\text{C}$

$T_b = 100^0\text{C} + 0.41^0\text{C} = 100\ .41^0\text{C}$

$$\Delta Tf = mKf$$

$\Delta Tf = 0.8m\ x\ \ 1.86^0\text{C}/m$

$\Delta Tf = 1.49^0\text{C}$

$T_f = 0^0\text{C} - 1.49^0\text{C} = -1\ .49^0\text{C}$

11.8.4Exhibition of osmotic pressure: Osmosis is the flow of solvent molecules to the region of solute molecules through semi- permeable membrane. The semi-permeable membrane stops the flow of solute molecules only. If a solution and its pure solvent are placed side by side in between a semi-permeable membrane, more solvent molecules would flow out from the pure solvent into the solution than vice versa. That flow of solvent from the pure solvent side makes the volume of the solution to rise while the volume of the solvent drops. When the height difference between the two sides becomes large enough, the net flow through the membrane ceases due to the extra pressure exerted by the excess height of the solution chamber and equilibrium is thereby reached. The pressure difference between the two regions at equilibrium is called the osmotic pressure of the solution. Figure 11.4shows a typical setup for measuring the osmotic pressure of a solution.

For dilute solutions, osmotic pressure is proportional to the molar concentration M of the solute
$\Pi \alpha M$
$\Pi = MRT$

Where;
Π = osmotic pressure of a solution
M = molarity of the solution
R is the ideal gas law constant
T is the absolute temperature. This equation is reminiscent of the ideal gas law we considered in our earlier chapter; Pv = nRT
Also, $\Pi = \frac{n}{v}RT$
OR $\Pi v = nRT$

Example 11.4

What is the osmotic pressure of a 0.333 M solution of $C_6H_{12}O_6$ at 25°C?
(R = 0.08206 L atm/mol K)

Solution

First we need to convert our temperature to kelvins:

$T = 25 + 273 = 298$ K

Now we can substitute into the equation for osmotic pressure:

$\Pi = MRT$

Π = 0.333M x 0.08206 L atm/mol Kx 298 K = 8.143atm

Example 11.5

What is the osmotic pressure of a 0.0522 M solution of $C_{12}H_{22}O_{11}$ at 55°C?

Solution

First we need to convert our temperature to kelvins:

$T = 55 + 273 = 328$ K

Now we can substitute into the equation for osmotic pressure:

$\Pi = MRT$

Π = 0.0522M x 0.08206 L atm/mol Kx 328 K = 1.405atm

PRACTICE QUESTION

1. If 115g of N_2 are mixed with 145g of O_2, what is the mole fraction of each component?

2. If 34.5 g of NaCl are mixed with 65.5 g of H_2O, what is the mole fraction of each component?
3. A solution is made by mixing 43.9 g of $C_6H_{12}C_6$ in 100.0 g of H_2O. If the vapour pressure of pure water is 26.5 torr at a particular temperature, what is the vapour pressure of the solution at the same temperature?
4. At 300°C, the vapour pressure of Hg is 32.97 torr. What mass of Au would have to be dissolved in 5.00 g of Hg to lower its vapour pressure to 25.00 torr?
5. If 123 g of $C_{10}H_{16}O$ are dissolved in 355 g of C_6H_6, what is the boiling point of this solution?
6. A solution of $C_2H_2O_4$ in CH_3COOH has a boiling point of 123.40°C. What is the molality of the solution?
7. If 25.0 g of $C_6H_{12}O_6$ are dissolved in 100.0 g of H_2O, what is the freezing point of this solution?
8. $C_8H_{17}OH$ is a nonvolatile solid that dissolves in C_6H_{12}. If 7.22 g of $C_8H_{17}OH$ is dissolved in 45.3 g of C_6H_{12}, what is the freezing point of this solution?
9. If 25.0 g of $C_6H_{12}O_6$ are dissolved in H_2O to make 0.100 L of solution, what is the osmotic pressure of this solution at 25°C?
10. At 298 K, what concentration of solution is needed to have an osmotic pressure of 1.00 atm?

CHAPTER12

INTRODUCTION TO NUCLEAR REACTION AND RADIOACTIVITY

After the discovery of the cathode rays, many scientists became interested in the study of different types of rays. Their researches led to the discovery of the radioactive rays. In 1846 Wilhelm Rontgen discovered that when cathode rays hit glass or metals new and very unusual rays were emitted. These rays were highly energetic and could penetrate matter. Also, the rays could darken covered photographic plates and they produced fluorescence in various substances. However they were not deflected by magnetic and electric fields, suggesting that rays did not consist of charged particles. Rontgen named the rays X- rays.

Soon after Rontgen discovery, Antoine Becquerel in 1896 while studying the fluorescent properties of substances, accidentally discovered that certain compound containing Uranium emitted radiation. The radiation could penetrate opaque materials like thick paper and thin metals sheet after which it will also darken photographic plates. The rays also had properties similar to X- ray by being highly energetic and not consisting of charged particles.

In 1898, Pierre and Marie Curie who were both Becquerel's students detected that thorium had radioactive properties and that the level of radiation in a naturally occurring uranium ore (also known as pitchblend), was quite higher than its uranium content. As a result of this observation, they subjected the uranium ore to further analysis and two new radioactive elements – polonium and radium were isolated. Radium was found to be several million times more radioactive than the same mass of uranium.

Further studies later revealed that the phenomenon was different from ordinary chemical reaction which involves electron transfer by atoms. This phenomenon involves changes in the atomic nuclei (that is new elements were formed by radioactive radiation),therefore, Becquerel named the phenomenon radioactivity. And elements which exhibit radioactivity were termed radioactive. Thus, radioactivity can be defined as the spontaneous disintegration of a radioactive element. It can also be defined as the emission of radiation from radioactive element.

RADIATIONS TYPES AND CHARACTERISTICS

Radioactive substances emits radiation spontaneously, independent of temperature and pressure. The energy released during radioactive emission is known as nuclear energy which is about a million times higher than the energy released during any chemical reaction. Radioactive radiations share some similar properties with light such as having effect on photographic plate, ionizing the gas through which the radiation passes and also causing flouresence in certain substances such zinc sulphide. It also leave a track in a cloud chamber – this can used as a means of identifying the type of radiation. Unlike light rays, however radioactive radiations can penetrate opaque materials. Three major radiations are emitted by radioactive elements which can be differentiated based on their behaviors in an electric field. They are:

i. Alpha rays
ii. Beta rays
iii. Gamma rays

Alpha(α) – rays

The α -rays are fast moving streams of positively charged particles , with each particle having a mass number of 4, an atomic number of 2 and 2 unit positive charge. That is each α – particle is a helium nucleus and it is 8,000 times the mass of a beta particle. Because of their large mass and their positive charge, the particles are attracted to a small extent towards the negative plate of an electric field. The same large size of alpha particles gives them the highest ionizing power (that is the greatest ability to damage tissue) and makes them less able to penetrate matter. As such can be stopped or absorbed by a thin sheet of paper or an aluminum foil that is only 0.1mm thick. And also the rays cannot be penetrated through the human skin. However, there is great danger when the beta emission source gets inside someone. The rays can cause fluorescence in some materials such as zinc sulphide. The emission of an α – particle result to the formation of a new element having 4 mass number and 2 atomic number short from the original radioactive element. examples are the emission of α – particle respectively from radium and polonium.

$${}^{224}_{88}\text{Ra} \longrightarrow {}^{224}_{88}\text{Ra} + {}^{4}_{2}\text{He}$$

$${}^{208}_{84}\text{Po} \longrightarrow {}^{204}_{82}\text{Pb} + {}^{4}_{2}\text{He}$$

Beta (β) –rays

Beta – rays are very fast moving streams of electrons with each particle having a mass number of zero with atomic number of -1 and a charge of -1. They are deflected significantly toward the positive plate of an electric field because they are negatively charged and much smaller than alpha particles. Also because of their small size, they have much less ionizing power (less ability to damage tissue) and much greater penetration power. The beta particles have penetrating range of about 3m in air and about 4mm in aluminium and can be stopped by a one-quarter inch thick sheet of aluminum. This indicates that the rays cannot be penetrated through the human skin. However, there is great danger when the beta emission source gets inside someone. They can cause fluorescence in some materials such as anthracene but not zinc sulphide. The emission of a β– particle results in the formation of a new element that has its atomic number increased by 1 and its mass number remaining the same. An example is the emission of a β - particle from thorium.

$${}^{234}_{90}\text{Th} \longrightarrow {}^{234}_{91}\text{Pa} + {}^{0}_{-1}\text{e}$$

Gamma (γ) – rays

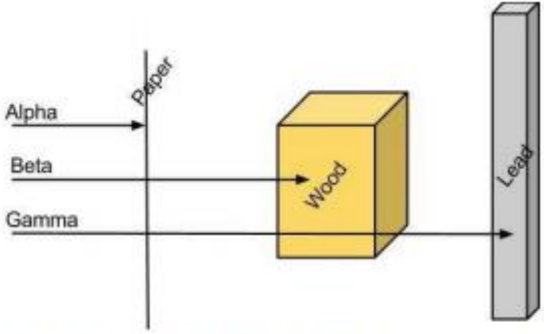
Gamma rays are not particles but a high energy form of electromagnetic radiation (similar to x-rays or visible light but except more powerful). Gamma rays are energy that has no mass or charge. Gamma rays have tremendous penetration power and require several inches of dense material (like lead) to shield them. Gamma rays may pass all the way through a human body without striking anything. They are capable of penetrating through layers of matter opaque to ordinary light. They are considered to have the least ionizing power and the highest penetration power. Their penetrating power allows them to penetrate about 100m through air and also 0.5m of iron or lead. They can cause fluorescence in some materials such as sodium iodide and zinc sulphide. Figure 11.1 shows the properties of these rays.

FIGURE 11.1 THE PROPERTIES OF THE MAJOR RADIOACTIVE RAYS

	Alpha (α)– rays	Beta (β)–rays	Gamma (γ)– rays
Nature	Helium nuclei, $^{4}_{2}He$	Electron, $^{0}_{-1}e$	Electromagnetic radiation
Electrical charge	+2	-1	No charge (0)
Mass	4unit	$^{1}/_{1840}$ unit	No mass (0)
Velocity	About $^{1}/_{20}$ the speed of light	Varies (from 3 - 99% of speed of light)	Speed of light
Relative penetration	1	100	10,000
Absorber	Thin paper	Thin metal	Large lead block

FIGURE 11.2 The effect of electric field on the three types of radiation

FIGURE 11.3 The three types of radiation and their absorbers



Alpha particles can be blocked with paper. Beta particles penetrate through paper, but are blocked by wood. Gamma particles are capable of penetrating paper and wood but can be blocked by a few inches of lead.
CC Tracy Poulsen

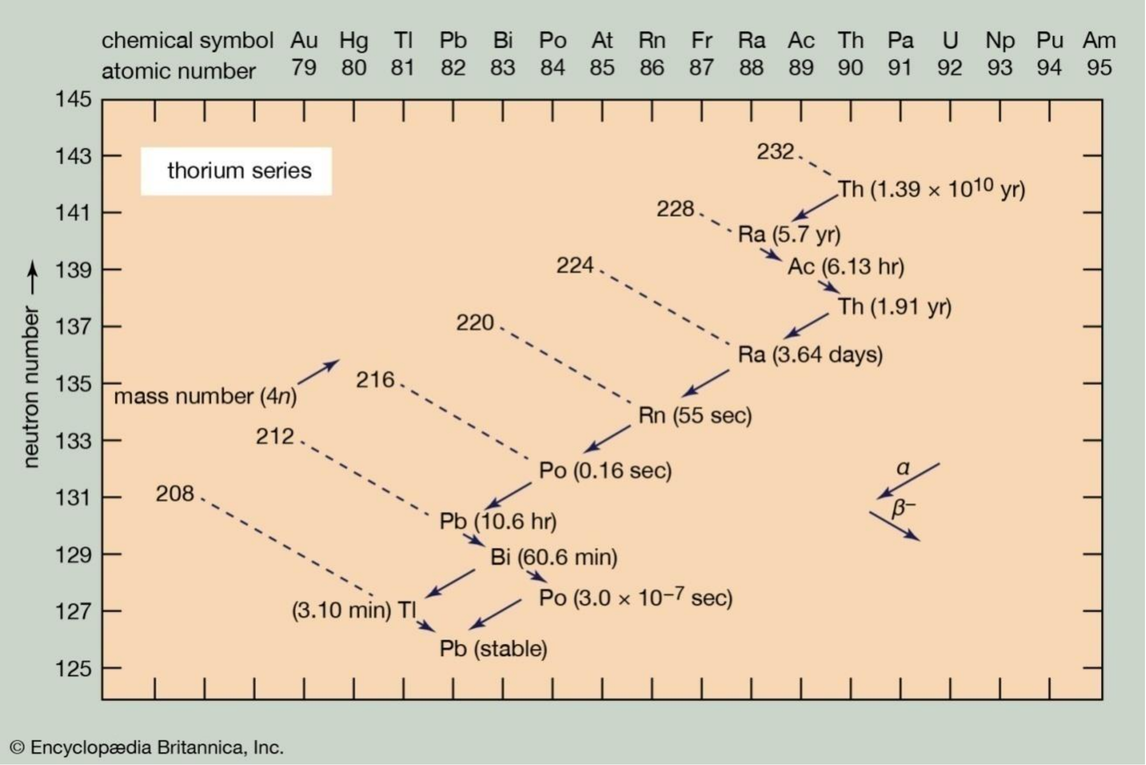
NATURAL RADIOACTIVE DECAY SERIES

Usually, elements (nucleus) formed during radioactive decay are also unstable and so would disintegrate further until a stable element is formed. There are a series of changes that would occur at varying rates, ranging from less than a second to millions of years before the final formation of a stable element. There are three natural occurring radioactive decay series which are named after the longest lived element in the series. They are;

The thorium series

The thorium series begins with thorium ($^{232}_{90}Th$) which has a half-life of 1.39 x 10^{10} years and ends with the stable nuclide of lead ($^{204}_{82}Pb$) after 12steps of disintegrations through the emission of alpha and beta particles. This series is sometimes termed 4n series because the mass number of each of the series is exactly divisible by 4.

FIGURE 11.4 The thorium series



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The uranium series

The uranium series begins with uranium (${}^{238}_{90}U$) which has a half-life of 4.5 x 10^9 years and ends with the stable nuclide of lead (${}^{206}_{82}Pb$) after 15steps of disintegrations through the same process as in Thorium. This series can also be called 4n + 2.

The actinium series

The actinium series is named after its first-discovered member, actinium -227. The series actually begins with uranium (${}^{235}_{90}U$) and after about 13steps of disintegrations through the emission of alpha and beta particles ends with lead (${}^{207}_{82}Pb$). This series is also called 4n + 3 series.

The neptunium series

RATE OF RADIOACTIVE DECAY/ half - life

Radioactive decay occurs at varying rates, ranging from less than a second to millions of years. For a particular radioactive element, spontaneous disintegration usually occurs at the same rate irrespective of the state or condition of the sample. That is a particular radioactive element would emit the same type of radiation at the same rate regardless of its chemical state, applied pressure, electromagnetic or gravitational field. Therefore, the rate of a radioactive decay can be used to characterize a radioactive element. This rate follows a first order rate law that requires the rate of radioactive radiation is proportional to the number of the radioactive atoms present. Given the equation for a radioactive decay process;

$$A \quad B+x+\Delta E \qquad \longrightarrow$$

This rate is usually expressed in terms of half-life of the radioactive element. The half – life of a radioactive element is the time taken for it to disintegrate to half the mass of the original size. In other words half – life is the time taken for half of the radioactive element to decay.