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Ministry of Higher Education and Scientific Research
MUSTAPHA STAMBOULI UNIVERSITY, MASCARA
FACULTY OF SCIENCE AND TECHNOLOGY

Polycopy of matter

Chemicals I (STRUCTURE of MATTER) Course and corrected application exercises

Presented by: Dr KHELLOUL NAWEL

For students: 1st year Common Base Licences (L1) (ST)

Academic year 2024/2025

Educational content

First year

Semester 1

Fundamental Teaching Unit 1

Structure of Matter

Structure of Mater programme (2 courses + 1 TD) / week:

Chapter 1: Basic Chemistry Terms. (2 weeks)

States and macroscopic characteristics of the states of matter

Changes in states of matter. notions of atom, molecule, mole, Avogadro number, atomic mass unit, atomic and molecular molar mass, molar volume, Weight law: Conservation of mass (Lavoisier), chemical reaction. Qualitative aspect of the matter. Quantitative aspect of the matter.

Chapter 2: Main Constituents of Matter (3 weeks)

Introduction: Faraday experiment: relationship between matter and electricity.

Identify the constituents of matter, including the atom and its physical properties (mass and charge). Rutherford's planetary model, Presentation, and characteristics of the atom (symbol, atomic number Z, mass number A, number of protons, neutrons, and electrons). Isotopy and relative abundance of different isotopes, Separation of isotopes and determination of an atom's atomic mass and average mass: Mass spectrometry: Bainbridge spectrograph, Binding and cohesive energy of nuclei, Stability of nuclei.

Chapter 3: Radioactivity- Nuclear Reactions (2 weeks)

Natural radioactivity (α, β, and γ radiation), artificial radioactivity and nuclear reactions, Kinetics of radioactive decay, Applications of radioactivity.

Chapter 4: The Electronic Structure of the Atom (2 weeks)

Wave-corpuscle duality, Interaction between light and matter, Bohr's atomic model: hydrogen atom, The hydrogen atom in wave mechanics, Polyelectronic atoms in wave mechanics.

Chapter 5: The Periodic Classification of the Elements (3 weeks)

Periodic classification by D. Mendeleiev, Modern periodic classification, Evolution and periodicity of the physicochemical properties of the elements, Calculation of the radii (atomic and ionic), the energies of successive ionization, electron affinity, and electronegativity (Mulliken scale) by the rules from Slater.

Chapter 6: Chemical Bonding (3 weeks)

The covalent bond in Lewis theory, the polarized covalent bond, dipole moment, and partial ionic character of the bond, Geometry of the molecules: Gillespie theory or VSEPR, The chemical bonding in the quantum model.

Table of contents

CHAPTER I Basic Chemistry Terms 1

I. Matter 1

I.1. Definition 1

I.1.2. Physical properties 1

I.1.3. Chemical properties 1

I.2. States of matter and separation methods 1

I.3. Change in the state of matter 2

I.3.1. Characteristics of state changes 3

I.4. The characteristic properties of matter and its states. 4

I.4.1. The Volume and the mass 4

I.4.1.1. Volume 4

I.4.1.2. Mass 4

I.4.2. The pressure and the temperature 4

I.4.2.1. The pressure 4

I.4.2.2. The temperature 4

I.5.Atomic concepts 4

I.5.1. The atom 4

I.5.2. Molecule 5

I.5.3. Mole 5

I.5.4. Avogadro's Number: 5

I.5.5. Molar mass atomic 6

I.5.6. The molecular mass of a compound 6

I.5.7. Atomic mass unit (uma) 6

I.5.8. molar Volume 6

I.6. The weight law 6

I.6.1. Law of Conservation of Mass: (Lavoisier) 6

I.6.2. Law of definite Proportions: Law of Proust 7
I.6.3. Law of multiple proportions: Dalton1804 7
I.7. Aspect qualitatif de la matière 7
I.7.1. pure substance 7
I.7.2. Elements 7
I.7.3. compound 8
I.7.4. Mixture 8
  I.7.4.1. Homogeneous mixture 8
  I.7.4.2. Heterogeneous Mixture 8
I.7.5. Solution 9
  I.7.5.1. Solvent 9
  I.7.5.2. Solute 9
  I.7.5.3. Dilution 9
  I.7.5.4. Solubility 10
  I.7.5.5. saturated solution 10
  I.7.5.6. unsaturated solution 10
I.8. Quantitative aspect of the matter 10
I.8.1. quantity of matter 10
I.8.2. Molar Concentration 10
I.8.3. Molarity 10
I.8.4. Molality 11
I.8.5. Mass concentration 11
I.8.6. Mass fraction 11
I.8.7. mole fraction 12
I.8.8. Normality 12
I.8.9. Density 13
  I.8.9.1. Density of solids and liquids relative 13

I.8.9.2. The density of a gas: ... 13
CHAPTER II Main Constituents of Matter ... 14
II. Introduction ... 14
II. 1. Faraday's Experiment: The Relationship Between Matter and Electricity ... 14
II.2. Discovery of Sub-atomic Particles ... 14
II. 2.1. Discovery of Electron ... 14
II.2.1.1. Crooks' experiment (1879) and cathodic ray properties: ... 14
II.2.1.2. Experience of J.J. Thomson: Charge to Mass Ratio of Electron qme) ... 15
II.2.1.3. Millikan's Experiment (1908) ... 19
II. 2.2. Proton ... 22
II.2.2.1 Goldstein's Experience ... 22
II.3.3 Neutron ... 23
II.3.3.1 Chadwick's Experience ... 23
II.3.4. Discovery of Nucleus ... 24
II.3.4.1. Rutherford’s Scattering Experiment ... 24
II.4. Presentation of the atom ... 26
II.4.2. Nuclear nomenclature ... 27
II.4.3. Characteristics of the atom ... 27
II.5. Isotopes ... 29
II.6. Average Atomic Mass ... 30
II.7. Natural Abundance ... 30
II.8. Separation of isotopes and determination of atomic mass ... 30
II.8.1. Mass spectrometry ... 30
II.8.2. Bainbridge mass spectrometer - Determination of isotopic masses of nuclei ... 30
II.9. Binding energy and mass defect ... 33
II.9.1. Mass defect (Δm) ... 33
II.9.2. Binding energy ... 34

II.9.3. The binding energy per nucleon 35

II.10. Sketching and interpreting the graph of average binding energy per nucleon against nucleon number 36

II.10.1. Binding energy curve (The Aston curve) 36

II.10.2. Band of Stability 37

CHAPTER III Radioactivity- Nuclear Reactions 38

III. Introduction 38

III.1. Radioactivity 39

III.1. 1. Natural radioactivity 39

III.2. Soddy and Fajans Law 40

III.3. The different types of disintegration 40

III.3.1. Alpha radioactivity 40

III.3.2. β decay 41

III.3.2.1. Beta minus β- radioactivity 41

III.3.2.2. Beta plus β + radioactivity 41

III.3.3. Gamma radioactivity 41

III.4. Artificial radioactivity and nuclear reactions 42

III.4.1. Nuclear transmutation: 43

III.4.1.1. Helium transmutation 43

III.4.1.2. Neutron emission: reactions (p, n) 45

III.4.1.3. Reaction (p, D) 46

III.4.1.4. Emission of protons: Reactions (n, p) 46

III.4.2. Fission Reaction 47

III.4.3. fusion Reaction 48

III.5. Radioactive decay kinetics 49

III.5.1. Law of radioactive decay 49

III.5.2. The radioactive constant λ 51

    - III.5.3. Activity (A) or decay rate 38
    - III.5.4. Half-life of Radioactive Decay T (or $t_{1/2}$) 38
    - III.5.5. Average (Mean) Life 39
  - III.6. Applications of Radioactivity 40
  - III.7. Damaging Effects of Radiation 43
- CHAPTER IV The Electronic Structure of the Atom 59
- IV. Introduction 59
  - IV.1 Dual Behavior of Electromagnetic Radiation (wave-corpuscle duality) 59
    - IV.1.1 Wave Nature of Electromagnetic Radiation and Electromagnetic Spectrum 59
    - IV.1.2. Particle Nature of Electromagnetic Radiation: Planck's Quantum Theory 62
    - IV.1.2 .1 Photoelectric Effect 63
    - IV.1.3. Interaction between light and matter 66
  - IV.2. Types of Spectrums 67
  - IV.3. emission Line Spectrum of Hydrogen 67
    - IV.3.1. Empirical Balmer-Rydberg relation 69
    - IV.3.2. The RITZ-RYDBERG formula 69
    - IV.3.3. Concept of a series of spokes 69
  - IV.4. The classical model of the atom 71
    - IV.4.1 Rutherford model 71
    - IV.4.2. Bohr atom model: hydrogen atom 72
      - IV.4.2.1. Postulates of Bohr atom model 73
      - IV.4.2.2. The radius of stationary orbits of the electron and the velocity of the electron 74
      - IV.4.2.3. Energy of the electron in a stationary orbit 76
      - IV.4.2.4. Quantification of the energy of the hydrogen atom 79
      - IV.4.2.5. Applications to hydrogenoids 82
    - IV.4.3. Limitations of Bohr's Model 83

IV.5. The hydrogen atom in wave mechanics 83

  IV.5.1. Wave-corpuscle duality and the Broglie relation 84

  IV.5.2 de Broglie Wavelength and Kinetic Energy 86

IV.6. Heisenberg’s Uncertainty Principle 86

IV.7. Schrodinger Equation for the hydrogen atom 88

  IV.7.1. Significance of the Uncertainty Principle 89

IV.8. Quantum numbers 89

  IV.8.1. Principal Quantum Number 89

  IV.8.2. The subsidiary or azimuthal quantum number (ℓ) 90

  IV.8.3. Magnetic Quantum Number (m) 90

IV.8.4. Spin quantum number (*s*) 91

IV.9. Shape of Orbitals 91

IV.10. Filling of Orbitals in Atom 94

  IV.10.1. Electronic Configuration of Elements in Periodic Table 94

  IV.10.2. Hund's rule of maximum multiplicity 96

  IV.10.3. Pauli Exclusion Principle 97

  IV.10.5. Valence electrons 98

  IV.10.6. Electron Configuration Exceptions 98

IV.11. Slater’s Rule 99

  IV.11.1. What is the nuclear charge? 99

  IV.11.2. What is the shielding effect (screening effect)? 99

  IV.11.3. What is the effective nuclear charge? 100

  IV.11.4. How to Find Shielding Constant? 100

    IV.11.4.1. s, p Orbitals 101

    IV.11.4.1. Shielding Constant for d or f-Orbital Electron 101

IV.12. Limitations of Slater’s Rule 102

CHAPTER V: The Periodic Classification of the Elements 107

V. Introduction 107
V.1. Periodic Classification of Elements 107
V.1.1. Dobereiner's Triads, 1829 107
V.1.2. Mendeleef's Classification (Periodic Table) 108
V.1.3. Moseley's Work 109
V.2. Modern Periodic Table 109
V.2.1. Periods in Periodic Table of Elements 110
V.2.2. Groups in the Periodic Table of Elements 112
V.2.2.1. Subgroups A 112
V.2.2.2. Subgroups B 113
V.2.3. Blocks of Periodic Table Elements 113
V.2.4. Families of the Periodic Table 114
V.3. Atomic characteristics and periodic Table Trends of Elements 118
V.3.1. Atomic radius (covalent radius) r_c 118
V.3.2. Ionic Radius 118
V.3.3. Ionization Energy (EI) 119
V.3.4. Electron Affinity of Elements in Periodic Table A or EA 122
V.3.5. Electronegativity χ 124
V.3.5.1. Periodic Trends in Electronegativity 124
V.3.5.2. Electronegativity scales. 125
V.4. Calculates the energy of poly electronics by Slater's rule 126
V.4.1. Calculation of ionization energies 126
V.4.2. Calculation of Electron Affinity 128
V.4.3. Calculation of ionic radii 130
CHAPTER VI Chemical Bonding 132
VI. Introduction 132
VI.1. Types of Chemical Bonds 132

- VI.1.1 covalent bonding 132
- VI.1.2 Dative bond or coordinate covalent bond 133
- VI.1.3 Ionic bonding 134
- VI.1.4 Metallic bond 135

VI.2. Lewis diagram........ 135

- VI.2.1. Lewis structure of atoms 135
- VI.2.2. Lewis structure of molecular compounds and ions........ 136
- VI.2.3. Formal charge........ 137
- VI.2.4. Octet rule........ 139

VI.3. Dipole moment: 141

- VI.3.1. Dipole Moment and Percentage Ionic Character 141
- VI.3.2. Percentage Ionic Character Formula........ 141

VI.4. Valence Shell Electron Pair Repulsion (VSEPR) theory 142

- VI.4.1. Applications of VSEPR theory........ 142
  - VI.4.1.1. AX_n type with simple bond........ 142
  - VI.4.1.2. AXn type with multiple bonds........ 143
  - VI.4.1.3. Molecules of AX_nE_m types. 143

VI.5. Chemical bonding in the quantum model........ 146

- VI.5.1. Formation and nature of bonds (Orbital Overlap)........ 146
  - VI.5.1.1. s-s overlap. σ-bond 146
  - VI.5.1.2. p-p overlap. π-bond 146

VI.6. Molecular Orbital Theory (T.O.M)........ 148

VI.7. Linear combination of atomic orbitals (LCAO method) 149

- VI.7.1. Energy level diagram for molecular orbitals........ 151
- VI.7.2. Atomic Structure and Chemical Bonding 151
- VI.7.3. Bond Order........ 152
- VI.7.4. magnetic properties 152

VI.7.5. Bonding in some Homonuclear di-atomic molecules: 152
VI.7.6. Molecular orbital for Heteronuclear Diatomic Molecules 156
VI.8. Theory of hybridization of atomic orbitals 159
VI.8.1. Hybridisation 159
VI.8.2. Types of Hybridization 160
VI.8.2.1. sp Hybridisation: 161
VI.8.2.2. sp^2 Hybridisation: 162
VI.8.2.3. sp^3 Hybridisation 163
VI.8.2.4. sp^3d Hybridisation: 164
VI.8.2.5. sp^3d^2 Hybridisation: 166
VI.8.2.6. sp^3d^3 Hybridisation: 167
References 168

PREFACE

In line with the LMD (Licence-Master-Doctorate) programmes defined by ministerial decree of the Ministry of Higher Education and Scientific Research, this course on "Matter Structure" (Chemistry 1) is more specifically is intended for first-year university students in the fields of Science and Technology (ST) and Material Sciences (SM) which aligns with the curriculum.

Each chapter has been prepared and structured in a simplified way to facilitate understanding and allow students to acquire the fundamental notions for understanding the structure of matter. This structure is intended to smooth out the difficulties inherent in scientific discourse while maintaining the necessary rigor. Corrected application exercises are provided for each chapter, enabling students to test their knowledge.

The book has been divided into six chapters.

Chapter I deals mainly with the macroscopic properties of states of matter, changes in states of matter, and the concepts of atoms, molecules, and Avogadro's number. The third part of this chapter deals with the concepts of atomic mass unit, molecular molar mass, atoms, molecules, and solutions.

In second chapter begins by exploring the basic building blocks of the atom (neutrons, protons, electrons) while highlighting the crucial experiments, including the J.J. THOMSON experiment and the Rutherford experiment, as well as the Rutherford planetary model that led to their identification.

Chapter III addresses radioactivity and covers various types of nuclear reactions.

Chapter IV focuses on the quantification of energy in the atomic model (wave-particle duality of light, hydrogen spectrum, and classical models of the atom) and the study of the wave model of the atom.

Chapter V describes the periodic classification of elements, evolution, and periodicity of the physicochemical properties of elements.

Chapter VI discusses chemical bonding: ionic bonding, covalent bonding, Lewis structure, the VSEPR method, and the hybridization of atomic orbitals.

It is possible that this first version has some imperfections. I would be grateful to everyone who would send me their comments and suggestions. Finally, during our teaching tenures, several concepts were clarified by interactions with the students and colleagues. We owe a word of gratitude to all our students and colleagues who inspired us to complete the book.

CHAPTER I Basic Chemistry Terms

I. Matter

I.1. Definition

Matter is anything in this world that takes up space (has volume) and has mass. Examples include pens, air, tables, and living organisms.

Matter is composed of microscopic entities and can be separated into two different categories: substances and mixtures.

A substance can again separate into elements and compounds, while in an element, an element can be separated into atoms and molecules

Matter is characterized by physical and chemical properties. Heat and light themselves are not forms of matter, but forms of energy.

I.1.2. Physical properties

a characteristic that a sample of matter exhibits when its composition does not change. A physical transformation changes matter at the macroscopic level (that is, as seen by the naked eye).

I.1.3. Chemical properties

A chemical property is a characteristic that a sample of matter presents and which results in a modification of its molecular composition following a reorganization of the atoms. A chemical change, also called a chemical reaction, operates on a microscopic scale but the resulting effects are often observable on a macroscopic scale.

I.2. States of matter and separation methods

The state of matter refers to the physical form and behavior of a substance based on its molecular structure, temperature, and pressure.

There are four main states of matter: solid, liquid, gas, and plasma. Each state has distinct characteristics:

I.2.1. Solid

In the solid state, particles are tightly packed together in a fixed arrangement. They have a definite shape and a definite volume; the intermolecular forces hold them in a rigid structure. The intermolecular force of attraction is powerful.

Solids are generally incompressible and have relatively low kinetic energy. They cannot flow.

I.2.2. Liquids

Liquids have particles that are close together but not as tightly packed as in solids. They have a definite volume but no fixed shape, instead taking the shape of their container. Liquids can flow and exhibit surface tension, and their particles have more freedom of movement than those in solids. The intermolecular space is very small (molecules are less closely packed). It is almost incompressible. The intermolecular force of attraction is not so strong. It can flow.

I.2.3. Gas

Usually, gas is the invisible state of matter. Gases have particles that are widely spaced and have high kinetic energy (Intermolecular space is very large molecules that are very loosely packed). They have neither a definite shape nor volume, instead expanding to fill the entire space available. Gases are compressible, meaning their volume can be reduced by increasing pressure. The particles in gases move randomly and rapidly. The intermolecular force of attraction is very weak. Intermolecular space is very large molecules that are very loosely packed. They can flow very easily.

I.2.4. Plasma

Plasma is a high-energy state of matter where atoms or molecules are ionized, resulting in the presence of positively charged ions and free electrons. Plasma is often found at high temperatures or in highly energized environments. It is electrically conductive and can exhibit complex behaviors such as generating magnetic fields. In addition to these states, there are also various other exotic states of matter that can exist under extreme conditions, such as supercritical fluids, quark-gluon plasma, and degenerate matter. The behavior of matter in different states is governed by principles of physics, including thermodynamics and quantum mechanics. Changes in temperature and pressure can cause phase transitions between the states of matter, such as melting, freezing, evaporation, and condensation.

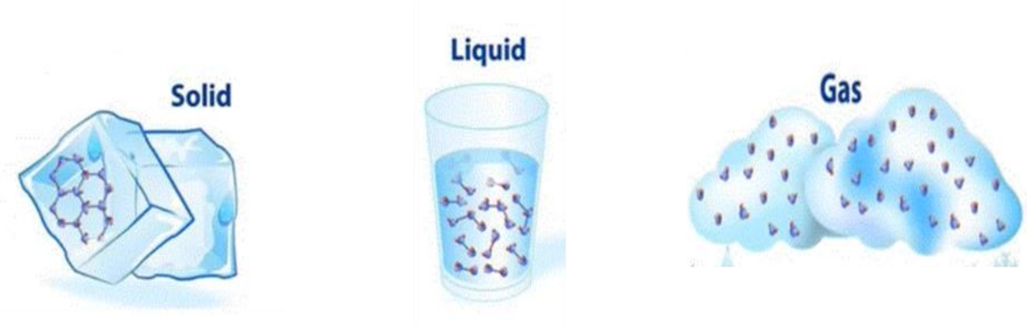


Figure I.1. State of matter diagram

I.3. Change in the state of matter

They have different states of matter, the three most important being solid, liquid, and gas. How can we change the state of matter? As you can see, these states of matter are classified according to their physical properties rather than chemical properties. The important question is what is the effect of a state change? We can change the state of matter by changing the temperature, and the other way is to change the pressure.

I.3.1. Characteristics of state changes

We will learn about the motion of solids, liquids, and gases. Solid particles oscillate only about their average position, liquid molecules move randomly in all directions, and gas molecules also move randomly in all directions. How can we increase or decrease the velocity or motion of a particle? We can increase or decrease the speed or motion of a particle by adding or removing thermal energy from the particle. The passage between states is shown in the diagram below:

What are the six changes in states of matter?

When a solid changes to a liquid, it is called melting

When a liquid changes to a solid, it is called freezing

When we provide high energy to a solid so that it directly changes into a gas, this process is called sublimation

When a liquid changes to a gas, it is called vaporization

When a gas changes to a liquid, it is called condensation

When we remove enough energy from a gas, it directly changes to a solid, it is called deposition

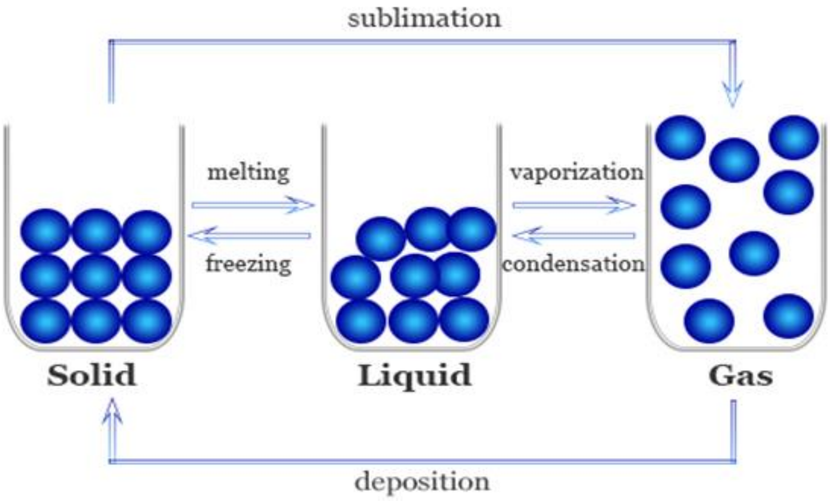


Figure I.2. States of Matter

I.4. The characteristic properties of matter and its states.

Matter and its states have four characteristic quantities:

I.4.1. The Volume and the mass

Volume and mass are two characteristic quantities of an object. The space each object occupies is determined by the measurement of its volume, and how heavy or light an object is by its mass.

I.4.1.1. Volume

Determines the space an object occupies. **Symbol:** V. Units: the cubic meter with symbol m^3 (International metric system), but also the liter (l or L). Measuring device: graduated container.

I.4.1.2. Mass

The mass of an object, whether solid or gas, measures the amount of matter in it.

symbol: m Unit: kilogram symbol kg (international metric system). Measuring device: balance.

I.4.2. The pressure and the temperature

I.4.2.1. The pressure

denoted P, corresponds to the ratio of a force (F) to the area of the surface (S) on which it is applied.

Symbol of the magnitude: P. Unit: the pascal symbol Pa (International Metric System). Measuring device: nanometer, barometer.

I.4.2.2. The temperature

corresponds to the degree of agitation of the molecules. The higher the temperature, the more the molecules are agitated and the more they disperse, increasing the molecular disorder.

The ambient temperature is the temperature of the environment.

Symbol of the magnitude: T. Unit: the kelvin of symbol K (International Metric System). Older scales: Celsius and Fahrenheit scales. Measuring device: thermometer

I.5.Atomic concepts

I.5.1. The atom

It is an ancient concept from the third century BC, developed by Democritus of Miletus and Leucippius. Introduced by Dalton in 1807 and clarified in the 19th century, it wasn't until the early 20th century that we had our first idea of its structure: an atomic nucleus surrounded by a cloud of electrons. The word atom is derived from the Greek word "atomos", which means indivisible, inseparable. Every substance is made of atoms; atoms are the smallest unit of matter, made up of three subatomic particles: proton, neutron, and electron.

In chemistry is the most basic thing. The properties of an atom are given a specific number called the atomic number to identify and understand its properties. The atomic number corresponds to the number of protons in the nucleus of an atom.

I.5.2. Molecule

What is a molecule?

A molecule is a microscopic particle that makes up most materials. Is definitely bigger than the atom (consists of two or more atoms, the same atoms, or different atoms) chemically bonded together, which means they must have a bond between them or they must undergo a certain reaction to be bound together. **These atoms cannot separate spontaneously: only a chemical transformation can modify the composition of a molecule.**

I.5.3. Mole

Scientifically, 1 mole is defined as the amount of substance that contains the same number of atoms, molecules, or particles as there are atoms in 12 grams of Carbon-12. 12 grams of carbon-12 is taken as the norm. One mole of an atom corresponds to 6.023×10^{23} atoms.

Or a standard scientific unit for measuring large quantities of very small entities such as atoms, molecules, or ions.

Under room temperature (≈ 298 K) and atmospheric pressure (1 atm), the molar volume of an ideal gas is approximately 24 $dm^3 \cdot mol^{-1}$.

The definition of a mole also determines the value of a universal constant that relates the number of units to the amount of material in a sample.

I.5.4. Avogadro's Number:

Avogadro's Number. But what’s the secret behind this number? A scientist named Lorenzo Romano Amedeo Carlo Avogadro came up with the concept. The name is very long. Therefore, we call him Avogadro. So, the number $6.023\ 10^{23}$ is known as Avogadro’s number. It is just a number used to represent quantities.

Avogadro's number is used to represent the number $6.023\ 10^{23}$ of any entity. So, we can walk into a store and say, "How many sheets of Avogadro do I want?" Of course. The only problem is that there aren't that many chocolates in the store, and we can't take them home. Going back to this concept, Avogadro's number is just another number used to represent quantities. But the number is so huge that using this in daily life is actually neither possible nor recommended.

So why does this number exist if we don't use it? Yes, this number is not commonly used in our daily life. However, it is a lifesaver for chemists who study atoms, molecules, electrons, and many such small entities. Hence, it is used to calculate the number of moles of any substance. Let's talk about one last concept.

We know that 1 mole of carbon-12 is equal to 12 grams of carbon-12. That's because 12 grams of carbon-12 has Avogadro's number of atoms.

The number of atoms in a mole is called the Avogadro Number: NA=6.023 10^{23} atoms.

$$\textbf{Number of mole} = \frac{\textbf{number of atoms}}{\textbf{Avogadro Number}}$$

I.5.5. Molar mass atomic

The mass of an element is the mass of one mole of atoms of that element.

I.5.6. The molecular mass of a compound

can be calculated by adding the atomic masses of constituent atoms. Or the sum of the masses in the periodic table.

I. 5.7. Atomic mass unit (uma)

The atomic mass unit (u or amu), which is defined as one-twelfth (1/12) of the mass of an atom of the carbon-12 isotope (^{12}C) in its ground state.

Carbon-12 isotope is the standard and is assigned the mass of exactly 12 atomic mass units.

$1\text{uma} = \frac{1}{12}\text{the mass of one carbon atom}$

$$1\text{ mol} = \text{Avogadro Number}$$

$$12\text{ gramms} \rightarrow \text{Avogadro Number}$$

$$\text{the mass of one carbon atom} \rightarrow \text{one carbon atom}$$

$$\text{the mass of one carbon atom} = \frac{12\ \times 1}{\mathrm{N_A}} = 1{,}992693\ 10^{-23}g$$

So

$$\text{uma} = \frac{12}{\mathrm{N_A}}.\frac{1}{12} = 1{,}6605402.10^{-24}\text{g} = 1{,}6605402.10^{-27}\ \text{Kg}$$

I.5.8. molar Volume

Molar volume (V_m) is the volume occupied by one mole of a substance. It depends on the state of matter and its state under defined conditions of temperature and pressure.

I.6. The weight law

The three main laws of chemical composition are the law of conservation of mass, the law of constant proportions, and the law of multiple proportions

I.6.1. Law of Conservation of Mass: (Lavoisier)

An element A and element B react together to give us a compound C

$$A + B \longrightarrow C$$

if we keenly observe that atoms of elements A and B do not exist individually in the reaction mixture, but come together to form a new compound C, even though the atoms of elements A and B appear to be degenerating, it's not the case in reality they are combining to give us the compound C.

$\sum$of the mass of the reactants =$\sum$of the mass of the products

The Law of Conservation of Mass dates from Antoine Lavoisier's 1789 discovery that mass is neither created nor destroyed in chemical reactions.

In other words, the mass of any one element at the beginning of a reaction will equal the mass of that element at the end of the reaction.

I.6.2. Law of definite Proportions: Law of Proust

The law of definite proportions is another law that led to modern atomic theory. So, the theory is that matter is made up of indivisible, indestructible particles called atoms. French chemist Joseph Proust 1797 invented the law of definite ratios, this law states that compounds always form a fixed ratio of their elements.

I.6.3. Law of multiple proportions: Dalton1804

This law was proposed by British chemist John Dalton (John Dalton, 1766-1844) in 1804, stating that when two elements A and B form a series of compounds, the ratio of masses of the second element that combine with 1 gram of the first element can always be reduced to small whole numbers.

I.7. Aspect qualitatif de la matière

Matter exists in the form of pure substances and mixtures. Pure substances exist as elements or compounds.

I.7.1. pure substance

exists when all atoms or molecules are of the same kind, i.e., they must be identical, and a pure substance must have a fixed composition and a unique set of properties. Pure substances can be divided into elements and compounds.

I.7.2. Elements

A pure substance composed of only one kind of atom. The key word here is that atoms cannot be broken down into simpler substances; in other words, elements are the simplest substances. Elements can be divided into atoms and molecules. Examples of atoms are sodium, neon, and argon. Examples of molecules are oxygen and chlorine.

(H_2, O_2, Cl_2, N_2, O_3).

I.7.3. compound

is a pure substance containing atoms of two or more elements chemically bonded together in a specific ratio. Can be divided into ionic form and molecular form. An example of a molecular compound is water and sodium chloride. In sodium chloride, we have Na, we have Cl, and the ratios have to be correct, so they have to be in the same type of fixed ratio.

Example: H_2O, NaOH, H_2SO_4, NH_3.

I.7.4. Mixture

is a group of two or more substances, each retaining its chemical properties, that are physically mixed together and are not chemically combined. It can be gas, liquid, or solid. Basically, they're just mixed together, and you can easily separate them.

The main difference between a mixture and a compound is that compounds are chemically bonded, but mixtures are physically mixed together.

We can have two types of mixtures, homogeneous and heterogeneous

I.7.4.1. Homogeneous mixture

The word Homo means the same thing: a mixture. A homogeneous is a mixture that has no visible boundaries between its components and has a uniform composition throughout the mass. A mixture is homogeneous when no changes in physical or chemical properties are detectable. This means you cannot see or observe the particles of a homogeneous mixture

An example of a homogeneous mixture is when you mix table salt and water, you get a homogeneous mixture.

The second example of a homogeneous mixture is air. We know that air is made up of different gases like oxygen, nitrogen, and carbon dioxide. Air is a homogeneous mixture because all these gases are combined together physically in such a way that they form a uniform composition throughout, and we cannot see the tickles up these gases.

Example

The air is a homogeneous mixture of different gases: the average composition is: Nitrogen N_2: 78.05%, oxygen O_2:20.97%, Carbon dioxide CO_2: 0.03%, rare gases (He: 0.00046%, Ne: 0.0016%, Ar: 0.93270%, Kr: 0.0011%, Xe: 0.00001%):0.94, hydrogen H_2: 0.01%.

I.7.4.2. Heterogeneous Mixture

is a mixture that has a non-uniform composition throughout its mass. This means we see particles of the substances contained within them.

The best example of a heterogeneous mixture is salad. When you mix different vegetables physically, you get a salad

The second example of a heterogeneous mixture is oil plus water. When you put some oil into the water, it is known as a heterogeneous mixture. Secondly, you can recognize the layer of oil above the water.

I.7.5. Solution

A homogeneous mixture of two or more substances in their gaseous, liquid, or solid phases. It is formed when a solute dissolves in a solvent. The particle size is 0.01-1 nm. The particles do not separate, nor can they be separated by filtration. The particles do not scatter light.

Example Milo drink

I.7.5.1. Solvent

It is the medium in which solutes dissolve, are present in larger quantities, and are in the same physical state (phase) as the solution.

I.7.5.2. Solute

A substance that can be dissolved in a solvent. A phase is a medium (liquid, gas, or solid) whose properties change continuously in space. If the solvent used is water, the solution is called an aqueous solution.

I.7.5.3. Dilution

It is a process of obtaining a new solution that is less concentrated than the initial solution, in which the concentration of a simple solution is decreased by adding a diluent.

The initial solution is called the mother solution, and the dilute solution is called the daughter solution.

Solutions are prepared by adding a certain amount of the stock solution to a diluent, usually water.

Adding a solvent to a solution does not change the amount of solute (number of moles), but it does change the concentration of the solution.

Moles of solute before dilution = moles of solute after dilution

$$\boldsymbol{D'o}\text{ù}: \boldsymbol{C_0} \times \boldsymbol{V_0} = \boldsymbol{C_1} \times \boldsymbol{V_1}$$

This equation can only be used in dilution situations; it cannot be directly applied to chemical reaction problems.

Example: how do you make 500 mL of an HCl solution with a concentration of 0.250 mol/L from a commercial solution of 12.1 mol/L?

I.7.5.4. Solubility

refers to the ability of a solute to dissolve in a solvent and form a solution. Solubility depends on the type of solvent used, as well as temperature and pressure

I.7.5.5. saturated solution

A solution that cannot dissolve a further amount of solute at a particular temperature is called a saturated solution.

For example, when you keep adding sugar to the water, a time will reach when no more sugar will dissolve in the water and sugar will settle down at the bottom. This solution is known as a saturated solution.

I.7.5.6. unsaturated solution

A solution that can dissolve an additional quantity of solute at a particular temperature is called an unsaturated solution. For example, when you take a glass of water and dissolve a spoonful of sugar in it. The sugar readily dissolves in the water. So, this solution is the unsaturated solution.

I.8. Quantitative aspect of the matter

I.8.1. quantity of matter

It is a quantity that makes it possible to determine the number of chemical entities, so like any quantity that has a unit, its unit is the mole, which we call mol and is represented by n.

$$n = \frac{N}{N_A}$$

$$n = \frac{m\ (g)}{M_{(g/mol)}}$$

I.8.2. Molar Concentration

is the number of moles present in a volume of solvent or solution.

$$C\left(\frac{mol}{L}\right) = \frac{number\ of\ mole\ of\ solute\ (mol)}{volume\ of\ solution\ (L)}$$

I.8.3. Molarity

represented by the symbol capital M, we define molarity as the number of moles of solute dissolved in one liter of solution, so it’s moles over volume, but the volume has to be in liters, not milliliters.

The formula of molarity is:

$$Molarity\ (M) = \frac{number\ of\ mole\ of\ solute\ (mol)}{volume\ of\ solution\ (L)}$$

where M is the molarity of a solution, n is the number of moles of a solute V is the volume of a solution.

Example

How many grams of H_2SO_4 (M=98g/mol) are present in 500 ml of a 4 M solution?

$$M = \frac{n}{V}, n = \frac{m}{M}$$

$$M = \frac{m}{V.M} \Longrightarrow m = M.V.M = 4 \times 500 \times 10^{-3} \times 98 = 196\ g$$

I.8.4. Molality

is equal to the moles of the solute (but here is how it differs from molarity) its moles divided by the kilograms. It measures the number of moles of a solute in 1 Kg of solvent.

$$\text{Molality (Mo)} = \frac{\text{number of mole of solute (mol)}}{\text{mass of solvent (Kg)}}$$

Example: Determine the molality of the solution containing 53,25 g of NaCl and 250 g of water

$$Molality\ (NaCl) = \frac{number\ of\ mole\ of\ solute\ (mol)}{mass\ of\ solvent\ (Kg)}$$

$$number\ of\ mole\ (NaCl) = \frac{masse}{M} = \frac{53.25}{58.5} = 0.91\ mol$$

$$Molality\ (NaCl) = \frac{0.91}{250.10^{-3}}$$

I.8.5. Mass concentration

is the mass of a species per unit volume of the solution. Denoted by the symbol C_m, it is expressed in $g.L^{-1}$.

$$C_m\ (g.L^{-1}) = \frac{m(grammes)}{V\ solution\ (litre)}$$

I.8.6. Mass fraction

is the mass or weight of the substance divided by the total mass of all of the substances present in the mixture or solution, although mass fraction is the correct term by custom, ordinary engineering usage frequently employs the term weight fraction.

The sum of the mole fractions of all the constituents of a solution is always equal to unity

$$w_i = \frac{m_i}{\sum_{i=1}^{n} m_i}$$

$$\sum w_i = 1$$

I.8.7. mole fraction

It is defined as the number of moles of a particular substance of solvent or solute present in a mixture or solution, divided by the total number of moles present in the mixture of solution. This definition holds for gases, liquids, and solids.

$$x_i = \frac{n_i}{\sum_{i=1}^{n} n_i}$$

- **Symbol x**
- **Unit none**
- **Mole fraction should be 0<x<1**

$$\sum_{i=1}^{n}(x_i) = 1$$

I.8.8. Normality

is defined as the number of grams equivalent of solute dissolved in 1 liter of solution, and depends on the type of chemical reaction considered.

For acids, the number of gram equivalents corresponds to the number of hydrogen ions (H^+ or H_3O^+) that the molecule can donate in a reaction.

The gram equivalent of a base corresponds to the mole fraction of hydroxide ions (OH^-), whereas in redox reactions, it is the number of electrons.

Denoted by big N, it can be calculated by multiplying the molar concentration or molarity by the equivalent number.

$$\mathbf{N = x.M}$$

x: represents the number of protons in the case of acids (H^+or H_3O^+) and the number of OH^- in the case of bases

For monoacids and monobases, we have N = C or N = M. For diacids (two bases) and triacids (three bases), the following rules apply: N=2M; N=3M.

$$HCl \longrightarrow Cl^- + H^+$$

$$H_3PO_4 \longrightarrow PO_4^{-3} + 3H^+$$

$$H_2SO_4 \longrightarrow SO_4^{-2} + 2H^+$$

$$Ca(OH)_2 \longrightarrow Ca^{+2} + 2OH^-$$

Example

What is the normality of a solution that contains 1.5 g of Ca $(OH)_2$ dissolved in 850 ml?

solution

$$Ca(OH)_2 \longrightarrow Ca^{+2} + 2OH^-$$

$$\mathrm{N} = \mathrm{x.M}$$

$$M = \frac{n}{V}$$

$$n = \frac{m}{M_{Ca(OH)_2}} = \frac{1.5}{74} = 0.02\, mol$$

$$M_{Ca(OH)_2} = 74\, g/mol$$

$$M = \frac{0.02}{850 \times 10^{-3}} = 0.023\, M$$

$$\mathrm{N} = 2 \times 0.023 = 0.046\ \mathrm{N}$$

I.8.9. Density

is defined as the mass of an object per its unit volume under certain temperature and pressure conditions. It is denoted by ρ, the unit is g/L.

$$\rho\left(\frac{g}{L}\right) = \frac{mass\ of\ solution}{volume\ of\ solution}$$

I.8.9.1. Density of solids and liquids relative

Density is defined as the ratio of the mass density of a substance to that of a reference material. It is a **dimensionless quantity** expressed as:

$$d = \frac{\rho}{\rho_{water}}$$

The choice of reference depends on the physical state of the substance:

- **Water** is used as the reference for solids and liquids.
- **Air** is used as the reference for gases

The density of water is 1 kg/L or 1g/mL.

I.8.9.2. The density of a gas:

For gases, measurements are made relative to air. Represented by d, there is no unit (dimensionless physical quantity).

The density of a gas relative to air is equal to the quotient of the mass m of a volume v of gas by the mass m_{air} of the same volume of air (reference substance), with m and m_{air} being measured under the same conditions of temperature and pressure.

$$d = \frac{mass\ of\ gas}{mass\ of\ air}$$

$$d = \frac{M}{29}$$

CHAPTER II Main Constituents of Matter

II. Introduction

Atoms are the fundamental building units of matter that comprise everything we meet on a daily basis. Your ballpoint pen and its ink, the page of your book, and even your body are made up of atoms since you are considered stuff.

II. 1. Faraday's Experiment: The Relationship Between Matter and Electricity

II.2. Discovery of Sub-atomic Particles

II. 2.1. Discovery of the Electron

II.2.1.1. Crooks' experiment (1879) and cathodic ray properties:

Sir William Crooks (1832-1919) was a British chemist and physicist. He was pioneer of vacuum tubes. He worked on spectroscopy.

In 1879, William Crookes (Sir William Crooks) performed his experiments by passing an electric current through a gas in a discharge tube at very low Pressure.

He took a glass tube fitted with two metallic electrodes and connected it to a high-voltage battery.

The pressure inside the tube is maintained at 10^{-4} atm, when a high voltage current is passed through the gas, shiny rays are emitted from the cathode, which travel toward the anode as shown in Figure 1. These rays were given the name “cathode rays” because they come from the cathode.

The properties of the cathode rays were determined, which are given below:

- These rays travel in straight lines perpendicular to the cathode surface.
- They can cast a sharp shadow of an opaque object if placed in their path.
- They are deflected towards a positive plate in an electric field, showing that they are negatively charged.
- A very fine mill, placed on the path of the radiation, starts moving: the radiation consists of particles having a kinetic energy and consequently a mass.
- They raise the temperature of the body on which they fall.
- Light is produced when these rays hit the walls of the discharge tube.
- It was found that the same type of rays was emitted no matter which gas and which cathode was used in the discharge tube.

All these characteristics indicate that the nature of cathode rays is independent of the nature of the gas present in the discharge tube or the cathode material. The fact that they cast the shadows of an opaque object suggested that these are not rays but they are fast-moving material particles. They are named electrons.

Since all the materials produce the same type of particles, it means that all materials contain electrons. As we all know, materials are composed of atoms, so electrons are the basic atomic particles.

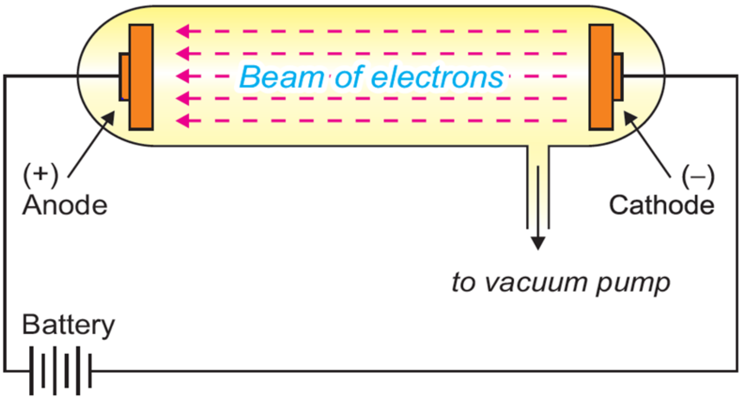


Figure II.1*:* Discharge tube used for the production of cathode rays.

II.2.1.2. Experience of J.J. Thomson: Charge to Mass Ratio of Electron $\frac{q}{m_e}$)

Thomson assisted in a series of experiments that are credited with contributing to the discovery of the electron. Thomson's most famous experiment was his 1897 cathode ray tube experiment. Thomson carried out quantitative studies of cathode rays and was able to determine the electrical charge (e) -to-mass (m_e) ratio of the particles coming out of the cathode ray tube and applying electrical and magnetic fields perpendicular to each other as well as to the path of electrons **(Fig. 2)**, regardless of the cathode material or the residual gas inside the tube.

In this experiment, Thomson created a high-vacuum cathode ray tube with two electrodes: a negatively charged cathode and a positively charged anode.

J.J. Thomson (1856- 1940) was a British physicist. He was awarded the 1906 Noble Prize in Physics for the discovery of electron and for his work on the conduction of electricity in gases

- ✓ **Experimental phase**

1. A cathode ray tube generates an electron beam by applying a very high potential difference (40,000 volts) between two electrodes at each end of the tube.

2. Electrons are emitted from the cathode and move to a perforated plate called the "anode" where they are projected onto a fluorescent screen, creating spots of light.

3. Thomson placed two metal plates on each side of the cathode ray tube to create an electric field.

The metal plates attached to the sides of the cathode ray tube are connected to a voltage source to create an electric field between them.

4. When the electric field is activated, the light spot on the fluorescent screen deflects towards the positive plate, indicating that the particles are deflected by the electric field, indicating that the electrons are negatively charged

5. Furthermore, using the polar parts of an electromagnet, between which there is a magnetic induction field

6. By measuring the division of the beam of electrons in the electrical field, Thomson was able to calculate the ratio of the charge to the mass of the electron.

He deduced that these particles were negatively charged corpuscles known as "electrons."

Thomson's experiment was also significant for the advancement of particle physics, leading to the discovery of many other subatomic particles over time.

✓ **Constitutions of experience**

The cathode, the anode, the fluorescent screen, and the two plates of the condenser, between which there is the electric field $E^{\rightarrow}$, the cross-section of the electromagnet pole piece, between which there is the magnetic induction field $B^{\rightarrow}$, as well as the field $E^{\rightarrow}$ and the effective field $B^{\rightarrow}$ common to the field.

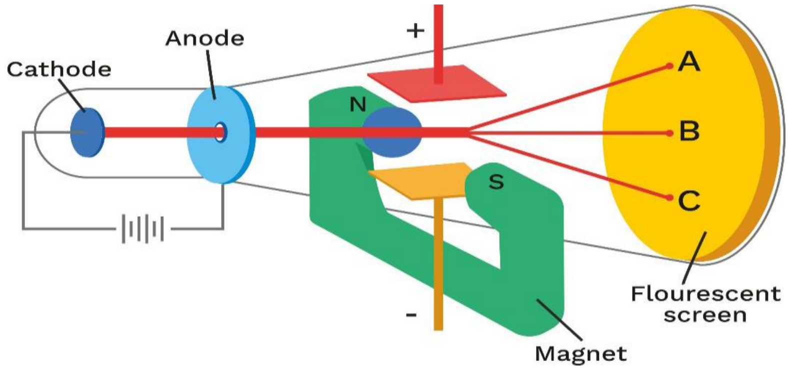


Figure. II.2. The apparatus to determine the charge-to-mass ratio of the electron

Thomson observed that cathode rays were deflected under the influence of electric and magnetic fields. By studying the deflection of cathode rays:

✓ **Only under the influence of an electric field**

The electron beam is deflected towards the positive trajectory plate (A), under the action of electric force (Fig. 1), where the electron "e" penetrates the capacitor with speed v_0 and is subjected to the electric force F_e such that

$$\mathbf{F_e} = \boldsymbol{q.E} = \boldsymbol{m_e \gamma}.$$

F_e: the electric force; **q**: the charge of the electron; **E**: the electric field **m_e**: the mass of the electron γ: acceleration

- ✓ **Effect of magnetic field**

The electron beam is deflected downwards from the trajectory (B) under the action of the magnetic force

$$\mathrm{F_m} = \boldsymbol{B.q.v}$$

F_m : the magnetic force**; q:** the charge of the electron**; B:** the magnetic field **υ:** the speed

- ✓ **Determination of the velocity of cathode rays**
- ✓ **Simultaneous action of electric and magnetic fields**

The electron beam cannot deviate from its trajectory (C), which occurs when

$$\begin{matrix} \mathrm{F_e} = \boldsymbol{q.E} \\ \boldsymbol{F_m = B.q.v} \end{matrix} \Leftrightarrow \boldsymbol{v} = \frac{\boldsymbol{E}}{\boldsymbol{B}}$$

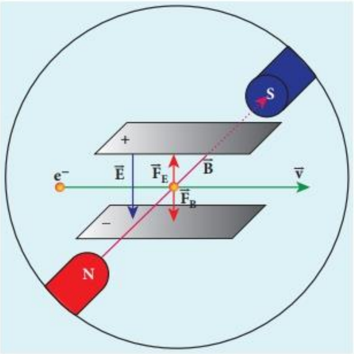


Figure. II.3. Electric force balancing the magnetic force- the path of the electron beam is a straight line

- ❖ **How to calculate q/me value**
- ❖ **Deflection of charge only due to a uniform electric field**

In J.J. Thomson's experiments, the electron beam was deflected using an electric field E, and its deflection Y was measured on a screen under a magnetic field. Electron e penetrates the capacitor with speed V_o and receives electric force F_e **(figure 4)**

The displacement of electrons requires two movements:

Along the Ox axis:

$v_0 = v_x \ \gamma = 0$

$$\gamma_x = \frac{d^2x}{dt^2} = 0 \Longrightarrow \frac{dx}{dt} = v_0 \Longrightarrow x = v_0 t \Longrightarrow t = \frac{x}{v_0}$$

$x = v_0.t$ It is a uniform rectilinear movement

Along the Oy axis:

The electron is subject to an electrostatic force and is projected on the Oy axis: FE parallel to Oy

$F_e(x) = 0\,; v_y = 0.$

$$F_e(y) = m_e\gamma_y = q.E \Rightarrow \gamma_y = \frac{q.E}{m_e}\,; \gamma_y = \frac{dv}{dt} \Rightarrow \frac{dv}{dt} = \frac{q}{m_e}.E \Rightarrow \int dv = \frac{q*E}{m_e}\int dt$$

$$\Rightarrow v = \frac{q*E}{m_e}*t$$

$$v = \frac{dy}{dt} = \frac{q*E}{m_e}*t \Rightarrow \int dy = v = \frac{q*E}{m_e}*t\,dt$$

$$\Rightarrow y = \frac{1}{2}\frac{q}{m_e}\,E.t^2$$

On the other hand

$$t = \frac{x}{v_0}$$

$$\mathrm{v}_0 = \frac{\mathrm{E}}{\mathrm{B}}$$

$$\Rightarrow y = \frac{1}{2}\frac{q}{m_e}\,E.\frac{x^2}{\frac{E^2}{B^2}}$$

for x=L; y=y₀

$$\Rightarrow y = \frac{1}{2}\frac{q}{m_e}\,\cancel{E}.\frac{x^2}{\frac{E^{\cancel{2}}}{B^2}}$$

$\Rightarrow \mathrm{Y} = \frac{1}{2}.\frac{\mathrm{q}}{\mathrm{m_e}}.\frac{\mathrm{L}^2}{\mathrm{E}}\,\mathrm{B}^2$ The electron e is deflected along the parabola with an accelerated uniform movement.

Determination the $\boldsymbol{\frac{q}{m_e}}$ value

From the following equation, we deduce the value of **q/m$_e$**

$$\mathrm{Y} = \frac{1}{2}.\frac{\mathrm{q}}{\mathrm{m_e}}.\frac{\mathrm{L}^2}{\mathrm{E}}\,\mathrm{B}^2$$

$$\frac{\mathrm{q}}{\mathrm{m_e}} = \frac{2\,\mathrm{Y}\,.\,\mathrm{E}}{\mathrm{L}^2\mathrm{B}^2} = +1{,}7589\,.\,10^{11}\,\frac{\mathrm{coulomb}}{\mathrm{Kg}}$$

The value of this ratio does not depend on the cathode material or residual gas in the cathode ray tube and whatever the intensity of the fields E and B.

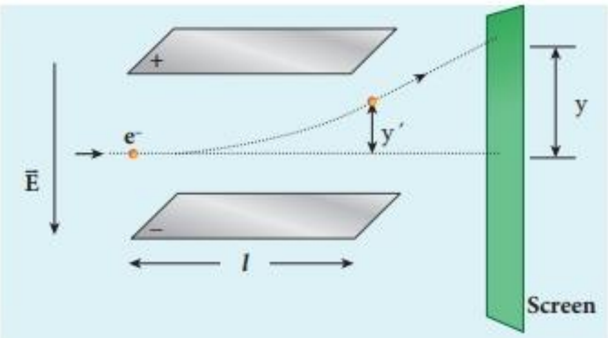


Figure. II.4. deviation of the path by applying a uniform electric field.

- **Deflection of charge only due to a uniform magnetic field**

Suppose that the electric field is switched off and only the magnetic field is switched on. Now the deflection occurs only due to the magnetic field. The force experienced by the electron in a uniform magnetic field applied perpendicular to its path is

$$\mathbf{F_m} = \boldsymbol{B.q.v}$$

Since this force provides the centripetal force, the electron beam undergoes a semi-circular path. Therefore, we can equate F_m to centripetal force $\frac{mv^2}{r}$.

$$\mathbf{F_m} = \boldsymbol{B.q.v} = \frac{\boldsymbol{mv^2}}{\boldsymbol{r}}$$

where *v* is the velocity of the electron beam at the point where it enters the magnetic field and *r* is the radius of the circular path traversed by the electron beam.

$$\boldsymbol{B.q.v} = \frac{mv^2}{r} \Longrightarrow \frac{q}{m} = \frac{v}{B.r}$$

II.2.1.3. Millikan's Experiment (1908)

In 1897, British physicist J.J. Thompson measured the ratio of electron charge to mass using a cathode ray tube. Later, in a series of experiments between 1908 and 1917, Millikan succeeded in measuring the charge of an electron with high precision, known as the Millikan oil drop. In his experiment, oil droplets in the form of mist, produced by the atomizer, were allowed to pass through a tiny hole in the upper plate of the electrical condenser. The downward motion of these droplets was observed through the telescope, equipped with a micrometer eyepiece. By measuring the speed at which these oil droplets fell, Millikan was able to determine the mass of the oil droplets from its term velocity.

In his experiment, a fine mist of oil was sprayed into the upper chamber with an atomizer. Tiny oil droplets fell through the hole in the upper floor, and Millikan was able to determine the mass of an oil drop from its terminal velocity. Next, Millikan used a beam of X-ray source to ionize the air inside the chamber. The electrical charge of these oil droplets is obtained by collisions with gaseous ions. The fall of these charged oil droplets can be retarded, accelerated, or made stationary depending on the charge of the droplets and the polarity and strength of the voltage applied to the plate. By carefully measuring the effect of electric field strength on the motion of oil droplets, Millikan concluded that the magnitude of electrical charge, q, on the droplets is always an integer multiple of the electrical charge "e".

Millikan was able to calculate the mass of the electron based on the electron charge and the electron charge-to-mass ratio determined by Thompson using a cathode ray tube. The mass of an electron is very small, $9{,}10.10^{-31}$ Kilograms.

There are different forces that act on the oil drop, including the gravitational, electrostatic force due to the electric field, and the viscous drag force, and forces that are pushed by Archimedes.

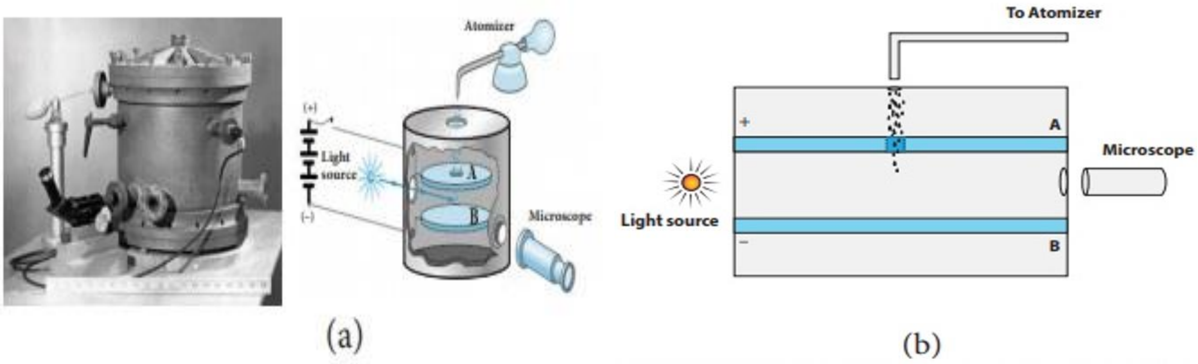


Figure. II.5. Millikan's experiment (a) real picture and schematic picture (b) Side view picture.

(ignoring buoyancy), Archimède's buoyancy is negligible.$\boldsymbol{\rho_{air} \ll \rho_{oil}}$

The drag force given by Stokes' law is

$F_{st} = 6.\pi.\eta.r.v$

η: Viscosity of air in poise

r: radius of the oil drop.

v: the velocity of the oil drop.

The gravitational force on the drop can be calculated using:

$F_g = m.g$

As it is very challenging to measure the mass of individual oil drops, it is helpful to re-express the mass of the oil drop in terms of the density of the oil as follows:

$$\rho_{oil} = \frac{m}{V} \Rightarrow m = \rho.V$$

Assuming that the oil drop is approximately spherical, its volume is given by the following formula:

$$V_{\text{sphere}} = \frac{4}{3}\,\pi.r^3$$

where r is the radius of the oil drop. Thus, the gravitational pull on the oil drop can be expressed as:

$\Longrightarrow F_g = \frac{4}{3}.\pi.r^3.g.\rho_{oil}$

- **Without the electric field's influence (E-field off)**

Calculating the Radius of the drop

When falling, the drop is subjected to the following two forces: the gravitational force due to Earth, F_g, and a drag force due to resistance to the motion from the surrounding air, F_{st}. These forces are directed in the up and down directions as shown in Fig. 6. For simplicity, we will use a positive sign for the up direction and a negative sign for the down direction.

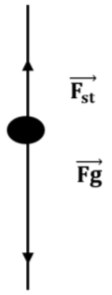


Figure. II.6. shows the forces acting on the drop when it is falling in air and has reached its terminal velocity.

The forces acting on the drop are

$F_g = \frac{4}{3}.\pi.r^3.g.\rho_{oil}$

$F_{st} = 6.\pi.\eta.r.v$

Therefore,

$\vec{F_g} + \overrightarrow{F_{st}} = 0 \;\Longrightarrow\; \frac{3}{4}\pi.r^3.\rho_{oil}.g = 6.\pi.\eta.r.v_0$

Radius of drop is:

$$r = \sqrt{\frac{9.\eta v_0}{2.\rho.g}}$$

- **Under the influence of an electric field ((E-field on)**

calculating the Charge of drop

Figure 2 shows the forces acting on the drop when it is rising under the influence of an electric field.

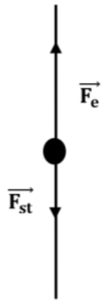


Figure. II.7. shows the forces acting on the drop

The electric field can be expressed as a function of the voltage V across the plates and the spacing d between them: $E = \frac{V}{d}$

$\overrightarrow{F_{st}} + \overrightarrow{F_e} = \vec{0} \Rightarrow F_{st} = F_e$

$\Rightarrow 6\pi.\eta.r.v = q.E \Rightarrow q = \frac{6\pi.\eta.r.v}{E}$ = q = $1.602.10^{-19}$ coulomb this is the elementary charge.

The mass of the electron can be deduced by combining the results of two seminal experiments: Based on J.J. Thomson's experiment and utilizing the value of q/m, in conjunction with the value of q determined through Millikan's experiment, this synthesis of experimental findings allows for the calculation of the electron's mass: me = $9.108.10^{-31}$ Kg.

II. 2.2. Proton

II.2.2.1 Goldstein's Experience

In 1886, Goldstein observed that, in addition to cathode rays, other rays were also present in the discharge tube. These rays were traveling in opposite directions to the cathode rays.

He used a discharge tube with a perforated cathode as shown in the figure. II.8.

He discovered that these rays passed through the holes present in the cathode and produced a glow on the walls of the discharge tube. He called these rays "canal rays"; they are positive ions obtained by stripping electrons from the molecules of the gases contained in the enclosure.

The positive ions are attracted by the cathode and possess sufficient kinetic energy to pass through the channel and hit the fluorescent screen, highlighting the existence of positive particles of the nucleus. These are protons.

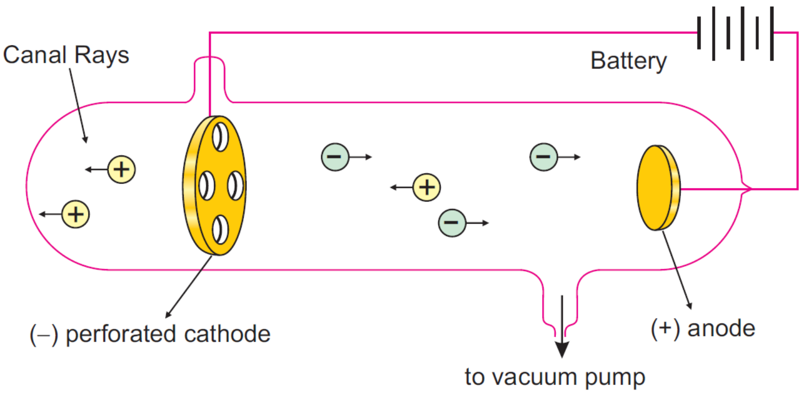


Figure. II.8. Discharge tube used for the production of canal rays.

II.3.3 Neutron

II.3.3.1 Chadwick's Experience

James Chadwick discovered the neutron in 1932 and observed that when he bombarded a thin sheet of beryllium with alpha particles, different kinds of particles were emitted.

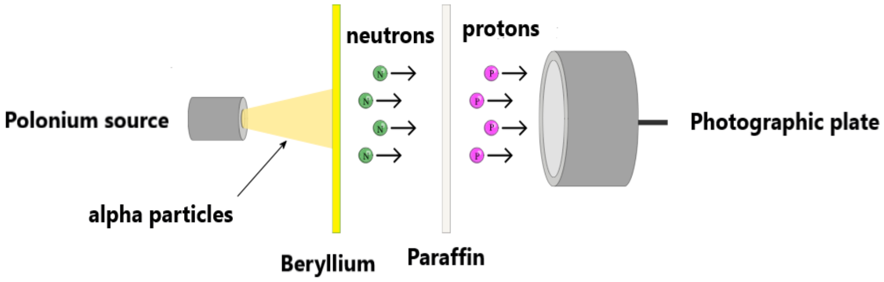
$$ {}^{9}_{4}Be + {}^{4}_{2}He \longrightarrow {}^{12}_{6}C + {}^{1}_{0}n $$

•These particles have about the same mass as protons and have no electric charge. Therefore, Chadwick called these particles neutrons.

•They are found in the nucleus along with protons.

•Neutrons are found in the nuclei of all atoms except hydrogen.

•Since protons and neutrons are both found in the nucleus, they are collectively called nucleons



Why did Chadwick use beryllium as a target?

When alpha particles interact with a beryllium target, they produce neutrons. In fact, alpha particles are made up of two protons and two neutrons, and when they collide with a beryllium nucleus, some of the neutrons are eliminated. Beryllium is a good target material for producing neutrons because it is relatively light and has a low atomic number. This means that it is less likely to absorb neutrons itself and more likely to produce neutrons.

Why did Chadwick use paraffin wax in front of the detector?

Paraffin wax is a good material for detecting neutrons because it contains a lot of hydrogen. Neutrons can collide with hydrogen nuclei and traverse them at high energy. Chadwick's detector consists of a cloud chamber filled with air, and as the rebounding hydrogen nuclei pass through the cloud chamber, they leave a trail of ionization. This trail can be seen and photographed, allowing Chadwick to count the number of neutrons detected. In addition to detecting neutrons, paraffin wax also helps slow them down.

This is important because neutrons travel very fast, and if not slowed down, they will pass through the detector without being detected.

II.3.4. Discovery of Nucleus

II.3.4.1. Rutherford's Scattering Experiment

Ernest Rutherford was interested in knowing how the electrons are arranged within an atom. Rutherford performed a 'Gold Foil' experiment to understand how negative and positive charges coexist in an atom. Rutherford designed an experiment for this purpose. In this experiment, the gold foil used by Rutherford was 0.00004 millimeters in thickness and was bombarded with alpha particles. Alpha particles are emitted by radioactive elements like radium and polonium. These are actually helium nuclei (He^{2+}). They can penetrate through matter to some extent. The effects of these αparticles were studied through flashes of light they produced on striking a photographic plate or a screen coated with zinc sulfide, as shown in the Figure. II.9.

He proved that the 'plum-pudding' model of the atom was incorrect.

Ernest Rutherford (1871 – 1937)
Rutherford was a British-New Zealand chemist. He performed a series of experiments using a - particles. He won the 1908 Noble Prize in Chemistry.
In 1911, he proposed the nuclear model of the atom and performed the first experiment to split atom. Because of his great contributions, he is considered the father of nuclear science.

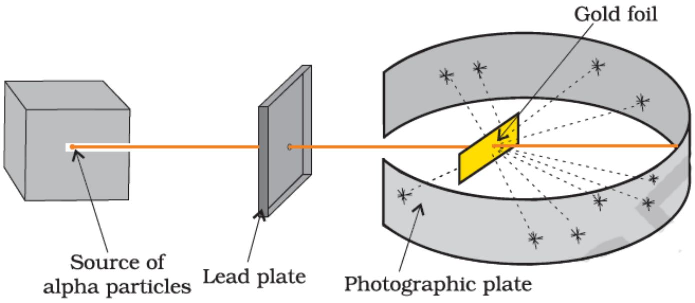


Figure. II.9. Rutherford's scattering experiment

Observations made by Rutherford were as follows:

- Most alpha particles pass through the gold foil (go straight) and are undeflected through the gold foil.
- Some of the alpha particles are deflected through a small angle.

- A few alpha particles (one in a thousand) are deflected(rebound) through an angle of more than 90°.
- Very few alpha particles returned (back-scattered) –that is, deflected back by 180°

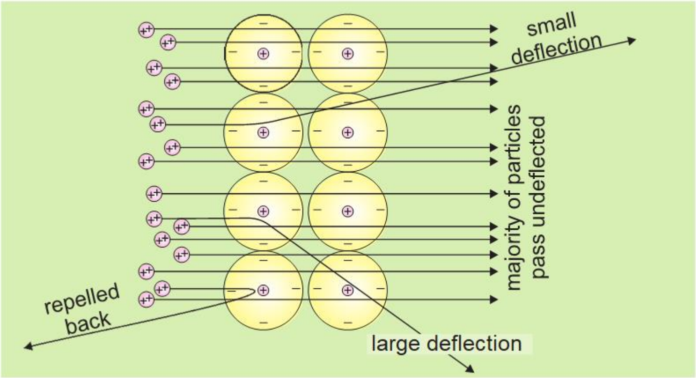


Figure. II.10. Scattering of alpha particles by the atoms of gold foil.

The conclusion made by Rutherford based on the above observation

Based on the observations, Rutherford drew the following conclusions regarding the structure of the atom, and he proposed his atomic model:

1 Since most of the particles passed through the foil undeflected, most of the volume occupied by an atom is empty.

2 The deflection of a few particles proved that there is a 'center of positive charges' in an atom, which is called the 'nucleus' of an atom.

3 The complete rebound of a few particles shows that the nucleus is very dense and hard.

4 Since a few particles were deflected, it shows that the size of the nucleus is very small compared to the total volume of an atom. The nucleus of an atom is 10,000 times smaller than the atom.

5 The electrons revolve around the nucleus in fixed, circular orbits.

6 An atom as a whole is neutral; the number of electrons in an atom is equal to the number of protons.

7 Except for electrons, all other fundamental particles that lie within the nucleus are known as nucleons.

From the experimental observations, Rutherford proposed that an atom has a lot of empty space and contains a tiny matter known as a nucleus whose size is of the order of 10^{-14}m. The nucleus is positively charged, and most of the mass of the atom is concentrated in the nucleus. The nucleus is surrounded by negatively charged electrons. Since static charge distribution cannot be in a stable equilibrium, he suggested that the electrons are not at rest and they revolve around the nucleus in circular orbits like planets revolving around the sun.

Drawbacks of Rutherford's Model of the Atom

Although Rutherford's experiment proved that the "plum pudding" model of the atom was incorrect, it still had the following flaws:

1. According to the classical radiation theory, electrons, as charged particles, should continuously release or emit energy and eventually fall into the nucleus.

2- If electrons liberated energy continuously, they should form a continuous spectrum, but in fact, a line spectrum is observed.

Although scientists had objections to Rutherford's proposed atomic model, it gave them thought-provoking ideas. They initiated the search to answer the following questions:

- How can an atom collapse, or why are atoms stable?
- ii. Why does an atom give a line spectrum?
- Scientists believe that there must be another atomic model. This shows that Rutherford's model is not perfect, and the Rutherford model cannot explain the stability of an atom.

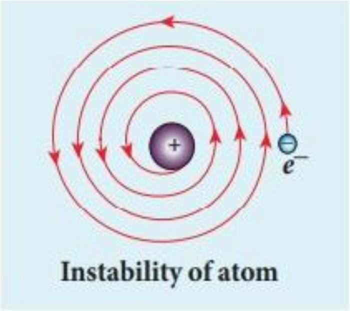
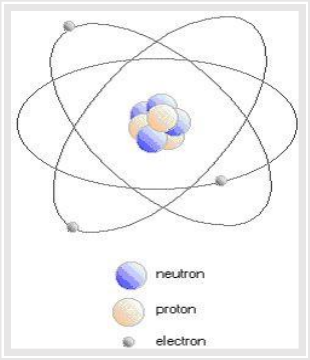


Figure. II.11. Spiral in motion of an electron around the nucleus

II.4. Presentation of the atom

II.4.1. The atom

The letter X is used to represent the symbol of any element. In symbolic notation, you will see different numbers around the symbol, with a superscript on the left-hand side as the atomic mass number (A) and a subscript (Z) on the left-hand side as the atomic number. The number on the top right of the symbol will always be the charge. The charge can be either positive or negative.



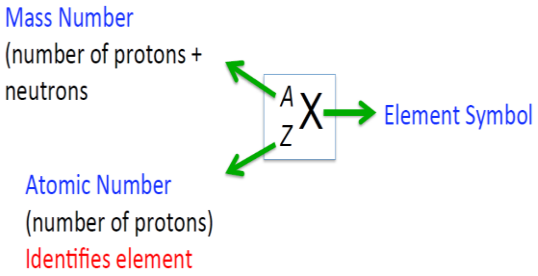
Atomic number - denoted by 'Z'. It is defined as the total number of protons present in the nucleus of an atom.

Mass Number - denoted by 'A'. Protons and neutrons are also called nucleons. Mass number is defined as the total number of protons and neutrons present in the nucleus of an atom.

This information will be important to help us determine the number of protons, neutrons, and electrons in an atom.

II.4.2. Nuclear nomenclature

In the notation for an atom, the atomic number, mass number, and symbol of the element are to be written as:

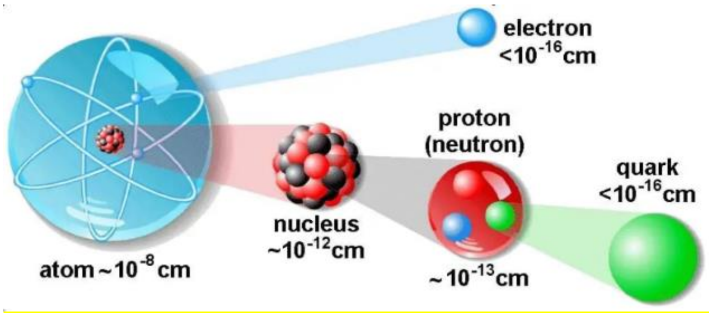


One important thing to notice about the symbols is that the first letter is always capitalized and the second letter is always lowercase.

When we are using symbolic notation, we will always start with the element symbol.

II.4.3. Characteristics of the atom

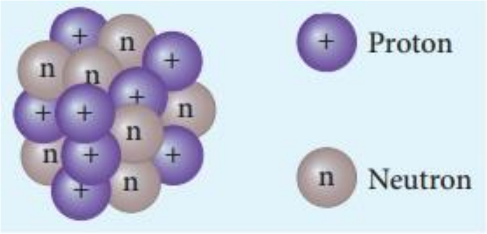
An atom is the smallest unit of an element that retains the properties of that element. Atoms are electrically neutral. Atoms are essentially made of the void. The size of atomic nuclei is negligible compared to atoms. The mass of an atom is concentrated in its nucleus. Atomic diameter: 10^{-10} m (1Å), nuclear diameter: 10^{-15} m.



It is composed of three primary subatomic particles:

- **nucleus**

The neutrons and protons in an atom are so closely packed together that they form a single cluster called the nucleus of the atom.



The two constituents of the nucleus, namely neutrons and protons, are collectively called nucleons.

- **Neutrons**

Neutrons have no charges; they have a mass nearly equal to that of a proton. The neutron is located in the nucleus of all atoms except hydrogen. They are represented as ‘n’. Hence, the mass of an atom is given by the sum of masses of protons and neutrons present in the nucleus. it serves 2 roles in the atom.

The first role is that it helps to buffer the positively charged protons in the nucleus.

The second role the neutron serves is that it contributes to the mass of the atom.

- **Protons**

A proton is a subatomic particle located in the nucleus of an atom. it is an essential component of matter, carrying a positive charge. Protons and neutrons together form the nucleus of an atom. The number of protons in the nucleus determines the identity of the element. The charge of a proton is the same as that of an electron but of opposite sign, making it an elementary particle in the field of particle physics.

- **Electron**

The electron is the final subatomic particle.

It is located outside the nucleus in the electron cloud and is primarily responsible for the chemical reactivity of elements.

It is also the main particle responsible for changing the charge of the atom.

Electrons are negatively charged, so adding an electron creates a negative charge, and removing an electron creates a positive charge.

Remember, changing the number of protons changes the properties of the element.

A change in the number of neutrons causes a change in mass, creating isotopes.

A change in the number of electrons changes the charge, turning the atom into an ion.

Particles	Location	Charge	Mass (Kg)
protons	Inside nucleus	$1{,}60\ x10^{-19}$	$1{,}673\ x\ 10^{-27}$
Neutrons	Inside nucleus	0	$1{,}675\ x\ 10^{-27}$
Electron	Outside nucleus	$-1{,}60\ x10^{-19}$	$9{,}109\ x\ 10^{-31}$

II.5. Isotopes

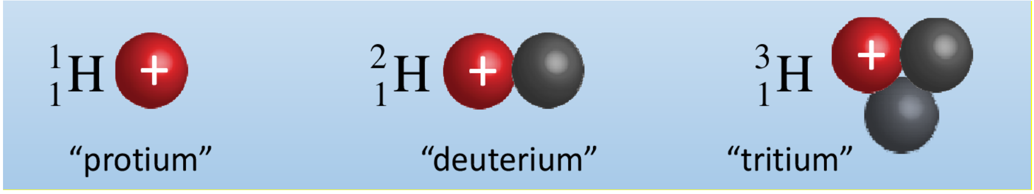
Definition

In nature, several atoms of some elements have been identified, which have the same atomic number but different mass numbers.

Isotopes are defined as atoms of the same element, having the same atomic number but different mass numbers. They have the same electronic configuration and number of protons, but they differ in the number of neutrons.

Many elements consist of a mixture of isotopes. Each isotope of an element is a pure substance it has similar chemical properties because these depend upon electronic configuration. However, they have different physical properties because these depend upon mass numbers.

masses are based on the atomic mass unit (amu)



Isobars

It can be defined as the atoms of different elements with different atomic numbers, which have the same mass number (different Z, identical A, different N).

isotones

Nuclides which have the same number of neutrons are called isotones (different Z, different A, identical N)

II.6. Average Atomic Mass

The mass of an atom of any natural element is taken as the average mass of all natural atoms of that element.

If an element has no isotopes, the mass of its atoms would be equal to the sum of the protons and neutrons it contains. However, if the element occurs in isotopic form, we need to know the percentage of each isotope form and then calculate the average.

Hence, the relative atomic mass of an element is an average value that takes account of the abundance of the isotopes of the element. It is calculated by working out the relative abundance of each isotope.

Example

The element chlorine is a mixture of 75.77% of ${}^{35}_{17}\mathrm{Cl}$ and 24.23% of ${}^{37}_{17}\mathrm{Cl}$. Calculate the average atomic mass of chlorine if no distinction is made between its different isotopes.

In fact, the chemist uses the average atomic mass or also known as the chemical atomic weight (35.453 u for chlorine), of an element. So, it must be remembered that the atomic mass that is mentioned in the periodic table is basically the average atomic mass.

II.7. Natural Abundance

Natural abundance refers to the atomic percentage of each isotope present in natural mixtures. This abundance is equivalent to the molar fraction of each stable isotope.

The relative atomic mass is therefore calculated using the equation:

$$M = \sum \frac{x_i * M_i}{100} = \frac{x_1 * M_1 + x_2 * M_2 + x_3 * M_3 + \cdots}{100}$$

$$\sum x_i = 100\%$$

x_i : relative abundance of each isotope (%).M_i : atomic mass of isotope

II.8. Separation of isotopes and determination of atomic mass

II.8.1. Mass spectrometry

A mass spectrometer can separate and measure the mass of isotopes of the same element. There are many types of mass spectrometers: Aston mass spectrometer, Dempster spectrometer, and Bainbridge Mass Spectrometer.

Isotopes are affected by electric and magnetic fields. The most empirical method for measuring the e/m ratio is the Bainbridge Spectrograph

II.8.2. Bainbridge mass spectrometer - Determination of isotopic masses of nuclei

An important instrument that utilizes the principles of magnetic and electric fields is called a mass spectrometer. A mass spectrometer is essentially a device used for the accurate determination of atomic masses. A schematic diagram of this spectrometer is shown in Figure. II.12.

Why the Bainbridge mass spectrograph?

It has a high resolving power

It is used to calculate the unknown mass of the particle

It is also used to find the number of isotopes present for the element

Principle

The mass spectrograph is a device that detects the isotopes of positive particles and determines the mass of the isotopes from the known mass

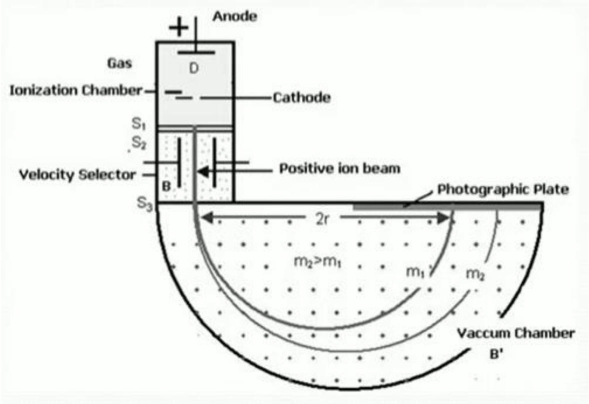


Figure. II.12. Principle schematic of the Bainbridge spectrograph.

Construction

It consists of the following parts

1- Ionization Chamber

The first step in measuring mass is essentially exposing a sample of molecules to a heat source or passing an electric current through the sample, which ionizes the molecules and creates a beam of positive particles in the form of a pencil beam, which is passed through a velocity selector.

2- Velocity Selector

The ions then pass through the hole into a region containing the velocity selector.

The velocity selector allows the ions of a particular velocity to come out of it, by the combined action of an electric and a magnetic field.

The velocity selector consists of two plane parallel plates P_1 and P_2, which produce a uniform electric field E, and an electromagnet, to produce a uniform magnetic field B (represented by the dots).

The electric field and magnetic field are so adjusted that the deflection produced by one field is nullified by the other so that the ions do not suffer any deflection within the velocity selector, and all the positive particles having the same velocity will enter through the velocity selector, and all other particles will be removed from the stream.

Let E and B be the electric field intensity and magnetic induction, respectively, and q be the charge of the positive ion.

The force exerted by the electric field is the electric force equal to **qE,** and the force exerted by the magnetic field is the magnetic force equal to **Bqv** where ***v*** is the velocity of the positive ion.

The action of forces in the velocity Selector

The force due to the electric field is

$$F_e = q\,E$$

The force due to the magnetic field is

$$F_m = q\,B\,v$$

As these forces are equal are opposite

$$q\,E = q\,B\,v$$

Hence

$$v = \frac{E}{B}$$

3- Analyzing Chamber

These positive ions, having the same velocity, are subjected to another strong uniform magnetic field of induction B′. Due to this magnetic field, these ions are deflected along a circular path of radius r and strike the photographic plate. The force due to the magnetic field B′qv provides the centripetal force.

We will apply Newton's second law of motion to calculate the mass of the ion.

According to the second law of motion, when an ion passes through this region of space, the net force acting on the ion is equal to the mass of the ion multiplied by its acceleration.

- **Hence**

$$F_m = q\,B'\,v = m\gamma$$

The only force acting on the ion is the magnetic force, and since it follows a curved path, γ is our centripetal acceleration.

$$\gamma = \frac{v^2}{r}$$

$$q\,B'\,v = m\,\frac{v^2}{r}$$

$$r = \frac{m\,v}{q\,B'}\ ,\quad m = \frac{q\,B'\,r}{v}$$

Isotope 1 : $\boldsymbol{r_1 = \frac{m_1\, v}{q\, B'}}$

Isotope 2 : $\boldsymbol{r_2 = \frac{m_2\, v}{q\, B'}}$ $\boldsymbol{m_2 > m_1}$

Ions with different masses trace semi-circular paths of different radii and produce dark lines on the plate. The distance between the opening of the chamber and the position of the dark line gives the diameter *2r* Figure. II.13. From which the radius *r* can be calculated:

$$2r_2 - 2r_1 = d$$

$$d = 2(r_2 - r_1) = \frac{v}{q\,B'}(m_2 - m_1) we\ havee\ : m_1 = \frac{q\,B'\,r_1}{v}\ and\ m_2 = \frac{q\,B'\,r_2}{v}$$

$$and\ v = \frac{E}{B}$$

$$\Longrightarrow \frac{q}{m} = \frac{E}{r.B'.B}$$

$$M_i = m_i\, N_A$$

Isotope 1 : $\boldsymbol{M_1 = \frac{q\, r_1\, B'\, N_A}{v}}$

Isotope 2 : $\boldsymbol{M_2 = \frac{q\, r_2\, B'\, N_A}{v}}$

Consequently, by comparing the position of the line produced by the particle of unknown mass with the position of the line produced by the particle of known mass, the unknown mass is determined.

4- Photographic Plate

The ions are deflected on the photographic plate and are captured by electrodes that act as ion collectors.

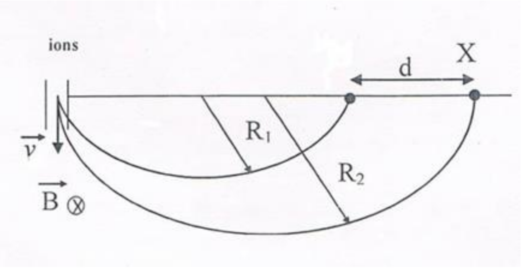


Figure. II.13. The circular paths of ions in the analyzer.

II.9. Binding energy and mass defect

II.9.1. Mass defect (Δm)

When nucleons combine to form a nucleus, the mass of the nucleus is less than the sum of the masses of the protons and neutrons that make it up. On the other hand, the sum of the masses of free protons and neutrons is greater than the mass of the original atomic nucleus.

Mass is converted into energy, and energy is converted into mass.

Mass defect (Δm): the difference between the mass of a nucleus and the sum of the masses of its isolated nucleons.

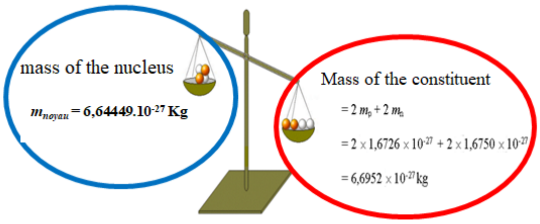
Where has this mass disappeared?

The answer was provided by Albert Einstein with the help of the famous mass-energy relation ($E = mc^2$). According to this relation, the "mass defect" is therefore mass that is converted into energy, and energy can be converted into mass according to Einstein's equation and released from its constituent particles during the formation of a nucleus.

The mass of an isolated nucleon is greater than the mass of the same nucleon held together in the nucleus.

$$\boldsymbol{\Delta m = Zm_P + Nm_n \ - m_{nucleu}}$$

Example of the helium nucleus ${}_{2}^{4}He$:



In the case of the Helium nucleus, when 2 protons and 2 neutrons combine to form the Helium nucleus, mass equal to mass defect disappears and the corresponding energy is released. This is called the binding energy of the nucleus (BE)

II.9.2. Binding energy

Binding energy: the energy required to separate the nucleus into its nucleons, or the energy released from its nucleons when a nucleus is assembled. This energy may be determined by using Einstein’s famous equation:

$$\boldsymbol{BE = \ \Delta m * C^2}$$

Where

BE is the change in energy (j)

Δm is the change in energy (Kg)

C is the speed of light (3.0 x 10^8 m/s)

In fact, to separate the nucleus into individual constituents, we must supply the energy

In subatomic physics, mass may be expressed using the atomic mass unit (amu)

$$1 \text{ amu} = \frac{1}{N_A} g$$

$$1 \text{ amu} = 1.66 \ \times 10^{-24} g = 1.66 \ \times 10^{-27} Kg$$

The main units used for Binding energy are:

The joule, the electro Volt (eV), and the Mega electro Volt

$$1\ \mathrm{eV} = 1.6\ \times 10^{-19}\,J$$

$$1\ Me\mathrm{V} = 10^{6}\ eV = 1.6\ \times 10^{-13}\,J$$

If Δm is expressed in Kg and c in m.s^{-1} BE, then it is obtained in joule

Example: Compute the binding energy of ${}^{16}_{8}O$ nucleus using the following data: atomic mass of oxygen atom, $M_A(O) = 15.9905$ u, and that of hydrogen atom, $m_H = 1.00785$ u.

$$\Delta \mathrm{m} = \mathrm{Zm_P} + \mathrm{Nm_n}\ - \mathrm{m_{nucleu}}$$

$\mathrm{m_P} = 1.0073\ \mathrm{mau}$

$\mathrm{m_n} = 1.0087\ \mathrm{mau}$

$\mathrm{m_{nucleu}} = 15.9905\ \mathrm{mau}$

$\Delta \mathrm{m} = 8 \times 1.0087 + 8 \times 1.0073 - 15.9905$

$\Delta \mathrm{m} = 0.137\ \mathrm{mau} = 0.137\ \times 1.66\ \times 10^{-27} = 0.227\ \times 10^{-27}\mathrm{Kg}$

$$\Delta \mathrm{E} =\ \Delta \mathrm{m} * \mathrm{C}^2$$

$$\Delta \mathrm{E} = 0.227\ \times 10^{-27} \times (3.10^{8})^2$$

$$\Delta \mathrm{E} = 2.11 \times 10^{-11}\mathrm{J}$$

II.9.3. The binding energy per nucleon

To judge the stability of a nucleus and to compare the different types of nuclei with each other, it is necessary to measure the binding energy per nucleon which is the energy required to separate a single nucleon from a particular nucleus and which is defined by the following relation:

$$\Delta E' = \frac{BE}{A}$$

The binding energy per nucleon BE/A of a nucleus is the binding energy BE divided by the number of nucleons A (mass number).

Higher values of binding energy per nucleon indicate greater stability for a nucleus. Nuclei with higher binding energy per nucleon are more tightly bound, meaning that it takes more energy to break them apart. As a result, these nuclei are generally more stable and less likely to undergo radioactive decay or nuclear reactions.

In most cases, the binding energy per nucleon is about 8 MeV

II.10. Sketching and interpreting the graph of average binding energy per nucleon against nucleon number

II.10.1. Binding energy curve (The Aston curve)

The "Aston curve" is a graph showing the relationship between the binding energy per nucleon and the mass number (number of nucleons) of the nucleus. Named after British scientist Francis William Aston, this curve illustrates how the binding energy per nucleon changes depending on the number of nucleons in the nucleus.

The Aston curve, or nuclear binding energy curve, usually shows a peak near the mass number where nuclei exhibit the highest stability and maximum binding energy per nucleon. This peak usually occurs around the element iron (Fe) in the periodic table.

This curve is critical to understanding nuclear stability and indicates that higher values $\Delta E'$of binding energy per nucleon correspond to more stable nuclei. This graphical representation helps us understand the energy required to keep the nucleus intact and the stability of different nuclei relative to their mass numbers.

The graph below shows the average value of -El/A as a function of A (Aston curve); this curve allows comparison of the stability of different core types and visualization of the most stable nuclei.

- When two light and unstable nuclei, with a mass number A<20, associate to form a heavier and more stable nucleus, two nuclei are combined to increase the average binding energy per nucleon. This is the phenomenon of nuclear fusion.
- Nuclear fusion occurs with the elements below Fe because joining smaller nuclei forms larger ones, which are higher on the graph (and thus more stable).
- When heavy and unstable nuclei with mass number A > 190 split into lighter nuclei, the system formed from these lighter nuclei is more stable than the initial heavy nuclei because the average binding energy per nucleon increases. This is the phenomenon of nuclear fission.
- Nuclear fission will occur with the elements above Fe because splitting bigger nuclei forms smaller ones, which are higher on the graph (and thus more stable).
- nuclei, with a mass number between 20<A<190, are stable nuclei and the binding energy per nucleon is > 8 MeV / nucleon.

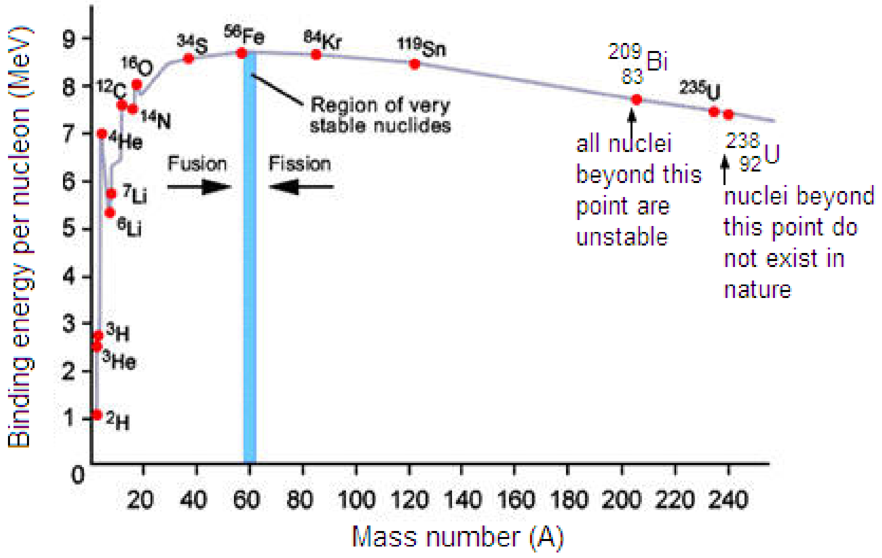


Figure. II.14. The Aston curve

II.10.2. Band of Stability

- **All nuclei with more than 83 protons are unstable**

Elements with 83 protons or fewer may also have unstable nuclei, depending on the ratio of neutrons to protons. If the number of neutrons is plotted against the number of protons for stable nuclei, a characteristic graph is obtained.

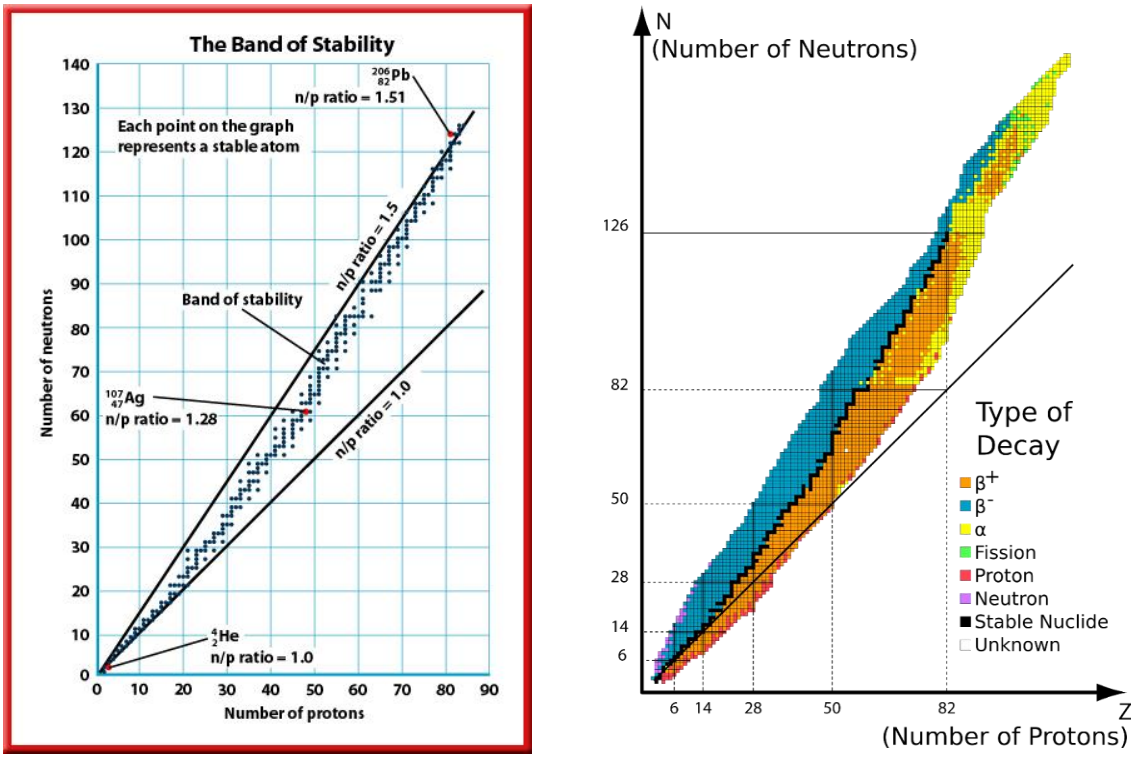


Figure. II.15. Neutron-Proton Stability Diagram N=f(Z)

CHAPTER III Radioactivity- Nuclear Reactions

III. Introduction

In the periodic table, there are nuclei, which are called stable, i.e., the properties of these nuclei do not change with the passage of time, unless the nuclei are otherwise disturbed. Yet there is another class of nuclei, whose number is much greater, which are unstable. They disintegrate spontaneously by emitting either electromagnetic radiations or some particles.

The phenomenon of spontaneous decay of a nucleus accompanied by the emission of alpha-particles, beta-particles, or gamma-rays is known as radioactivity. It could be either natural or artificial.

Radioactivity was the first of many startling discoveries that led the way into the world of nuclear reactions. Today, radioactive materials help us to look inside ourselves, and radioactive dating gives us clues into eras long past. Research in radioactivity has also opened the door to one of the most powerful forces known to the human race. Today, it is more important than ever that we learn how to use this power constructively.

On March 1, 1896, Henry Becquerel a French physicist made one of the most important discoveries of our time by accident. He was attempting to find out whether the rays emitted by fluorescent uranium salts were the same as the X-rays discovered in 1895 by the German physicist Wilhelm Roentgen.

Becquerel put a photographic plate that was completely sealed in paper in a drawer near a rock, identified as uranium salt, and left them there.

After a few days, he developed the plates and discovered strange bright spots. Becquerel discovered that uranium gives off invisible rays.

He concluded that uranium emitted invisible radiation, different from X-rays, spontaneously and inexhaustible. The phenomenon he discovered was named radioactivity (from the Latin radius, meaning ray).

Following Henri Becquerel’s work, in 1898, experiments conducted by Marie and Pierre Curie revealed other radioactive substances by isolating polonium and radium, unknown radioactive elements present in uranium ore.

Transmutations can be:

- **Spontaneous (natural): radioactive decays**
- **Caused: nuclear reactions**

III.1. Radioactivity

In the binding energy curve, the stability of the nucleus that has $Z > 82$ starts to decrease, and these nuclei are called unstable nuclei. Some of the unstable nuclei decay naturally by emitting some kind of particles to form a stable nucleus. The elements of atomic number $Z > 82$ and isotopes of lighter nuclei belong to naturally occurring radioactive nuclei. Each of these radioactive nuclei decays to another nucleus by the emission of a $^{4}{}_{2}He$ nucleus (α -decay) or an electron or positron (α-decay) or gamma rays (β - decay).

The phenomenon of spontaneous emission of highly penetrating radiations such as α, β, and γ rays by an element is called radioactivity. The substances which emit these radiations are called radioactive elements. These radioactive elements can be heavy elements ($Z > 82$), isotopes of lighter and heavy elements, and these isotopes are called radioisotopes. For example, carbon isotope $^{14}{}_{6}C$ is radioactive but $^{12}{}_{6}C$ is not.

Radioisotopes have a variety of applications such as carbon dating, cancer treatment, etc. When a radioactive nucleus undergoes decay, the system's mass decreases – that is, the mass of the initial nucleus before decay is always greater than the sum of the mass of the final nucleus and that of the emitted particle. When this difference in mass $\Delta m < 0$, it appears as the energy according to Einstein’s relation $E = |\Delta m|\ c^2$.

The phenomenon of radioactivity was first discovered by Henri Becquerel in 1896. Later, Marie Curie and her husband Pierre Curie did a series of experiments in detail to understand the phenomenon of radioactivity.

The phenomenon of spontaneous decay of a nucleus accompanied by the emission of alpha particles, beta particles, or gamma rays is known as radioactivity, which releases high-energy particles or rays.

It can be either natural or artificial.

Most elements in nature have no radioactive isotopes.

Some elements have some stable isotopes and some radioactive ones, e.g., potassium.

Some elements have only radioactive isotopes, e.g., uranium.

III.1. 1. Natural radioactivity

In nature, the nuclei of most atoms are stable.

However, certain atoms have unstable nuclei due to an excess of either protons or neutrons or an excess of both. They are described as radioactive and are known as radioisotopes or radionuclides. The nuclei of radioactive atoms change spontaneously into other atomic nuclei, which may or may not be radioactive. For instance, uranium 238 changes into a succession of different radioactive nuclei until it reaches a stable form, lead 206. This irreversible transformation of a radioactive atom into a different type of atom is known as disintegration. It is accompanied by the emission of different types of radiation.

A chemical element can therefore have both radioactive isotopes and non-radioactive isotopes. For example, carbon-12 is not radioactive, but carbon-14 is. Because radioactivity only affects the nucleus and not the electrons, the radioactive isotopes are the same as those of stable isotopes.

Natural radioactivity is the process by which certain elements spontaneously emit radiation from their atomic nuclei. This phenomenon occurs in unstable atomic nuclei as they try to obtain a more stable configuration. Several naturally occurring elements are radioactive, such as uranium, thorium, radium, and potassium. Isotopes of these elements have unstable nuclei that undergo radioactive decay, eventually transforming into more stable elements. Radioactive decay is a random process, and the rate of decay is measured by half-life, which is the time it takes for half of the radioactive material to decay.

Natural radioactivity is all around us, and it's present in various sources, including rocks, soil, air, and even within our bodies. While exposure to natural radioactivity is generally low and manageable, high levels of exposure can pose health risks, potentially causing cell damage and increasing the risk of cancer. Consequently, monitoring and understanding natural radioactivity are crucial for assessing its impact on the environment and human health.

III.2. Soddy and Fajans Law

In a radioactive transformation, there is a conservation of the total number of nucleons and of the overall charge.

$${}_{Z}^{A}X \longrightarrow {}_{Z-2}^{A-4}Y + {}_{2}^{4}He$$

In a balanced nuclear equation, both the atomic number and the mass number must be conserved.

III.3. The different types of disintegration

In the end, it turned out that radiation from radioactive substances can be classified into three fundamentally different groups.

Similar notation for subatomic particles

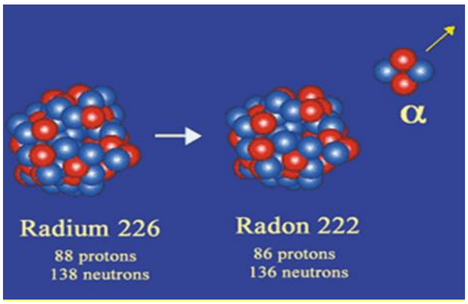
Proton ${}_{1}^{1}P$ Neutron ${}_{0}^{1}n$ Electron ${}_{-1}^{0}e$

III.3.1. Alpha radioactivity

Alpha radiation is the emission of helium nuclei that have two protons and two neutrons. The nuclei have two positive charges. Atoms with radioactive nuclei with too many protons and neutrons often emit alpha radiation. They transform into another chemical element with a lighter nucleus.

$$^{A}_{Z}X \longrightarrow {}^{A-4}_{Z-2}Y + {}^{4}_{2}He$$

- **α particle = helium nucleus $^{4}_{2}He$**



III.3.2. β decay

β decay is the emission of an electron e- or positron e+ to convert a neutron to a proton or a proton to a neutron inside the nucleus

III.3.2.1. Beta minus β^{-} radioactivity

Beta minus radiation consists of negatively charged electrons.

Certain atoms with nuclei that have too high several neutrons emit beta minus radiation. One of the neutrons within the nucleus disintegrates into a proton plus an electron. The electron is ejected, so the atom is transformed into a different chemical element.

- **Net effect: A neutron is changed into a proton.**

$$^{A}_{Z}X \longrightarrow {}_{Z+1}^{A}Y + {}_{-1}^{0}e \qquad\qquad {}^{1}_{0}n \longrightarrow {}^{1}_{1}p + {}_{-1}^{0}e$$

III.3.2.2. Beta plus β^{+} radioactivity

Beta plus radiation consists of positrons (particles with the same mass as electrons but positively charged). Some atoms with nuclei too heavily loaded with protons emit beta-plus radiation. One of the protons within the nucleus disintegrates into a neutron plus a positron. The positron is ejected, so the atom is transformed into a different chemical element.

Note that for both types of beta disintegration, the nucleus keeps the same number of nucleons (and therefore the same mass number).

$$^{A}_{Z}X \longrightarrow {}_{Z-1}^{A}Y + {}_{+1}^{0}e \qquad\qquad {}^{1}_{1}p \longrightarrow {}^{1}_{0}n + {}_{+1}^{0}e$$

- **Net effect: A proton is changed into a neutron.**

III.3.3. Gamma radioactivity

Gamma radiation is an electromagnetic wave, just like visible light or X-rays, but with more energy.

This type of radiation often follows alpha or beta disintegration. After the emission of the alpha or beta particle, the nucleus is still excited because its protons and neutrons are not yet in equilibrium. The excess energy is then rapidly released through the emission of gamma radiation. This is gamma radioactivity.

- Gamma ray: is no change in mass or atomic number

$$ {}^{A}_{Z}X^{*} \longrightarrow {}^{A}_{Z}X + \gamma $$

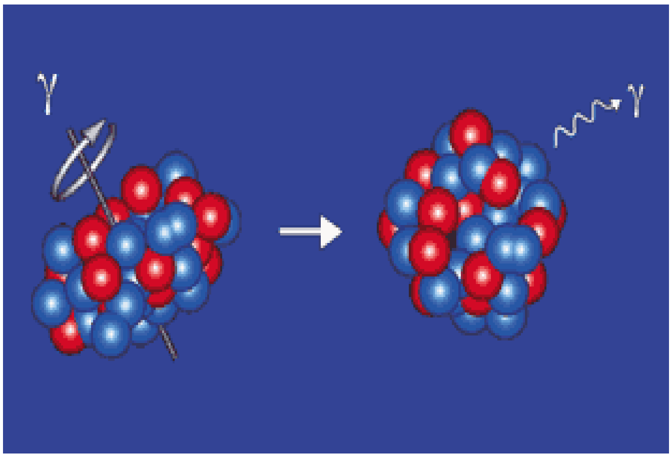


Table 1: Summary of Radioactive Decay Processes

Process	Symbol	Charge in Atomic Number	Charge in Mass Number	Charge in Number of Neutrons
α emission	${}^{4}_{2}He$ or α	-2	-4	-2
β emission	${}^{0}_{-1}e$ or β^{-*}	+1	0	-1
γ emission	${}^{0}_{0}\gamma$ or γ	0	0	0
Positron emission	${}^{0}_{1}e$ or β^{+*}	-1	0	+1

Effects of Different Types of Radiation

γ Max damage, due to high energy, deep penetration	β Penetrate only a few mm	α Little penetration only irritates the outer skin. but bad is generated internally

III.4. Artificial radioactivity and nuclear reactions

In 1934, Frédéric Joliot-Curie and Irène Joliot-Curie were the first to discover the phenomenon. They bombarded aluminum 27 with α particles to produce phosphorus 30.

Artificial radioactivity is created artificially by bombarding stable elements with various particle beams: neutrons, protons, α particles, electrons. There are three types of nuclear reaction: nuclear transmutation, nuclear fission, and nuclear fusion.

III.4.1. Nuclear transmutation:

The change of one element into another by particle bombardment (neutron, α particle, proton, nucleus)

- Most of the ~3300 known radioisotopes are made through artificial nuclear transmutation in particle accelerators.
- All elements with atomic numbers greater than 92 (transuranium elements) have been artificially made.

III.4.1.1. Helium transmutation

Proton release: reaction (α, p)

The (α, p) reaction is a nuclear reaction in which an alpha particle (α) interacts with a target nucleus, resulting in the release of a proton (p). This reaction is also known as an alpha-particle-induced proton emission reaction.

The (α, p) reaction typically occurs when accelerated α particles, which are helium nuclei consisting of two protons and two neutrons, collide with a nuclear target. During the interaction, one of the alpha particle's protons is transferred to the target nucleus, while the alpha particle itself may be modified or scattered in the process.

This reaction can be used to study the properties of atomic nuclei and produce specific radioactive isotopes. For example, by using particle accelerators, a target containing an appropriate target nucleus can be bombarded with energetic α particles to induce the (α, p) reaction and produce specific radioactive isotopes of the target nucleus.

The (α, p) reaction is an important reaction in the field of nuclear physics and nuclear reaction research. It enables the study of nuclear properties, the production of radioactive isotopes, and the understanding of nuclear reaction mechanisms.

$$\boldsymbol{{}^{A}_{Z}X + {}^{4}_{2}He \longrightarrow {}^{A+3}_{Z+1}Y + {}^{1}_{1}H}$$

$${}^{14}_{7}N + {}^{4}_{2}He \longrightarrow {}^{17}_{8}O + {}^{1}_{1}H \text{ Or } {}^{14}_{7}N\ (\alpha, p),\ {}^{17}_{8}O$$

Neutron liberate: reaction (α, n)

The (α, n) reaction is a nuclear reaction in which an alpha particle (α) interacts with a target nucleus, resulting in the release of a neutron (n). This reaction is also called alpha-particle-induced neutron emission reaction.

In the (α, n) reaction, an accelerated alpha particle collides with a target nucleus, transferring energy and momentum to the nucleus. The target nucleus absorbs the alpha particle, becomes excited, and then undergoes a process called nuclear deexcitation or gamma decay. During this process, the target nucleus emits a neutron, reducing its atomic number by one.

The (α, n) reaction is particularly important in nuclear physics and nuclear engineering. It is used to produce neutron-rich isotopes for a variety of applications including neutron capture experiments, neutron source development and nuclear medicine. It is also used in the study of nuclear structure and reactions, as well as in the production of isotopes for research and industrial purposes.

Furthermore, (α, n) reaction plays an important role in nuclear reactions in stellar environments, such as in supernovae or during nucleosynthesis processes. It contributes to the formation of heavy elements by providing a mechanism for neutron capture and subsequent beta decay.

Overall, the (α, n) reaction is a fundamental process involving the interaction of an α particle with a target nucleus, resulting in the emission of neutrons and having various applications and impacts in nuclear science and astrophysics.

$$ {}^{A}_{Z}X + {}^{4}_{2}He \longrightarrow {}^{A+3}_{Z+1}Y + {}^{1}_{0}n $$

$$ {}^{27}_{13}Al + {}^{4}_{2}He \longrightarrow {}^{30}_{15}P + {}^{1}_{0}n $$

Reaction without capture

A reaction without capture refers to a nuclear reaction where the incident particle does not become incorporated or captured by the target nucleus. Instead, the reaction involves the exchange of energy, momentum, or particles between the incident particle and the target nucleus.

In such reactions, the incident particle interacts with the target nucleus, transferring some of its energy and momentum. This interaction can result in various outcomes, such as elastic scattering, inelastic scattering, or particle emission. The incident particle may be deflected or change energy while the target nucleus remains intact.

Reactions without capture are important in nuclear physics as they provide valuable information about the properties of atomic nuclei, such as their size, shape, and internal structure. They are also used in experimental techniques to probe nuclear interactions, study nuclear reactions, and investigate nuclear properties.

Transmutation by Proton capture

Transmutation by proton capture refers to a nuclear process in which a nucleus captures a proton, resulting in the transformation of the nucleus into a different element. This process is also known as proton-induced transmutation or (p, γ) reaction.

In this type of reaction, a proton collides with a target nucleus and becomes incorporated into the nucleus, increasing its atomic number by one. The captured proton combines with the target nucleus, resulting in the formation of a new nucleus. Typically, the newly formed nucleus is in an excited state and subsequently undergoes gamma decay, emitting a gamma ray photon to transition to a lower energy state.

The transmutation by proton capture plays a significant role in nuclear reactions and nuclear applications. It is commonly utilized in nuclear medicine for the production of radioactive isotopes used in diagnostic imaging and cancer treatment.

By bombarding stable target nuclei with protons, specific isotopes can be created that have desirable properties for medical purposes.

Proton capture reactions are also important in stellar nucleosynthesis, where they contribute to the formation of elements in stellar environments. In particular, proton capture reactions are responsible for the production of lighter elements, such as helium, lithium, and beryllium, in the nuclear fusion processes occurring within stars.

Helium emission: reactions (p, α)

These are nuclear reactions in which protons (p) bombard the nucleus and eject alpha particles.

An example is: $\mathbf{{}_{7}Li + p \rightarrow \alpha + \alpha}$.

Here a proton hits a lithium-7 nucleus, producing an alpha particle and leaving behind an alpha particle as well (2 alpha particles total).

These reactions typically occur in light nuclei, where protons have enough energy to overcome the binding energy of the nucleus and eliminate alpha particles.

In order for these reactions to occur, protons require kinetic energy of several MeV. This is possible in particle accelerators or in stellar nuclear fusion.

The emission of an alpha particle usually leaves the daughter nucleus in an excited state, which then decays to the ground state via gamma emission.

These types of (p, α) reactions are very useful for studying nuclear structure and stellar nucleosynthesis processes. Cross-sections and reaction rates provide information about nuclear properties.

III.4.1.2. Neutron emission: reactions (p, n)

These are nuclear reactions where a proton (p) hits a target nucleus and a neutron (n) is emitted.

An example is $\mathbf{{}_{7}Li + p \rightarrow {}_{8}Be + n}$.

Here a proton collides with a lithium7 nucleus, causing a neutron to be knocked out and leaving behind an unstable beryllium-8 nucleus.

For these reactions to happen, the incoming proton needs enough energy to overcome the neutron binding energy in the target nucleus. Typically, several MeV of energy is required.

Neutron emission reactions tend to occur with lighter nuclei where the neutron separation energy is lowest. As nuclei get heavier, (p,n) reactions become less energetically favorable.

The residual nucleus after the neutron emission is often left in an excited state and emits gamma radiation as it decays to the ground state.

These reactions are useful for producing neutron beams for research, using proton beams on low **Z** targets like lithium or beryllium.

They also play a role in stellar nucleosynthesis processes, especially proton-induced reactions during novae outbursts. The flux of protons can induce (p,n) reactions on elements like oxygen and neon.

In addition, some radioisotopes can be produced by (p,n) reactions, taking advantage of the residual radioactive nuclei created after neutron emission.

III.4.1.3. Reaction (p, D)

These are proton-induced nuclear reactions where a deuteron (D, a hydrogen-2 nucleus) is emitted from the target nucleus after being hit by a proton.

An example is 7Li + p → 8Be + D. Here the proton hits lithium-7, causing the emission of a deuteron and leaving beryllium-8.

For the reaction to occur, the proton needs enough energy to overcome the deuteron's binding energy in the target nucleus. Usually, several MeV of energy is required.

Light nuclei like lithium, beryllium, and boron are common targets for (p, D) reactions, as their low binding energies favor deuteron emission.

The residual nucleus after the deuteron emission is often left in an excited state and releases energy by gamma emission as it drops to the ground state.

These reactions are useful for generating monoenergetic deuteron beams for nuclear physics experiments when an accelerated proton beam hits a target.

They also play a role in nucleosynthesis in stellar environments like novae, where high fluxes of protons can induce deuteron emission.

In addition, some radioisotopes like carbon-11 can be produced by (p, D) reactions on targets like boron-10.

The reaction cross-sections and rates give information about the nuclear structure and forces binding nucleons in the nucleus.

III.4.1.4. Emission of protons: Reactions (n, p)

The (n, p) reaction, also known as neutron-induced proton emission often denoted as (n, p) reactions, is a nuclear reaction in which a neutron (n) interacts with a target nucleus, resulting in the emission of a proton (p). It is a type of neutron capture reaction that leads to the conversion of a neutron into a proton within the target nucleus.

In the (n, p) reaction, a neutron is absorbed by the target nucleus, causing it to become excited. The excess energy is then released by the emission of a proton. The target nucleus transforms into a different nucleus with one additional proton, while the number of neutrons remains the same or may change depending on the specific reaction.

One common example of a (n, p) reaction is the capture of a neutron by a nucleus followed by the emission of a proton. For instance:

$$n + X \longrightarrow X^{*} \longrightarrow X + pn + X \longrightarrow X^{*} \longrightarrow X + p$$

The (n, p) reaction is important in various fields of nuclear science and technology. It is used in nuclear reactors to control neutron populations and to produce specific radioisotopes through neutron activation. Neutron activation analysis, a technique used for elemental analysis, relies on (n, p) reactions to induce proton emissions that can be detected and measured.

In nuclear astrophysics, (n, p) reactions are significant in stellar nucleosynthesis. Neutrons are captured by atomic nuclei in stellar environments, and subsequent (n, p) reactions can occur, leading to the synthesis of heavier elements. These reactions play a crucial role in the formation of elements beyond iron in stars.

Furthermore, the study of (n, p) reactions contributes to our understanding of nuclear structure, nuclear reaction mechanisms, and the properties of atomic nuclei. Experimental investigations and theoretical models are employed to analyze these reactions, providing insights into the behavior of nucleons within atomic nuclei.

This type of reaction is important in various nuclear processes, including nuclear fission, nuclear fusion, and nuclear reactions in stars. It plays a crucial role in nuclear physics, astrophysics, and nuclear engineering, contributing to the understanding of nuclear reactions and the behavior of atomic nuclei under different conditions.

III.4.2. Fission Reaction

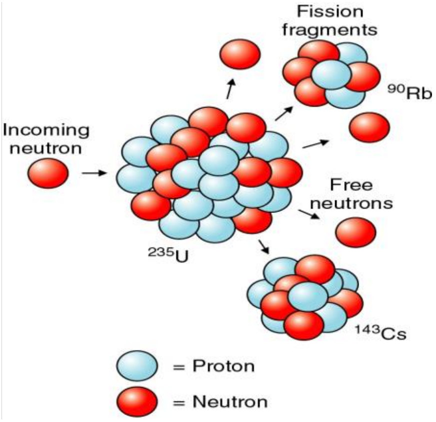
A fission reaction is a nuclear reaction in which a heavy atomic nucleus splits into two or more lighter nuclei, accompanied by the release of a significant amount of energy. This process is typically initiated by bombarding the nucleus with a neutron, which causes it to become unstable and undergo fission like uranium-235 or plutonium-239, which absorbs a neutron, forming an excited compound nucleus. The compound nucleus then undergoes a process called nuclear fission, where it splits into two or more smaller fragments, usually nuclei of intermediate mass, such as xenon and strontium isotopes. Along with the smaller nuclei, several neutrons are also released. Neutrons produced by fission can trigger other fissions, leading to a chain reaction.

The fission of heavy elements releases enormous amounts of energy because the binding energy per nucleon is greater for heavier nuclei.

It's worth noting that there are different types of fission reactions, such as spontaneous fission, induced fission, and ternary fission, depending on the conditions and mechanisms involved.

However, the most common and widely studied type of fission reaction is induced fission, which occurs when a nucleus absorbs a neutron.

fission reactions have important applications in nuclear power generation, nuclear weapons, and scientific research, and they play a crucial role in our understanding of nuclear physics and energy production.



III.4.3. fusion Reaction

Nuclear fusion is the process by which two light atomic nuclei combine to form a heavier nucleus, releasing enormous amounts of energy in the process.

Fusion requires immense temperatures and pressures to overcome the positive charges of the nuclei and allow them to get close enough to fuse. It occurs naturally in stars like the sun.

In a fusion reaction, nuclei are brought close enough together that the strong nuclear force, which binds protons and neutrons within the nucleus, can overcome the electrostatic repulsion between positively charged protons. This allows the nuclei to merge and form a more massive nucleus.

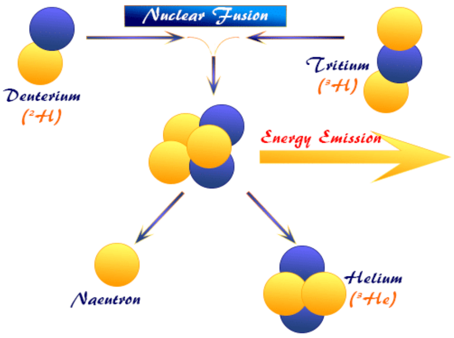
The most well-known and extensively studied fusion reaction is the fusion of hydrogen isotopes: deuterium (D) and tritium (T). When deuterium and tritium nuclei collide and fuse, they form a helium nucleus (two protons and two neutrons) and release a high-energy neutron. This reaction is the primary pathway for energy production in current experimental and theoretical fusion reactors.

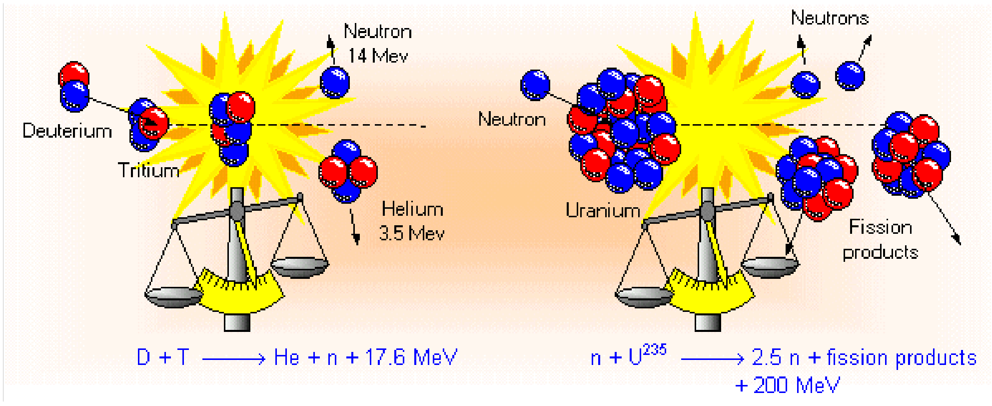
When two nuclei fuse, the mass of the resultant nucleus is less than the sum of the masses of the original nuclei.

This "missing" mass is converted to energy according to Einstein's equation E=m c^2.

For fusion to occur, the nuclei must have enough kinetic energy to overcome the repulsive Coulomb force and get within a very short distance for the strong nuclear force to attract them together.

Successful realization of fusion power would offer numerous advantages, including abundant fuel resources, reduced radioactive waste compared to fission reactions, and minimized greenhouse gas emissions. However, significant technological and engineering hurdles still need to be overcome before fusion energy becomes a practical and commercially viable source of electricity.





III.5. Radioactive decay kinetics

III.5.1. Law of radioactive decay

According to the nature of quantum mechanics, one cannot accurately predict when a radioactive nucleus will decay. However, we can accurately calculate the probability of a nucleus decaying within a certain time interval. Consider a sample containing a large number of identical radioactive nuclei. (For example, an ordinary macroscopic sample with mass 10–100 g will contain ~ 10^{23} nuclei.) Let the probability of a nucleus decaying per unit time be λ. This probability depends only on the properties of the nucleus. It does not depend on the number of nuclei present in the sample. Thus, r is a constant for a given radioactive nucleus for all time. The quantity r is called the decay constant. The decay constant can be precisely calculated using quantum mechanics. In the following, we assume the decay constant has a definite (usually different) value for each radioactive nucleus.

Let the number of undecayed nuclei at time t′ be N′. Let ΔN′ nuclei decay in a short time Δt′. Then, from the definition of λ

$$\lambda = \frac{\frac{|\Delta N|}{N}}{\Delta t} = \frac{\frac{|\Delta N|}{\Delta t}}{N}$$

$$\frac{|\Delta N|}{\Delta t} = \lambda\, N$$

Since N is decreasing, ΔN is negative. So, the decay velocity is written:

$$-\frac{\Delta N}{\Delta t} = \lambda N$$

Or

$$\frac{\Delta N}{\Delta t} = -\lambda N$$

where λ is a constant of proportionality and is known as the decay constant of the element. Negative sign indicates that as **t** increases, **N** decreases.

Taking the limit $\Delta t' \to 0$, we have

$$\frac{dN}{dt} = -\lambda N \qquad (3)$$

Rewriting Eq (3)

$$\frac{dN}{N} = -\lambda dt$$

To solve this differential equation, we separate the variables and, by integrating both sides, we have:

$$\int \frac{dN}{N} = -\lambda \int dt$$

$$\ln(N) = \lambda t + C \qquad (4)$$

where C is a constant of integration and is evaluated by the fact that at t = 0, the number of atoms of the radioactive element is N0. Using this condition, we get

$$C = \ln(N_0)$$

Substituting this value of C in Eq. (4), we get

$$\ln N = -\lambda t + \ln N_0$$

Or

$$\ln \frac{N}{N_0} = -\lambda t$$

Radioactive decay law

$$\boldsymbol{N = N_0 e^{-\lambda t}}$$

The exponential nature of this equation shows that it takes an infinite time for the whole of the radioactive material to disintegrate.

This law can be written in a form depending on the mass of the radioactive element, since:

In 1 mole of the element, we have N_A, the number of Avogadro

$$1\,mol \longrightarrow N_A$$

$$n\ mol\ de\ l'élément \left(\frac{m}{M}\right) \longrightarrow N$$

Thus: $\frac{m}{M} = 1\,mol \times \frac{N}{N_A}$ so $N = \frac{m.N_A}{M}$ and in the same way $N_0 = \frac{m_0.N_A}{M}$ substitute N et N_0 with its formula it follows that:

$$\frac{m.\cancel{N_A}}{\cancel{M}} = \frac{m_0.\cancel{N_A}}{\cancel{M}}.e^{-\lambda t}$$

Then

$$m = m_0\, e^{-\lambda t}\ \textbf{or}\ n = n_0\, e^{-\lambda t}$$

With:

n: number of moles of the element

m: the mass of the radioactive element at time t≠0

m_0: the mass of the radioactive element at the moment t=0

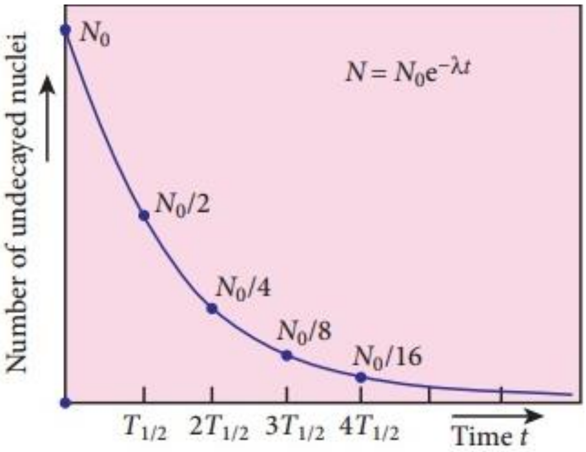


Figure.III.1. Law of radioactive decay

III.5.2. The radioactive constant λ

The radioactive constant λ is the fraction of nuclei that decay per unit of time for a specific kind of nucleus.

$$\lambda = \frac{ln2}{T}$$

III.5.3. Activity (A) or decay rate

The activity of a sample is the rate at which the radioactive nuclei decay per unit of time.

If N is the number of nuclei at a certain time t,

Activity A: $A = -\frac{dN}{dt} = \lambda N$ (1)

Substituting for N from $N = N_0 e^{-\lambda t}$ in Eq (1)

we get

$$A = -\frac{dN}{dt} = \lambda N_0 e^{-\lambda t}$$

Substituting $A_0 = \lambda N_0$

The exponential relation for activity is

$$A = A_0 e^{-\lambda t}$$

In this relation, A_0 is the activity at t = 0. The exponential factor shows that activity is decreasing with time in the same fashion as N.

Where $A_0 = \lambda N_0$ is the initial activity. Note that the activity also follows the exponential decay law.

Activity is measured in becquerels (Bq) or curies (Ci). 1 Bq = 1 decay/s. 1 Ci = 3.7×10^{10} Bq.

Unit

- **The SI unit of activity is becquerel (Bq)**

  1 becquerel = 1 Bq = 1 disintegration/s (dps or disintegrations per second).

- **Traditional unit of activity is Curie (Ci) and becquerels (Bq):**

  1 curie (Ci) = 3.7 10^{10} disintegration/s = 3.7 10^{10} Bq

activities of radioactive sources are defined in terms of millicurie (1 mCi = 10^{-3} Ci) and microcurie (1 Ci = 10^{-6} Ci).

III.5.4. Half-life of Radioactive Decay T (or $t_{1/2}$)

The half-life of a radioactive nucleus is the time period taken for half the nuclei originally present to decay (or for the activity to drop to one-half of its original value).

When one half of the atoms have decayed, the source has gone through what is called one "***half-life***".

Every radionuclide has a characteristic half-life.

After a half-life has elapsed, when t = $t_{1/2}$, the activity A drops to $\frac{1}{2}A_0$ by definition

$$\frac{1}{2}A_0 = A_0 e^{-\lambda t_{1/2}}$$

$$e^{\lambda t_{1/2}} = 2$$

Taking natural logarithms of both sides of this equation

$$\lambda t_{1/2} = \ln 2$$

Half-life $t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$

Therefore, the half-life of a radioactive material depends upon the disintegration constant λ. The larger the value of the disintegration constant, the smaller the half-life,

i.e. nuclei of radioactive material will decay faster and vice versa. Half-life of a radioactive material is its intrinsic property and it cannot be altered by any physical or chemical means. After each half-life, the number of radioactive atoms reduces to half. For example, if we take on 1st Jan. 2006, 10,000 atoms of a radioactive material whose half-life is 1 year, then on 1st Jan. 2007, the number of radioactive atoms left becomes 5000. On 1st Jan. 2008, the number will be 2500 and on 1st Jan.

2009, it will be 1250, and so on. It is clear that after infinite half-lives, the number of radioactive nuclei will reduce to zero.

III.5.5. Average (Mean) Life

The average life is calculated by summing the lives of all the nuclei and dividing by the total number of nuclei. Suppose N_1 nuclei decay in time t_1, dN_2 nuclei decay in time t_2, dN_3 nuclei decay in time t_3, and so on, then the average life or mean life will be

$$\tau = \frac{t_1 dN_1 + t_2 dN_2 t_3 dN_3 + \cdots}{dN_1 + dN_2 + dN_3 + \cdots}$$

In integral form

$$\tau = \frac{\int_{00}^{N_0} t\, dN}{\int_0^{N_0} dN} = \frac{1}{N_0}\int_0^{N_0} t dN$$

$$dN = -\lambda N_0 e^{-\lambda t} dt$$

Now for $t = \infty$, $N = 0$ and $t = 0$, $N = N_0$

Therefore,

$$\tau = -\frac{1}{N_0}\int_{\infty}^{0} \lambda t N_0 e^{-\lambda t}\, dt$$

$$\tau = \lambda \int_{\infty}^{0} t\, e^{-\lambda t}\, dt \quad (1)$$

The integral in eq (1) can be evaluated by parts

$$\int_0^{\infty} t\, e^{-\lambda t}\, dt = \left[t\frac{e^{-\lambda t}}{-\lambda}\right]_0^{\infty} - \int_0^{\infty} 1\frac{e^{-\lambda t}}{-\lambda} dt$$

$$= (0 - 0) + \left[\frac{1}{\lambda} \times \frac{e^{-\lambda t}}{-\lambda}\right]_0^\infty$$

$$= -\frac{1}{\lambda^2}(0 - 1) = \frac{1}{\lambda^2}$$

Therefore, the value of average life form eq (1) is

$$\boldsymbol{\tau = \frac{1}{\lambda} = \frac{t_{1/2}}{0.693}}$$

III.6. Applications of Radioactivity

Applications of radioactivity are varied and interesting. Before discussing these applications, we discuss some of the well-known cases where radioactivity has been utilized.

Napoleon I Bonaparte, Emperor of France, died in 1821 at St. Helena. The exact cause of his death was not known at that time. It was only recently that, by analyzing various elements present in his scalp hair using radioactive techniques, scientists were able to confirm that he died of repeated arsenic poisoning.

In 1963, American President J.F. Kennedy was shot dead. It was not clear whether one or two assassins shot him because there were two bullet marks on his body. It was only by analyzing the bullet pieces recovered from his body using a radioactive technique that it was confirmed that he was shot dead by a single assassin.

Dinosaurs went extinct on Earth about 65.5 million years ago. The asteroid collision theory to account for the extinction of dinosaurs, which was first proposed by Walter Alvarez in the late 1970s, links the extinction event at the end of the Cretaceous period to an asteroid impact approximately 65.5 million years ago. Alvarez proposed that a sudden increase in iridium levels, recorded around the world in the period’s rock stratum, was direct evidence of the impact. The bulk of the evidence no suggests that a 10 km-wide asteroid hit in the vicinity of the Yucatán Peninsula, creating the 170 km-wide Chicxulub Crater and triggering the mass extinction. The Yucatán Peninsula separates the Caribbean Sea from the Gulf of Mexico.

The impact caused extinctions both directly (by heat from the meteorite impact) and also indirectly (via a worldwide cooling brought about when matter ejected from the impact crater reflected thermal radiation from the sun).

We are familiar with unmanned space missions to the moon and Mars. In these missions, one of the purposes is to know the elemental composition of the planet's soil. For this purpose, these flights are equipped with α emitting radioactive sources. The soil of the planet is exposed to α particles. By measuring the energy of the back-scattered α-particles, scientists can get a clear picture of the elements present in a planet's soil.

Having discussed some of the interesting applications of radioactivity, we discuss below some of the typical applications of radioactivity in various fields.

III.6.1. Medicine

Some of the best uses of radioactivity are in the fields of medicine and archaeology. In medicine, radioactive isotopes help us a great deal. Doctors use radioactive isotopes to diagnose and treat several illnesses.

Gamma rays are used to kill rapidly dividing cancer cells.

For diagnostic purposes, X-rays are the most common example, which locate any fractured bone inside the body. X-rays are also used to study the gastrointestinal tract.^{132}I and ^{123}I are used to study malfunctioning thyroid glands. Kidney function is also studied using a compound containing ^{131}I.

A more recent development is Positron Emission Tomography (PET), which is a more precise and accurate technique for locating tumors in the body. A positron emitting radionuclide (e.g. ^{18}F) is injected to the patient and it accumulates in the target tissue. As it emits positrons which promptly combine with nearby electrons, it results in the simultaneous emission of two g-rays in opposite directions. These γ-rays are detected by a PET camera and give precise indication of their origin, i.e. depth also. This technique is also used in cardiac and brain imaging.

The most common therapeutic use of radioisotopes is in treating cancer. In this technique, cancerous cells are destroyed using g-rays from a ^{60}Co radioactive source. Sometimes wires or sealed needles containing radioactive isotope such as ^{192}Ir or ^{125}I are directly placed into the cancerous tissue. The radiations from the radioisotope attack the tumor as long as the needle/ wire is in place.

When the treatment is complete, these are removed. This technique is frequently used to treat mouth, breast, lung, and uterine cancer.

^{32}P is used to treat excess of red blood cells produced in the bone marrow.

III.6.2. Food and Agriculture

One of the more controversial uses of radiation today is food irradiation. High doses of g-radiation do not make food radioactive. Gamma Irradiation kills bacteria, insects, and parasites, and retards spoilage in some foods like potatoes, onions, cooked food, etc. Irradiated foods are regularly eaten by astronauts on space missions, as well as by hospitalized patients with weak immune systems who need extra protection from microorganisms in food.

The irradiation process involves exposing food to intense controlled amounts of gamma rays from ^{60}Co or ^{137}Cs, X-rays, or electron beams from particle accelerators. The process has about the same effect on food as canning, cooking, or freezing. It kills pests and extends shelf life, but also reduces the food's nutritional value somewhat by destroying vitamins A, B1 (thiamine), C, and E. No radiation remains in the food after treatment.

III.6.3. Geology and Element Identification

Radioactivity is used to identify the location of deposits of uranium and other radioactive minerals. This is useful in mining exploration. The intensity of detected radiation also is an indication of the amount of radioactive element that may be located there.

III.6.4. Insect Control

About 10% of the world's crops are destroyed by insects. In efforts to control insect plagues, authorities often release sterile laboratory-raised insects into the wild. These insects are made sterile using ionizing radiation. They are irradiated with this radiation before they hatch. Female insects that mate with sterile male insects do not reproduce, and the population of the insect pests can be quickly curbed as a consequence. This technique of releasing sterile insects into the wild called the sterile insect technique (SIT), is commonly used in protecting agricultural industries in many countries around the world.

III.6.5. Reactors

Atomic nuclei are storehouses of huge amounts of energy. This huge amount of energy can be explored when a heavy nucleus is broken into two or more lighter fragments or when two light nuclei are fused into a heavier one. Let us calculate energy released when we break a heavy nucleus into two lighter fragments.

III.6.6. Radiocarbon Dating

The principle of radioactive decay is applied in the technique of radioactive dating, a process widely used by scientists to determine the age of materials and artifacts.

Radioactive dating is defined as the method of determining the age of biological or geological samples by using the radioactive technique.

There are many radioisotopes by which we can determine the age of a given object, but the two most commonly used methods are:

Radiocarbon dating.

Certain natural radioactive elements can be used as chronometers for looking back in time. Methods of dating have been developed based on the decay of the radioactivity contained in the objects or remains being studied.

It is possible to go back tens of thousands of years using carbon-14, and even further using other methods such as thermoluminescence and uranium/thorium dating.

Carbon-14 dating is used to study the history of Man and his environment during a period between 5,000 and 50,000 years ago.

The use of radioactive 14C for dating was first done by William Libby at the
University of Chicago, USA, in 1947.

Carbon is very widespread in our environment and in particular, is a constituent of the carbon dioxide gas molecule present in the atmosphere.

This carbon consists mainly of carbon-12. However, a small proportion of radioactive carbon-14 is naturally present. There is the same ratio of carbon-14 to carbon-12 in the atmosphere and in the living world (plants and animals) during the life of each individual because of necessary exchanges between them (respiration, photosynthesis and food).

When an organism dies, carbon-14 is no longer renewed through exchanges with the outside world. As it gradually disintegrates, the proportion contained within the organism diminishes.

So by measuring the carbon-14 to carbon-12 ratio we can ascertain the date of death. The less carbon-14 there is in the fossil to be dated, the longer ago death occurred.

The relatively short half-life of $_{14}$C (5730 years) means that the amount of $_{14}$C remaining in materials and objects older than about 30,000 years is too small to be measured experimentally. Thus, carbon dating has the following two limitations:

It cannot measure the age of an object older than about 30,000 years.

It cannot measure the age of non-living objects like rocks and minerals.

III.7. Damaging Effects of Radiation

Nuclear radiation is ionizing radiation. It has enough energy to strip electrons from atoms. When a nuclear particle passes through matter (meat) via radiation, it actually collides with electrons, thereby ionizing the atoms it strikes. It destroys organic molecules: tissues, these effects are: - Pathological effects: development of lesions, cancer, and leukemia - Genetic effects: changes in genes. Likewise, all radiation has the following properties: Alpha-radiation: has low penetration into the skin and is very dangerous if swallowed Beta-radiation: more penetrating (1 cm inside flesh), stopped by interaction with atomic nuclei γ rays: Very penetrating and can penetrate the human body. All this radiation can cause cancer

- Ionizing power: the ability of radiation to ionize molecules and atoms. More massive particles have more potential to interact with and ionize other molecules.
- Penetrating power: the ability of radiation to penetrate matter. Smaller particles can penetrate more deeply.

- Acute radiation damage: damage to cells resulting from exposures to large amounts of radiation in a short period of time
- Increased cancer risk: Lower radiation doses over a longer period of time can cause damage to somatic cells and increase cancer risk.
- Genetic defects: damage to DNA in reproductive cells that shows an effect in offspring

CHAPTER IV The Electronic Structure of the Atom

IV. Introduction

Historically, results observed from the studies of interactions of radiations with matter have provided immense information regarding the structure of atoms and molecules. Neils Bohr utilized these results to improve upon the model proposed by Rutherford. Two developments played a major role in the formulation of Bohr's model of the atom. These were:

(i) Dual character of electromagnetic radiation, which means that radiations possess both wave-like and particle-like properties.

(ii) Experimental results regarding atomic spectra.

IV.1 Dual Behavior of Electromagnetic Radiation (wave-corpuscle duality)

Electromagnetic radiation exhibits a dual nature known as wave–particle duality. On one hand, wave theory explains phenomena such as interference and diffraction, where light behaves like a continuous wave spreading through space. On the other hand, quantum theory describes light as discrete packets of energy called photons, which successfully explain black body radiation and the photoelectric effect (as demonstrated by Albert Einstein in 1921).

To resolve this apparent contradiction, scientists accepted that light possesses both wave-like and particle-like properties. When light propagates, it shows wave behavior; when it interacts with matter, it behaves like particles. These two aspects are complementary, meaning light can manifest either character depending on the experimental conditions.

It is then necessary to consider the wave and corpuscular aspects as complementary: the light sometimes manifests a wave character, sometimes a corpuscular character. We then speak of wave-particle duality.

- **Wave**

A wave is an oscillation or periodic movement that can transport energy from one point in space to another without any conveying of matter between the points. Common examples of waves are all around us. Shaking the end of a rope transfers energy from your hand to the other end of the rope, dropping a pebble into a pond causes waves to ripple outward along the water's surface.

In each of these cases, kinetic energy is transferred through matter (the rope, or water) while the matter remains essentially in place.

IV.1.1 Wave Nature of Electromagnetic Radiation and Electromagnetic Spectrum

In the mid-19th century, physicists studying thermal radiation from heated objects did not yet understand its fundamental nature. The key breakthrough came from James Clerk Maxwell in the 1860s and 1870s. Building on Faraday's work, Maxwell theoretically demonstrated that accelerating electric charges generate linked, fluctuating electric and magnetic fields. These fields propagate through space as electromagnetic waves at the speed of light, as in Fig. IV.1. Maxwell's theory unified electricity and magnetism, correctly proposing that light itself is an electromagnetic wave. These waves are transverse (with perpendicular electric and magnetic components), require no medium to travel through, and carry energy. This framework explained that thermal radiation is simply one part of a continuous spectrum of electromagnetic waves, which also includes other types distinguished by their different wavelengths. We will consider here only a few simple properties.

1- The oscillating electric and magnetic fields produced by oscillating charged particles are perpendicular to each other and both are perpendicular to the direction of propagation of the wave. A simplified picture of the electromagnetic wave is shown in Fig. IV.1.

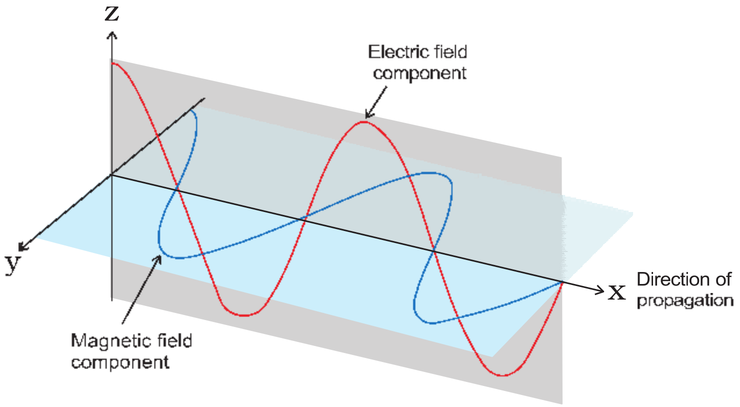


Fig. IV.1. The electric and magnetic field components of an electromagnetic wave.

2- Unlike sound waves or waves produced in water, electromagnetic waves do not require a medium and can move in a vacuum.

3- It is now well established that there are many types of electromagnetic radiation, which differ from one another in wavelength (or frequency).

These constitute what is called the electromagnetic spectrum (Fig. IV.2). We are surrounded by electromagnetic radiation as never before. Different regions of the spectrum are identified by different names. Some examples are the radio frequency region around 10^6 Hz, used for broadcasting; the microwave region around 10^{10} Hz used for radar; the infrared region around 10^{13} Hz used for heating; and the ultraviolet region around 10^{16} Hz, a component of the sun’s radiation. The small portion around 10^{15} Hz, is what is ordinarily called visible light. It is only this part that our eyes can see (or detect). Special instruments are required to detect non-visible radiation.

Studies link electromagnetic radiation to cancer, Alzheimer's, Autism, chronic fatigue, Headaches, and other Health Issues.

4- Different kinds of units are used to represent electromagnetic radiation.

These radiations are characterized by the properties, namely, frequency (ν) and wavelength (λ).

(1) Wavelength (λ)

It is defined as the distance between the two nearest crests or nearest troughs. It is measured in terms of an Å (Angstrom), pm (Picometer), nm (nanometer), cm (centimeter), m (meter).

$$\mathbf{1Å = 10^{-10}\ m,\ 1Pm = 10^{-12}\ m}$$

$$\mathbf{1nm = 10^{-9}\ m,\ 1cm = 10^{-2}\ m}$$

(2) Frequency (ν)

The frequency of a wave is the number of waves that pass through a point in 1 sec. it is measured in terms of Hertz (Hz), sec^{-1}, or cycle per second (cps)

1 Heartz = 1 sec^{-1} = 1 cps.

$$\boldsymbol{\nu = \frac{c}{\lambda}}$$

(3) Time period (T)

The time taken for one complete oscillation of a wave is known as period (T). Time is taken by a wave to travel a distance equal to one wavelength.

$$T = \frac{1}{\lambda}$$

(4) Velocity (c)

It is defined as the distance covered by a wave in 1 sec.

$$\nu = \frac{\lambda}{T}$$

These components have the same wavelength, frequency, speed, and amplitude, but they vibrate in two mutually perpendicular planes.

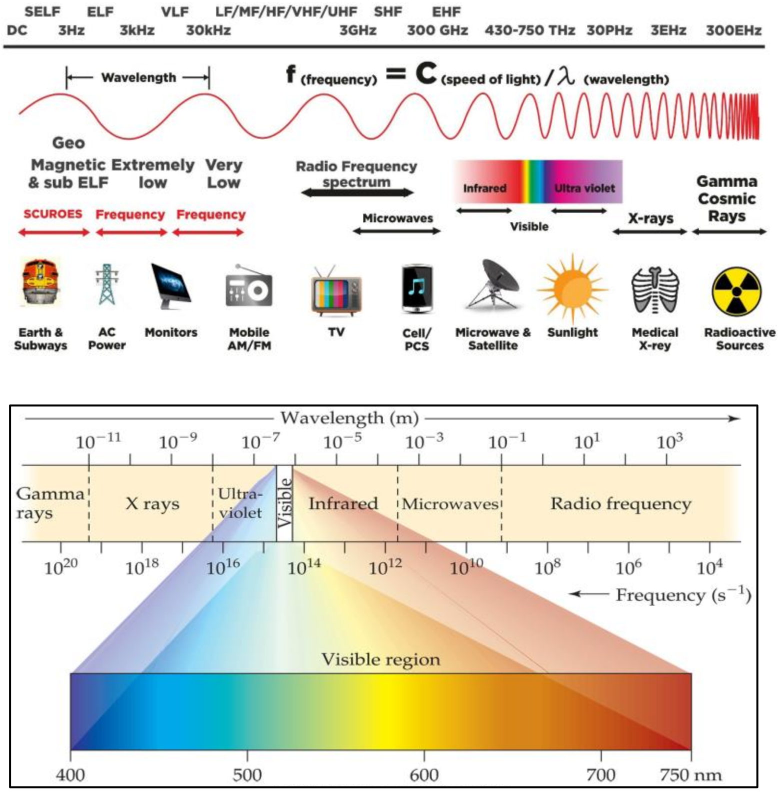


Fig.IV.2. The spectrum of electromagnetic radiation. The visible region is only a small part of the entire spectrum.

IV.1.2. Particle Nature of Electromagnetic Radiation: Planck's Quantum Theory

The wave nature of electromagnetic radiation can explain some of the experimental phenomena, such as diffraction and interference

It is noteworthy that Max Planck gave the first concrete explanation of the phenomenon of black-body radiation in 1900.

Max Planck arrived at a satisfactory relationship by assuming that absorption and emission of radiation arise from an oscillator, i.e., atoms in the wall of the black body. Their frequency of oscillation is changed by interaction with oscillators of electromagnetic radiation. Planck assumed that radiation could be subdivided into discrete chunks of energy. He suggested that atoms and molecules could emit or absorb energy only in discrete quantities and not in a continuous manner. He gave the name quantum to the smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation. The energy (E) of a quantum of radiation is proportional to its frequency (ν) and is expressed by the following equation.

$$E = \nu\, h$$

The proportionality constant, 'h' is known as Planck's constant and has the value 6.626×10^{-34} J.s.

On the other hand, light had been considered to be electromagnetic waves. However, after the discovery of light quanta (photons), it was clarified that light has a wave nature at one time and a particle nature at another time. Therefore, light has a kind of **duality**.

IV.1.2 .1 Photoelectric Effect

During his experiments on electromagnetic waves, Hertz noticed that sparks occurred more readily in the air gap of his transmitter when ultraviolet light was directed at one of the metal balls.

Late in the nineteenth century a series of experiments revealed that electrons are emitted from a metal surface when light of sufficiently high frequency (ultraviolet light is required for all but the alkali metals) falls upon it. This phenomenon is known as the photoelectric effect and the emitted electrons are called photoelectrons.

Figure IV.3 illustrates the type of apparatus employed to study the photoelectric effect more precisely.

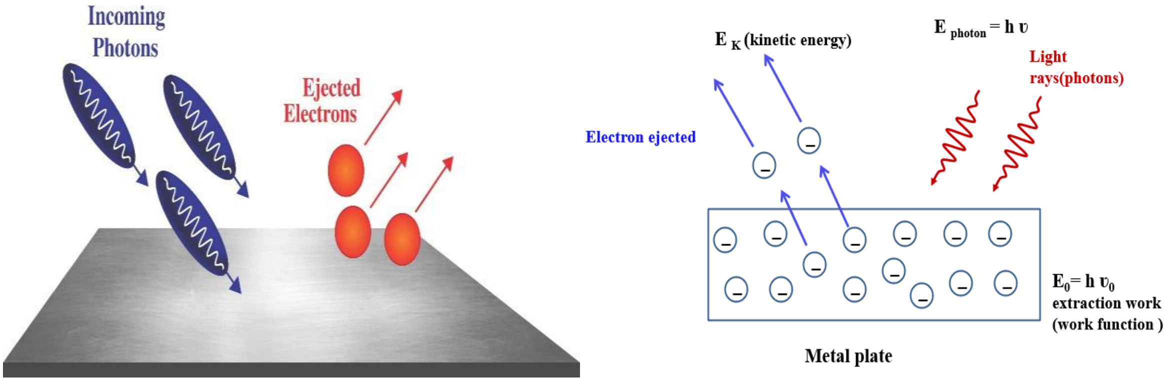


Figure IV. 3. The different energies constituting the photoelectric effect

The results observed in this experiment were:

(1) The electrons are ejected from the metal surface as soon as the beam of light strikes the surface, i.e., there is no time lag between the striking of a light beam and the ejection of electrons from the metal surface.

(2) The number of electrons ejected is proportional to the intensity or brightness of light.

(3) For each metal, there is a characteristic minimum frequency, $\nu0$ (also known as threshold frequency) below which the photoelectric effect is not observed. At a frequency $\nu > \nu0$, the ejected electrons come out with certain kinetic energy.

Einstein (1905) was able to explain the photoelectric effect using Planck's quantum theory of electromagnetic radiation as a starting point.

Shining a beam of light onto a metal surface, therefore, be viewed as shooting a beam of particles, the photons. When a photon of sufficient energy strikes an electron in the atom of the metal, it transfers its energy instantaneously to the electron during the collision, and the electron is ejected without any time lag or delay. The greater the energy possessed by the photon, the greater be transfer of energy to the electron and the greater the kinetic energy of the ejected electron. In other words, the kinetic energy of the ejected electron is proportional to the frequency of the electromagnetic radiation. Since the striking photon has energy equal to h.ν and the minimum energy required to eject the electron is h.ν0 (also called work function, W_0), then the difference in energy ($h\nu - h\nu_0$) is transferred as the kinetic energy of the photoelectron. Electrons could be ejected from the clean surface of a metal when light having a frequency greater than some threshold frequency was shone on it.

Following the conservation of energy principle, the kinetic energy of the ejected electron is given by the equation.

$$E_K = \frac{1}{2} m_e v^2$$

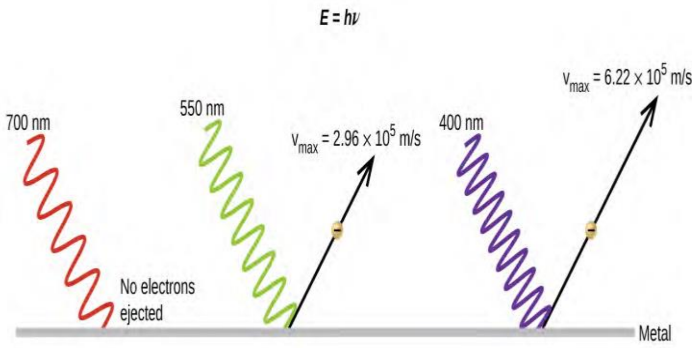


Figure. IV. 4. Photons with low frequencies do not have enough energy to cause electrons to be ejected via the photoelectric effect.

One can analyze the photoelectric effect by using the energy conservation law. The total energy of the incoming photon must be equal to the kinetic energy of the ejected electron plus the energy required to eject the electron from the metal. It is described mathematically by the photoelectric equation:

$$E_{photon} = W_0 + E_K$$

The components of this equation are as follows:

1. Energy of a photon (E): It represents the energy carried by a single photon of light. It is directly proportional to the frequency (ν) of the light wave and can be calculated using the equation E = hν, where h is Planck's constant (= 6.62×10^{-34} J·s)
2. Work function (W_0): It refers to the minimum amount of energy required to remove an electron from a specific material.

3. Kinetic energy of the ejected electron (E_K): It represents an electron's kinetic energy after emitting from the material.

$$E_{photon} = W_0 + E_K$$

$$E_{photon} = h\nu$$

$$W_0 = h\nu_0$$

$$E_K = \frac{1}{2}m_e \mathrm{v}^2$$

$$h\nu = h\nu_0 + \frac{1}{2}m_e \mathrm{v}^2$$

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

$$\frac{1}{2}m_e \mathrm{v}^2 = hc\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)$$

$$E_K = hc\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)$$

Where

m_e is the mass of the electron and v is the velocity associated with the ejected electron.

electrons could be ejected from the clean surface of a metal when light having a frequency greater than some threshold frequency was shone on it.

Example1

The threshold frequency ν_0 for a metal is 6×10^{14} s^{-1}. Calculate the kinetic energy of an electron emitted when radiation of frequency $\nu = 1.1 \times 10^{15}$ s^{-1} hits the metal.

Solution

$$E_{photon} = W_0 + E_K$$

$$E_{photon} = h\nu$$

$$W_0 = h\nu_0$$

$$E_K = E_{photon} - W_0$$

$$E_K = h(\nu - \nu_0)$$

$$E_K = 6.62 \text{ x } 10^{-34}\,(1.1 \times 10^{15} - 6 \times 10^{14})$$

Example

What is the velocity of photoelectrons ejected from copper metal by an electromagnetic wave of frequency 4.0 x 10^{16} Hz? The work function of copper is 7.53 x 10^{-19} J.

Given: ν = 4.0 x 10^{16} Hz, W_0 = 7.53 x 10^{-19} J

We use the following equation:

$\frac{1}{2}m_ev^2 = h\nu - W_0 \Rightarrow \frac{1}{2} \times 9.1 \times 10^{-31}$ kg x $v^2 = 6.62 \times 10^{-34}$ J·s x 4.0×10^{16} s^{-1} – 7.53×10^{-19} J $\Rightarrow v = 7.52 \times 10^6$ m·s^{-1}

Therefore, the electron moves with a velocity of 7.52×10^6 meters per second.

Note that the kinetic energy of the photoelectron increases linearly with frequency as long as the photon energy is greater than the work function.

For any light frequency above the threshold, the kinetic energy of the ejected electron is proportional to the energy of the incoming photon.

Example 1

Calculating the Energy of Radiation

When we see light from a neon sign, we observe radiation from excited neon atoms. If this radiation has a wavelength of 640 nm, what is the energy of the emitted photon?

Example 2

A radiation of wavelength 300 nm is incident on a silver surface. Will photoelectrons be observed?

IV.1.3. Interaction between light and matter

The speed of light depends upon the nature of the medium through which it passes. As a result, the beam of light deviates or refracts from its original path as it passes from one medium to another. It is observed that when a ray of white light is passed through a prism, the wave with shorter wavelength bands more than the one with a longer wavelength. Since ordinary white light consists of waves with all the wavelengths in the visible range, a ray of white light is spread out into a series of colored bands called the spectrum.

The light of red color, with the longest wavelength deviated the least, while violet light, which has the shortest wavelength deviated the most.

The spectrum of white light, that we can see, ranges from violet at 7.50×10^{14} Hz to red at 4×10^{14} Hz. Such a spectrum is called the continuous spectrum. Continuous because violet merges into blue, blue into green, and so on. A similar spectrum is produced when a rainbow forms in the sky. Remember that visible light is just a small portion of electromagnetic radiation. When electromagnetic radiation interacts with matter, atoms, and molecules may absorb energy and reach a higher energy state. With higher energy, these are in an unstable state.

To return to their normal (more stable, lower energy states) energy state, the atoms and molecules emit radiations in various regions of the electromagnetic spectrum.

IV.2. Types of Spectrums

The spectrum of radiation emitted by a substance that has absorbed energy is called an emission spectrum. Atoms, molecules, or ions that have absorbed radiation are said to be “excited”. To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it and the wavelength (or frequency) of the radiation emitted, as the sample gives up the absorbed energy, is recorded.

1- Emission spectrum

are of great interest in the study of electronic structure. Each element has a unique line emission spectrum. The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms in the same way as fingerprints are used to identify people.

The exact matching of lines of the emission spectrum of the atoms of a known element with the lines from an unknown sample quickly establishes the identity of the latter. German chemist, Robert Bunsen (1811-1899) was one of the first investigators to use line spectra to identify elements. Elements like rubidium (Rb), cesium (Cs), thallium (Tl), indium (In), gallium (Ga), and scandium (Sc) were discovered when their minerals were analyzed by spectroscopic methods.

2- Absorption spectrum

An absorption spectrum is like the photographic negative of an emission spectrum. A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelength which corresponds to the radiation absorbed

by the matter, leaving dark spaces in the bright continuous spectrum.

The study of emission or absorption spectra is referred to as **spectroscopy**. The spectrum of the visible light, as discussed above, was continuous as all wavelengths (red to violet) of the visible light are represented in the spectra. The emission spectra of atoms in the gas phase, on the other hand, do not show a continuous spread of wavelength from red to violet, rather they emit light only at specific wavelengths with dark spaces between them.

Such spectra are called **line spectra** or **atomic spectra** because the emitted radiation is identified by the appearance of bright lines in the spectra.

IV.3. Emission Line Spectrum of Hydrogen

Another paradox within the classical electromagnetic theory that scientists in the late nineteenth century struggled with concerned the light emitted from atoms and molecules. When solids, liquids, or condensed gases are heated sufficiently, they radiate some of the excess energy as light. Photons produced in this manner have a range of energies and there by produce a continuous spectrum in which an unbroken series of wavelengths is present. Most of the light generated from stars (including our sun) is produced in this fashion. You can see all the visible wavelengths of light present in sunlight by using a prism to separate them.

In contrast to continuous spectra, light can also occur as discrete or line spectra having very narrow line widths interspersed throughout the spectral regions. Exciting a gas at low partial pressure using an electrical current, or heating it, will produce line spectra.

Each emission line consists of a single wavelength of light, which implies that the light emitted by a gas consists of a set of discrete energies. For example, when an electric discharge passes through a tube containing hydrogen gas at low pressure, the H_2 molecule dissociates, and the energetically excited hydrogen atoms produced emit electromagnetic radiation of discrete frequencies.

Atoms only keep this excess energy for a very short time: they release it in the form of light, and it is said that they de-excite themselves. The emitted radiation consists of a series of lines of different wavelengths.

Passing the light through a prism produces a line spectrum, indicating that this light is composed of photons of four visible wavelengths, as shown in Figure IV.5. **This is the emission spectrum of the hydrogen atom**.

The hydrogen spectrum consists of several series of lines named after their discoverer.

The origin of discrete spectra in atoms and molecules was extremely puzzling to scientists in the late nineteenth century, since, according to classical electromagnetic theory, only continuous spectra should be observed. Even more puzzling, in 1885, Johann Balmer was able to derive an empirical equation that related the four visible wavelengths of light emitted by hydrogen atoms to whole integers. The Balmer series of lines is the only lines in the hydrogen spectrum that appears in the visible region of the electromagnetic spectrum.

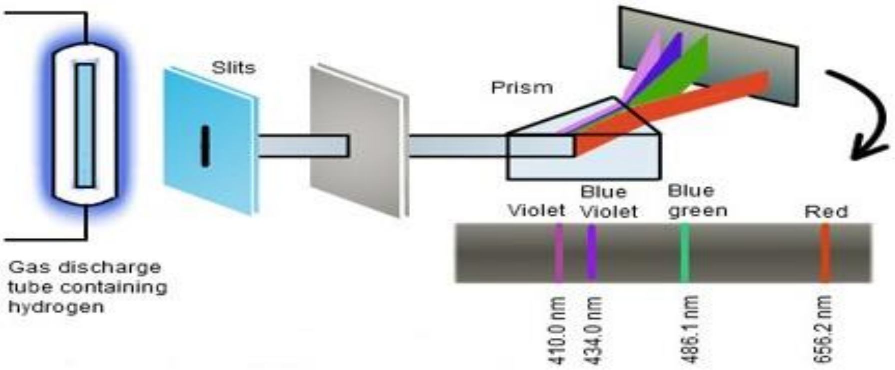


Figure IV.5. Experimental tools for H_2 experimentation with an electric discharge

The visible lines of the hydrogen spectrum obey the following formula:

$$\frac{1}{\lambda} = 1.097 \times 10^{7} \left(\frac{1}{2^2} - \frac{1}{n^2}\right) m^{-1}$$

where n is an integer equal to or greater than 3 (i.e., n = 3,4, 5....)

IV.3.1. Empirical Balmer-Rydberg relation

Balmer first demonstrated that the graphical representation of the inverse of the wavelengths as a function of $1/n^2$ (where n is an integer between 3 and 6) is a straight line.

$$\frac{1}{\lambda} = 1.097 \times 10^{7} \left(\frac{1}{4} - \frac{1}{3^2}\right)$$

IV.3.2. The RITZ-RYDBERG formula

Other discrete lines of hydrogen atoms are found in the ultraviolet and infrared regions. Swedish spectroscopist Johannes Rydberg generalized Balmer's work and developed an empirical formula that predicted all series of lines in the hydrogen spectrum, not just those limited to the visible region line, and can be described by the following expression:

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

where, n_1 and n_2 are integers, $n_1 < n_2$, n_1=1,2........ and $n_2 = n_1 + 1, n_1 + 2$....

R_H is a Rydberg's constant, its value is 1.097×10^{7} m^{-1}.

The first five series of lines corresponding to n_1 = 1, 2, 3, 4, 5 are the Lyman, Balmer, Paschen, Bracket, and Pfund series, respectively.

The basis of this equation is entirely empirical, meaning it is based exclusively on experimental measurements and is not linked to any theory.

However, it can predict the position of the lines of the hydrogen spectrum, which is the only element to which it is applicable.

IV.3.3. Concept of a series of spokes

(i) Lyman series

When the electron jumps from any of the outer orbits to the first orbit, the spectral lines emitted are in the ultraviolet region of the spectrum, and they are said to form a series called the Lyman series.

Here, n_1 = 1, n_2 = 2,3,4

The wave number of the Lyman series is given by

$$\frac{1}{\lambda} = R_H \left(\frac{1}{1^2} - \frac{1}{n_2^2}\right)$$

(iii) Balmer series

When the electron jumps from any of the outer orbits to the second orbit, we get a spectral series called the Balmer series. All the lines of this series in hydrogen have their wavelength in the visible region. Here n_1=2, n_2 = 3,4,5

The wave number of the Balmer series is,

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n_2^2} \right)$$

(iv) Paschen series

This series consists of all wavelengths which are emitted when the electron jumps from outermost orbits to the third orbit. Here n_2 = 4,5,6… and n_1 = 3. This series is in the infrared region with the wave number given by

$$\frac{1}{\lambda} = R_H \left(\frac{1}{3^2} - \frac{1}{n_2^2} \right)$$

(v) Brackett series

The series obtained by the transition of the electron from n_2 = 5, 6... to n_1 = 4 is called the Brackett series. The wavelengths of these lines are in the infrared region. The wave number is,

$$\frac{1}{\lambda} = R_H \left(\frac{1}{4^2} - \frac{1}{n_2^2} \right)$$

(vi) Pfund series

The lines of the series are obtained when the electron jumps from any state n_2 = 6, 7... to n_1=5. This series also lies in the infrared region. The wave number is,

$$\frac{1}{\lambda} = R_H \left(\frac{1}{5^2} - \frac{1}{n_2^2} \right)$$

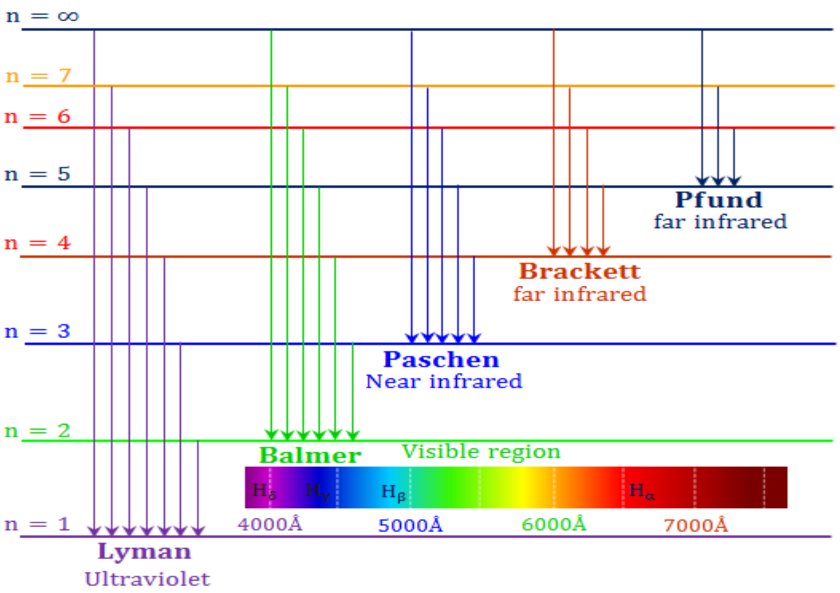


Fig. IV.6. The Lyman, Balmer, and Paschen series of transitions for hydrogen atoms.

Table IV.1 The Spectral Lines for Atomic Hydrogen

Series	**n1**	**n2**	**Spectral region**
Lyman (1916)	1	≥ 2 (2,3, 4… ∞)	Ultraviolet (UV)
Balmer (1885)	2	≥ 3 (3,4, 5… ∞)	visible
Paschen (1908)	3	≥ 4 (4,5, 6… ∞)	Infrared (IR)
Brackett (1922)	4	≥ 5 (5,6, 7… ∞)	Infrared
Pfund (1924)	5	≥ 6 (6,7, 8… ∞)	Infrared

IV.4. The classical model of the atom

There have been various atomic models throughout the history of atomic physics, namely from the early 19th century until the first part of the 20th century, when a final model of the atom being used nowadays (or accepted as the most accurate one) was invented. Although the awareness of atom existence goes way back to the antique period of world history (Greek conception of the atom), this article will be mainly about five basic atomic models, from which each one has somehow contributed to how we perceive the structure of the atom itself - Dalton´s Billiard Ball Model, J.J Thomson's "plum pudding" model, Rutherford's Planetary model, Bohr's Atomic model, Electron Cloud Model/Quantum Mechanics Model.

IV.4.1 Rutherford model

Following the work of Ernest Rutherford and his colleagues in the early twentieth century, the picture of atoms consisting of tiny dense nuclei surrounded by lighter and even tinier electrons continually moving about the nucleus was well established. This picture was called the planetary model since it pictured the atom as a miniature “solar system” with electrons orbiting the nucleus like planets orbiting the sun. The simplest atom is hydrogen, consisting of a single proton as the nucleus about which a single electron moves. The electrostatic force attracting the electron to the proton depends only on the distance between the two particles. The electrostatic force has the same form as the gravitational force between two mass particles except that the electrostatic force depends on the magnitudes of the charges on the particles (+1 for the proton and −1 for the electron) instead of the magnitudes of the particle masses that govern the gravitational force. Since forces can be derived from potentials, it is convenient to work with potentials instead, since they are forms of energy. The electrostatic potential is also called the Coulomb potential. Because the electrostatic potential has the same form as the gravitational potential, according to classical mechanics, the equations of motion should be similar, with the electron moving around the nucleus in circular or elliptical orbits (hence the label “planetary” model of the atom).

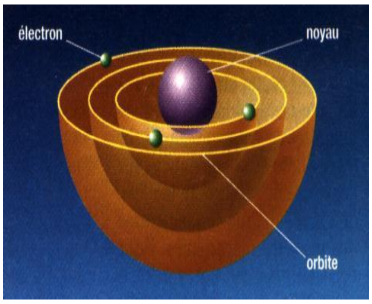


Figure IV.7. Planetary model of the atom according to Rutherford

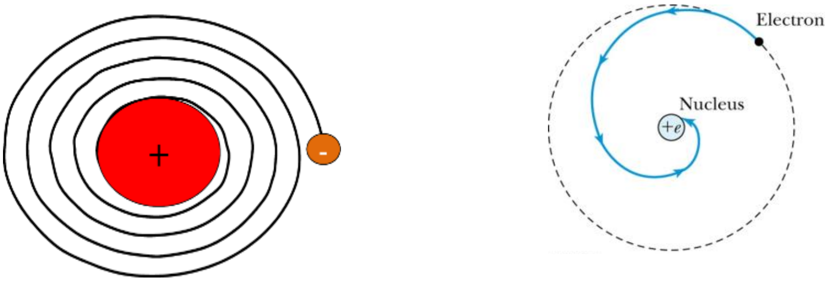


Figure IV.8. Trajectory of the electron according to the Rutherford model

According to Rutherford, the electron moving in an elliptical orbit would be accelerating (by changing direction), and, according to classical electromagnetism, it should continuously emit electromagnetic radiation. This loss in orbital energy should result in the electron’s orbit getting continually smaller until it spirals into the nucleus. This phenomenon should cause the electron to fall on the nucleus (Figure IV.8), which is contradictory to the reality of the atomic structure.

IV.4.2. Bohr atom model: hydrogen atom

Keeping in view the defects in Rutherford's Atomic Model, Neil Bohr presented another model of the atom in 1913. To overcome the limitations of the Rutherford atom model in explaining the stability and also the line spectrum observed for a hydrogen atom, Niels Bohr made modifications to the Rutherford atom model. He is the first person to give a better theoretical model of the structure of an atom to explain the line spectrum of the hydrogen atom. The following are the assumptions (postulates) made by Bohr.

The Quantum Theory of Max Planck was used as the foundation for this model. According to Bohr's model, the revolving electron in an atom does not absorb or emit energy continuously. The energy of a revolving electron is 'quantized' as it revolves only in orbits of fixed energy, called 'energy levels' by him.

IV.4.2.1. Postulates of Bohr atom model

Niels Bohr (1913) was the first to explain quantitatively the general features of the structure of hydrogen atom and its spectrum. He used Planck’s concept of quantization of energy.

Bohr’s model for the hydrogen atom is based on three postulates, which are the basis of the explanation proposed for the interpretation of the emission line spectrum of the hydrogen atom:

The hydrogen atom consists of a tiny nucleus and an electron moves around the nucleus in circular orbits of fixed radius 'r' and energy under the influence of the Coulomb electrostatic force of attraction. This Coulomb force gives the necessary centripetal force for the electron to undergo circular motion.

The Coulomb electrostatic force of attraction: $F_a = \frac{Ze^2}{4\pi\varepsilon_0 r^2}$

The centripetal force: $F_c = \frac{mv^2}{r}$

Electrons in an atom revolve around the nucleus only in certain discrete orbits called stationary orbits where it does not radiate electromagnetic energy. Only those discrete orbits allowed are stable orbits.

The angular momentum of the electron in these stationary orbits is quantized – that is, it can be written as an integer or integral multiple of $\frac{h}{2\pi}$ called as reduced Planck’s constant – that is, ħ (read it as h-bar) and the integer n is called as principal quantum number of the orbit.

$l = n\hbar$ where $\hbar=\frac{h}{2\pi}$

This condition is known as the angular momentum quantization condition.

According to quantum mechanics, particles like electrons have a dual nature. The standing wave pattern of the de Broglie wave is associated with an orbiting electron in a stable orbit.

The circumference of an electron’s orbit of radius r must be an integral multiple of de Broglie wavelength – that is

$$2\pi r = n\lambda$$

But the de Broglie wavelength (λ) for an electron of mass m moving with velocity v is $\lambda = h / mv$ where h is called Planck's constant.

$$2\pi r = n\left(\frac{h}{mv}\right)$$

$$mvr = n\frac{h}{2\pi}$$

For any particle of mass m undergoing circular motion with radius r and velocity v, the magnitude of angular momentum l is given by

$$l = r(mv)$$

$$mvr = l = nh$$

3- The energy of orbits is not continuous but discrete. This is called the quantization of energy. An electron can jump from one orbit to another orbit by absorbing or emitting a photon whose energy is equal to the difference in energy (ΔE) between the two orbital levels (Figure IV .9 and IV.10)

$$\Delta \mathrm{E} = \mathrm{E}_{final} - \mathrm{E}_{initial} = h\nu = h\frac{c}{\lambda}$$

Where c is the speed of light, λ is the wavelength of the radiation used, and ν is the frequency of the radiation. Thus, the frequency of the radiation emitted is related only to changes in the atom's energy, and it does not depend on the frequency of the electron's orbital motion.

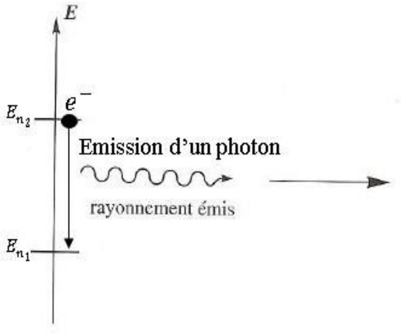


Figure IV.9. Emission process

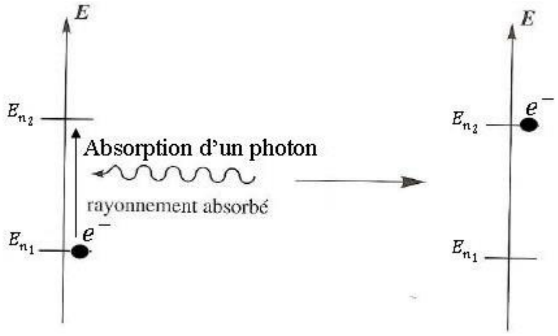


Figure IV.10. Absorption process

The absorption or emission of a photon corresponds to a change in the electron's orbit. The energy absorbed (or emitted) of the photon equals the difference in energy between the two levels.

IV.4.2.2. The radius of stationary orbits of the electron and the velocity of the electron

Consider an atom that contains the nucleus at rest and an electron revolving around the nucleus in a circular orbit of radius r_n as shown in Figure **IV.11**. The nucleus is made up of protons and neutrons. Since a proton is positively charged and a neutron is electrically neutral, the charge of a nucleus is purely the total charge of protons.

Let *Z* be the atomic number of the atom; then +*Ze* is the charge of the nucleus. Let –*e* be the charge of the electron. From Coulomb's law, the force of attraction between the nucleus and the electron is

$$\overline{F}_{\text{Coulomb}} = \frac{1}{4\pi\varepsilon_0}\frac{(+Ze)(-e)}{{r_n}^2}\hat{r}$$

$$\overline{F}_{\text{Coulomb}} = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{{r_n}^2}\hat{r}$$

This force provides necessary centripetal force

$$\overline{F}_{\text{centripetal}} = \frac{mv^2}{r_n}\hat{r}$$

where m be the mass of the electron that moves with a velocity υ in a circular orbit. Therefore,

$$\overline{F}_{\text{Coulomb}} = \overline{F}_{\text{centripetal}}$$

$$\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{{r_n}^2} = \frac{mv^2}{r_n}$$

$$mv^2 = \frac{Ze^2}{4\pi\varepsilon_0 r_n}$$

$$r_n = \frac{4\pi\varepsilon_0(mvr_n)^2}{Zme^2}$$

From Bohr's assumption, the angular momentum quantization condition,$m = v_n r_n = l_n = nh$

$$r_n = \frac{4\pi\varepsilon_0(n\hbar)^2}{Zme^2} = \frac{4\pi\varepsilon_0 n^2\,\hbar^2}{Zme^2}$$

$$K = \frac{1}{4\pi\varepsilon_0} = 910^9\,SI$$

$$r_n = \frac{(\varepsilon_0 h^2)}{(\pi me^2)}\frac{n^2}{Z} \qquad \left(\hbar = \frac{h}{2\pi}\right)$$

where $n \in \mathrm{N}$. Since, ε_0, *h, e* and π are constants. Therefore, the radius of the orbit becomes

$$r_n = a_0\frac{n^2}{Z}$$

$$where\ \ a_0 = \frac{\varepsilon_0 h^2}{\pi me^2} = 0.529\ \text{Å}$$

This is known as Bohr radius which is the smallest radius of the orbit in an atom. Bohr radius is also used as unit of length called Bohr. 1 Bohr = 0.53 Å. For hydrogen atom (Z = 1), the radius of nth orbit is

$r_n = a_0.n^2$

For $n = 1$ (first orbit or ground state),

$r_1 = a_0 = 0.529$ Å

For n = 2 (second orbit or first excited state),

$r_2 = 4a_0 = 2.116$ Å

For n = 3 (third orbit or second excited state),

$r_3 = 9a_0 = 4.761$ Å

and so on.

Thus, the radius of the orbit from the center increases with n, that is, $r_n \propto n^2$ as shown in Figure IV .12.

Further, Bohr's angular momentum quantization condition leads to $mvr_n = mvr_n n^2 = n\frac{h}{2\pi}$

$$v = \frac{h}{mr_n n 2\pi}$$

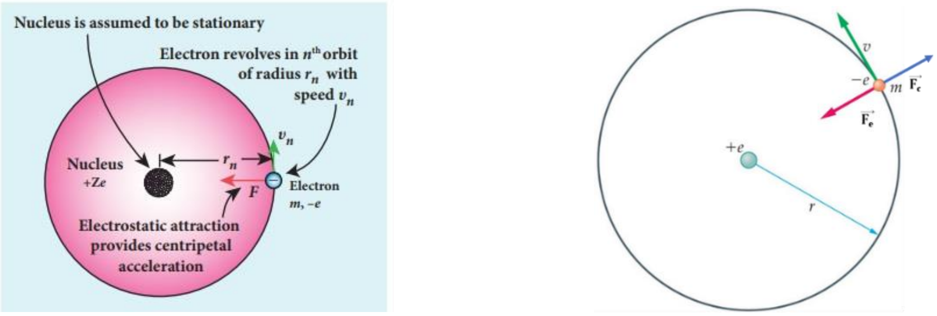


Figure IV.11. Electron revolving around the nucleus

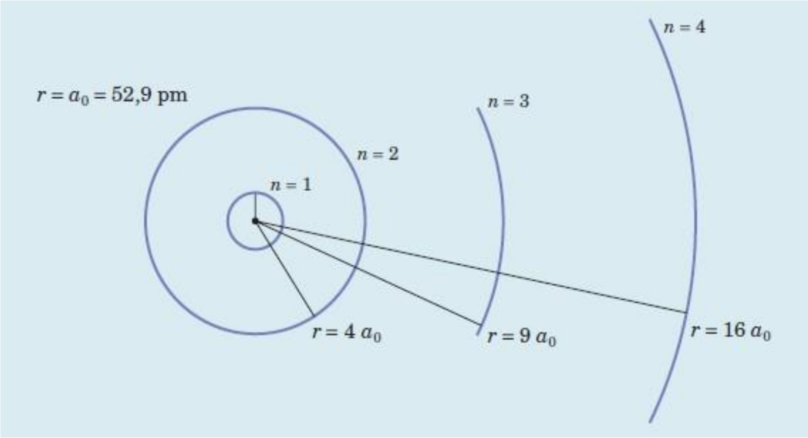


Figure IV.12. Variation of the radius of the orbit principal quantum number.

IV.4.2.3. Energy of the electron in a stationary orbit

The total energy of an electron revolving in a particular orbit is

T.E. = K.E. + P.E.

The kinetic energy K.E. of an electron: $K.E = \frac{1}{2}mv^2 = \frac{me^4}{8\varepsilon_0^2 h^2}\frac{Z^2}{n^2}$

and the potential energy P.E. of an electron: $P.E = -\frac{K\,Ze^2}{r_n} = -\frac{1}{4\pi\varepsilon_0}\frac{(+Ze)(-e)}{r_n} = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_n}$

$$r_n = \frac{(\varepsilon_0 h^2)}{(\pi m e^2)}\frac{n^2}{Z}$$

$$P.E = -\frac{1}{4\varepsilon_0^2}\frac{Z^2 m e^4}{h^2 n^2}$$

This implies that:$T.E = K.E + P.E = \frac{1}{2}mv^2 - \frac{K\,Ze^2}{r_n}$

But $mv^2 = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_n}$

Substituting value of mv^2 in the equation of total energy:

$$T.E = \frac{1}{2}\left(\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_n}\right) - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_n}$$

So: $T.E = -\frac{1}{2}\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_n}$

Substituting value of 'r' in the equation of T.E.

$$T.E = -\frac{1}{2}K\frac{Ze^2}{r_n}$$

$$r_n = \frac{(\varepsilon_0 h^2)}{(\pi m e^2)}\frac{n^2}{Z}$$

$$\boldsymbol{K = -\frac{1}{4\pi\varepsilon_0} = 9.10^9\ SI}$$

$$T.E = -\frac{K}{2}\frac{Ze^2}{\frac{(\varepsilon_0 h^2)}{(\pi m e^2)}\frac{n^2}{Z}}$$

$$T.E = -\frac{2\pi^2 e^4 m K^2}{h^2}\frac{Z^2}{n^2}$$

Substituting the values of mass and charge of an electron (*m* and *e*), permittivity of free space ε0 and Planck’s constant *h* and expressing in terms of *eV*, we get

$\frac{2\pi^2 e^4 m K^2}{h^2} = 13.6\ eV$

For hydrogen atom (Z=1)

$$\boldsymbol{E = -13.6\frac{1}{n^2}\ eV}$$

$$\boldsymbol{E = -21.8\ 10^{-19}\frac{1}{n^2}\ joule}$$

For the first orbit (ground state), the total energy of electron is E1= – 13.6 eV.

The energy of an electron of the hydrogen atom, in its ground state, is -13.6 eV.

The states corresponding to a higher n are qualified as excited states and correspond to the state of an excited electron, having received an excess of energy.

$$E_n = E_1 \frac{1}{n^2} = \frac{-13.6}{n^2}$$

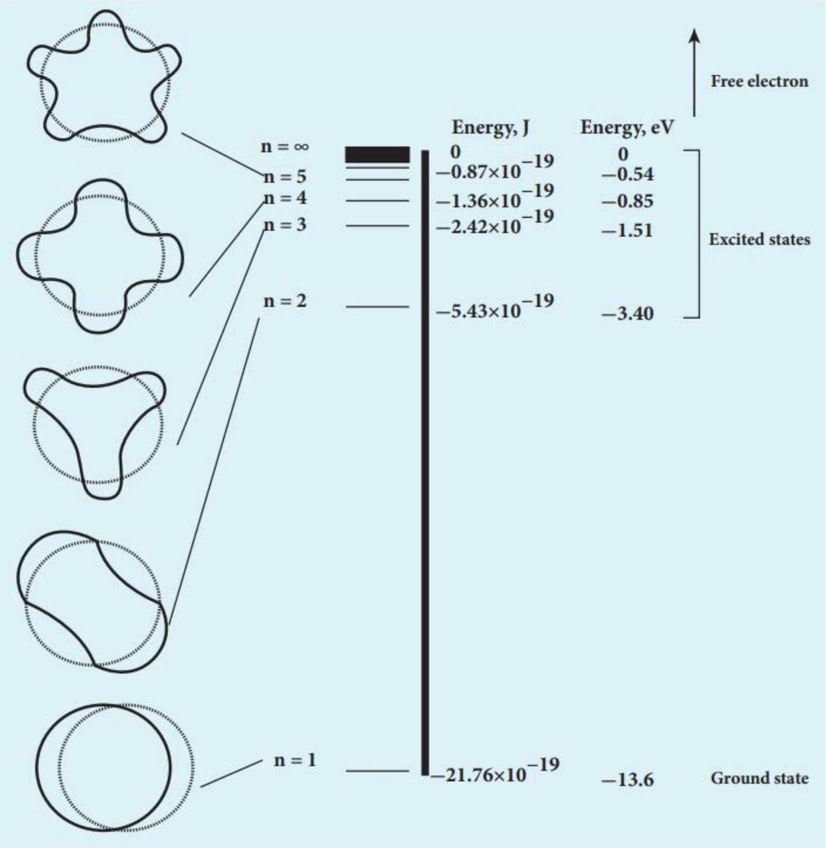


Figure IV.13. shows the energy level diagram and the shape of the orbits for increasing values of n.

It shows that the energies of the excited states come closer and closer together when the principal quantum number n takes higher values.

- **Excitation energy**

The energy required to excite an electron from lower energy state to any higher energy state is known as excitation energy.

The excitation energy for an electron from the ground state (n = 1) to the first excited state (n = 2) is called first excitation energy, which is

$$E_I = E_2 - E_1 = 10.2\ eV$$

Similarly, the excitation energy for an electron from the ground state (n = 1) to second excited state (n = 3) is called second excitation energy, which is

$$E_U = E_3 - E_1 = 12.1\ eV$$

- **Ionization energy**

An atom is said to be ionized when an electron is completely removed from the atom – that is, it reaches the state with energy $E_{n\rightarrow\infty}$. or the minimum energy required to remove an electron from an atom in the ground state is known as binding energy or ionization energy.

$$E_{\textbf{ionization}} = E_\infty - E_1 = 0 - (13.6 -) = +13.6\ eV$$

When an electron is in nth state of an atom, the energy spent to remove an electron from that state – that is, its ionization energy is

$$E_{\textbf{ionization}} = E_\infty - E_n = 0 - \left(\frac{-13.6}{n^2}\right) eV$$

At normal room temperature, the electron in a hydrogen atom (Z=1) spends most of its time in the ground state.

The amount of energy spent to remove an electron from the ground state of an atom *(E = 0* for *n→∞)* is known as first ionization energy (13.6 *e*V).

According to Bohr's 3rd postulate, when the electron of hydrogen passes from an energy level E_{n_i} to an energy level E_{n_f} the energy involved is expressed as:

$$|\Delta E| = \left|E_{n_f} - E_{n_i}\right| = h\nu = \frac{hc}{\lambda} = \frac{2K^2e^4\pi^2m}{h^2}\left(\frac{1}{n_i^2} - \frac{1}{n_j^2}\right)$$

he frequency and the wave number corresponding to this radiation are given by :

$$\nu = \frac{\left|E_{n_f} - E_{n_i}\right|}{h} = \bar{\nu} = \frac{1}{\lambda} = \frac{\left|E_{n_f} - E_{n_i}\right|}{hc} = \frac{1}{hc}\frac{2K^2e^4\pi^2m}{h^2}\left(\frac{1}{n_i^2} - \frac{1}{n_j^2}\right)$$

$$\Rightarrow \bar{\nu} = \frac{1}{\lambda} = \frac{2K^2e^4\pi^2m}{c\,h^3}\left(\frac{1}{n_i^2} - \frac{1}{n_j^2}\right) = 10973740\left(\frac{1}{n_i^2} - \frac{1}{n_j^2}\right)$$

We deduce $R_H = \frac{2K^2e^4\pi^2m}{c\,h^3} = 10973740\ m^{-1}$

$$\bar{\nu} = \frac{1}{\lambda} = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_j^2}\right)$$

Thus, we find the empirical formula of Ritz and the different series of lines of the emission spectrum of the hydrogen atom. The calculated value of the Rydberg constant is close to the experimental value given empirically by Balmer RH=109677.6 cm^{-1}.

IV.4.2.4. Quantification of the energy of the hydrogen atom

The energy of an atom is the least (largest negative value) when its electron is revolving in an orbit closest to the nucleus i.e., the one for which n = 1.

For n = 2, 3... the absolute value of the energy E is smaller, hence the energy is progressively larger in the outer orbits.

The lowest state of the atom, called the ground state, is that of the lowest energy, with the electron revolving in the orbit of the smallest radius, the Bohr radius, a_0. The energy of this state (n = 1), E1 is –13.6 eV. Therefore, the minimum energy required to free the electron from the ground state of the hydrogen atom is 13.6 eV. It is called the ionization energy of the hydrogen atom. This prediction of Bohr's model is in excellent agreement with the experimental value of ionization energy.

When a hydrogen atom receives energy by processes such as electron collisions, the atom may acquire sufficient energy to raise the electron to higher energy states. The atom is then said to be in an excited state. for n = 2; the energy E2 is –3.40 eV. It means that the energy required to excite an electron in a hydrogen atom to its first excited state equals

E2 – E1 = –3.40 eV – (–13.6) eV = 10.2 eV.

Similarly, E3 = –1.51 eV and E3 – E1 = 12.09 eV, or to excite the hydrogen atom from its ground state (n = 1) to second excited state (n = 3), 12.09 eV energy is required, and so on.

From these excited states, the electron can then fall back to a state of lower energy, emitting a photon in the process. Thus, as the excitation of the hydrogen atom increases (that is as n increases) the value of minimum energy required to free the electron from the excited atom decreases.

The principal quantum number n labels the stationary states in the ascending order of energy. the highest energy state corresponds to n =∞) and has an energy of 0 eV. This is the energy of the atom when the electron is completely removed (r = ∞)

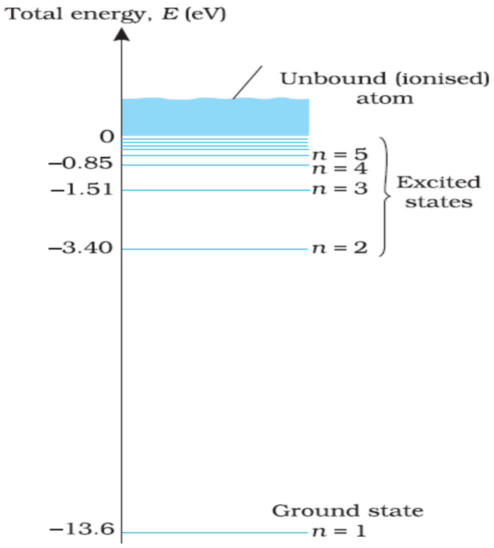


Figure IV.14. The energy level diagram for the hydrogen atom.

Example 1

Calculate the energy of a photon required to excite a hydrogen atom from the n = 2 state to the n = 6 state.

$$E_{6\to 2} = E_6 - E_2 = \frac{-13.6}{n_6^2} - \frac{-13.6}{n_2^2} = -13.6\left(\frac{1}{n_6^2} - \frac{1}{n_2^2}\right)$$

$$= -13.6\left(\frac{1}{6^2} - \frac{1}{2^2}\right) = 3.023\ eV$$

Example 2

The atom is in the third excited state. Indicate all the possible downward transitions of the atom.

$$E_4 \longrightarrow E_3$$

$$E_4 \longrightarrow E_2$$

$$E_4 \longrightarrow E_1$$

$$E_3 \longrightarrow E_2$$

$$E_3 \longrightarrow E_1$$

$$E_2 \longrightarrow E_1$$

Example 3

Calculate the energy of a photon capable of exciting the atom to the 3rd excited state when it is in the ground state.

the 3rd excited state n=4

$$E_{4\to 1} = E_4 - E_1 = \frac{-13.6}{n_4^2} - \frac{-13.6}{n_1^2} = -13.6\left(\frac{1}{n_4^2} - \frac{1}{n_1^2}\right)$$

$$= -13.6\left(\frac{1}{4^2} - \frac{1}{1^2}\right) = 10.2\ eV$$

Exercise

According to the Bohr model, the allowed energy levels of the hydrogen atoms are given by

$$E_n = \frac{-13.6}{n^2}\ eV\ , where\ n = 1,2,3\ \ldots$$

Using this model, we will calculate one of the possible wavelengths in the line spectrum of the hydrogen atom. Follow the directions below. When necessary, use this value of Planck's constant

h= $6.62\text{x}10^{-34}$ j.s .and speed of light c=3x108 m/s

h= $4.136\text{x}10^{-15}$ eV.s

Hint

a. Suppose that the electron jumps from energy level ni=4 down to energy level nf=2.

What is the difference in the energy level?

The electron lose energy

$$\Delta E = E_2 - E_4$$

$$\Delta E = \frac{(-13.6)}{n_2^2} - \frac{(-13.6)}{n_4^2}$$

$\Delta E = \frac{(-13.6)}{(2)^2} - \frac{(-13.6)}{(4)^2}$=2.55 eV

b. The energy lost by the electron goes into the photon being emitted. What is the frequency of this photon?

The frequency of the photon is

$$\Delta E = h\nu \Rightarrow \nu = \frac{\Delta \mathrm{E}}{h}$$

c. Given the answers to a and b above, the wavelength of the photon being emitted in this transition is

$$\nu = \frac{\mathrm{c}}{\lambda}$$

IV.4.2.5. Applications to hydrogenoids

The hydrogenoid is a monoatomic ion with only one electron like hydrogen. It therefore has an electronic structure similar to that of the hydrogen atom. It is always a cation.

$$r_n = a_0 \frac{n^2}{Z}$$

$$E = -13.6 \frac{Z^2}{n^2}$$

$$\bar{\nu} = \frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

Example

I- In the emission spectrum of the hydrogen atom, calculate the wavelength corresponding to the 5th line of the Lyman series.

II- The ionization energy of a hydrogenoid ion is equal to 54.4 eV.

1- Determine its atomic number Z, knowing that the energy of the ground state of the hydrogen atom is equal to -21.76. 10^{-19} Joule.

2- One of the limit lines, of the emission spectrum of this hydrogenoid, has a wavelength of 2050 Å. Calculate:

a) The number of the series to which this line belongs. What is the name of the series?

b) The wavelength of the first line of this series.

IV.4.3. Limitations of Bohr’s Model

Bohr’s model of the hydrogen atom provides insight into the behavior of matter at the microscopic level, it was undoubtedly an improvement over Rutherford's nuclear model because it takes into account the stability and line spectra of hydrogen atoms and hydrogen-like ions (such as He^+, Li^{2+}, Be^{3+}, etc.), but it does not consider the electron-electron interaction in atoms with more than one electron. However, Bohr’s model was too simple to account for the following points:

It fails to account for the finer details (double peaks, i.e. two closely spaced lines) of the hydrogen atom spectrum observed by using sophisticated spectroscopic techniques. This model is also unable to explain the spectrum of atoms other than hydrogen, such as helium, which has only two electrons. Furthermore, Bohr's theory could not explain the splitting of spectral lines in the presence of a magnetic field (Zeeman effect) or an electric field (Stark effect).

He could not explain the ability of atoms to form molecules through chemical bonds.

- The model is indeed valid only for chemical species comprising a single electron, i.e. the hydrogen atom and the ions He^+, Li^{+2}, Be^{+3}.

he didn't rely on a solid theory to demonstrate his main postulate: the model couldn't explain why electronic orbits with angular momentum equal to $nh/2\pi$ are stable and non-radiant.

However, two of Bohr's postulates were used to develop the model of wave mechanics and quantum mechanics, the current model of the atom:

The electronic energy levels are quantified (postulate 2)

energy is emitted or absorbed when an electronic level change occurs (postulate 3).

In other words, the BOHR model, even refined, does not give satisfactory results: classical physics is unable to explain the observed phenomena, one needs a better theory that can explain the salient features of the structure of complex atoms. The call to quantum chemistry is then essential

IV.5. The hydrogen atom in wave mechanics

Because of the shortcomings of Bohr’s model, attempts were made to develop more suitable and general atomic models. Two important developments that have significantly contributed to the formulation of such models are:

1. Dual behavior of matter,
2. Heisenberg uncertainty principle.

We know how matter behaves in the macroscopic world—objects that are large enough to be seen by the naked eye follow the rules of classical physics. A billiard ball moving on a table will behave like a particle: It will continue in a straight line unless it collides with another ball or the table cushion, or is acted on by some other force (such as friction). The ball has a well-defined position and velocity (or a well-defined momentum, $p = mv$, defined by mass m and velocity v) at any given moment.

When waves interact with each other, they show interference patterns that are not displayed by macroscopic particles such as the billiard ball. For example, interacting waves on the surface of water can produce interference patterns. This is a case of wave behavior on the macroscopic scale, and it is clear that particles and waves are very different phenomena in the macroscopic realm.

IV.5.1. Wave-corpuscle duality and the Broglie relation

As technological improvements allowed scientists to investigate the microscopic world in greater detail, it became increasingly clear by the 1920 s that tiny pieces of matter obeyed a different set of rules from those we observe for large objects.

The unquestionable separation of waves and particles no longer applies to the microscopic world. Louis de Broglie was one of the first to draw attention to the peculiar behavior of the microscopic world.

He asked the question in his 1925 doctoral dissertation.: If electromagnetic radiation can have particle properties, can electrons and other submicroscopic particles exhibit wavelike character?

In his 1925 doctoral dissertation

Broglie, in 1924 proposed that matter, like radiation, should also exhibit dual behaviour i.e., both properties wave–particle duality of light that Einstein used to resolve the photoelectric-effect paradox to material particles.

He predicted that a particle with mass m and velocity v (that is, with linear momentum p) should also exhibit the behavior of a wave with a wavelength value λ, given by the following formula, where h is the known Planck's constant:

$$E = \frac{h\,c}{\lambda}$$

$$\mathrm{E} = \mathrm{m\,v^2}$$

$$\mathrm{E} = \frac{\mathrm{h\,v}}{\lambda} = \mathrm{m\,v^2}$$

$$\boldsymbol{\lambda} = \frac{\mathbf{h}}{\mathbf{m\,v}} = \frac{\mathbf{h}}{\mathbf{P}}$$

where

λ: Broglie wavelength ‘m)

m is the mass of the particle (Kg)

v its velocity (m/s)

p its momentum.

h: Planck's constant ($6{,}626 \times 10^{-34}$ J.s)

Bohr had postulated the electron as being a particle orbiting the nucleus in quantized orbits, de Broglie argued that Bohr’s assumption of quantization can be explained if the electron is considered not as a particle, but rather as a circular standing wave such that only an integer number of wavelengths could fit exactly within the orbit (Figure IV.15).

For a circular orbit of radius r, the circumference is 2πr, and so de Broglie’s condition is:

$$2\pi r = n\,\lambda\,, n = 1,2,3,\ldots$$

Since the de Broglie expression relates the wavelength to the momentum and, hence, velocity, this implies:

$$2\pi r = n\,\lambda = \frac{nh}{P} = \frac{nh}{m\,v} = \frac{nhr}{mvr} = \frac{nhr}{L}$$

This expression can be rearranged to give Bohr’s formula for the quantization of the angular momentum:

$$L = \frac{nh}{2\pi} = n$$

Classical angular momentum L for a circular motion is equal to the product of the radius of the circle and the momentum of the moving particle P.

$$L = rP = rmv \quad \text{(for a circular motion)}$$

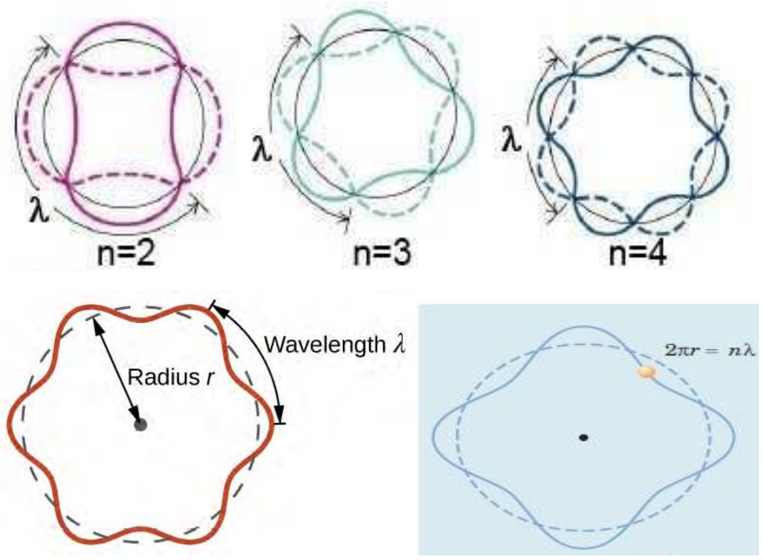


Figure IV.15. Representation of the electron considered as a standing wave

IV.5.2 de Broglie Wavelength and Kinetic Energy

When the particle-like light photon or electron is subjected to the potential difference V, it acquires a velocity v and generates two types of energies, potential and kinetic energy.

The energy of an electron

$$KE = \frac{1}{2}mv^2$$

$$mv^2 = 2KE$$

$$m^2v^2 = 2mKE$$

Again, $\boldsymbol{\lambda} = \frac{\mathbf{h}}{\mathbf{m\,v}}$

From the above two relations, wavelength $\boldsymbol{\lambda} = \frac{\mathbf{h}}{\sqrt{2mKE}}$

The above formula is derived from the de Broglie wave equation and kinetic energy is used to calculate the wavelength of a photon or an electron.

Example 1

Calculate the momentum and the de Broglie wavelength in the following cases:

i) an electron with kinetic energy 2 eV.

ii) a bullet of 50 g fired from a rifle with a speed of 200 m/s

iii) a 4000 kg car moving along the highway at 50 m/s

Example 2

Find the de Broglie wavelength associated with an alpha particle which is accelerated through a potential difference of 400 V. Given that the mass of the proton is 1.67×10^{-27} kg.

IV.6. Heisenberg's Uncertainty Principle

Shortly after de Broglie proposed the wave nature of matter, two scientists at Bell Laboratories, C. J. Davisson and L. H. Germer, demonstrated experimentally that electrons can exhibit wavelike behavior by showing an interference pattern for electrons travelling through a regular atomic pattern in a crystal. When an electron is considered to be a wave as suggested by de Broglie, it is not possible to identify the exact position and velocity of the electron more precisely at a given instant since the wave extends throughout a region of space.

Werner Heisenberg a German physicist in 1927, stated uncertainty principle which is the consequence of dual behavior of matter and radiation.

He determined that there is a fundamental limit to how accurately one can measure both a particle's position and its exact momentum (or velocity) simultaneously.

The more accurately we measure the momentum of a particle, the less accurately we can determine its position at that time, and vice versa. This is summed up in what we now call the

Heisenberg uncertainty principle: It is fundamentally impossible to determine simultaneously and exactly both the momentum and the position of a particle.

For a particle of mass m moving with velocity vx in the x direction (or equivalently with momentum px), the product of the uncertainty in the position, Δx, and the uncertainty in the momentum, Δpx, must be greater than or equal to $\frac{h}{2\pi}$

$$\Delta x \times \Delta P_x \geq \frac{h}{2\pi}$$

$$\text{or } \Delta x \times m\Delta v \geq \frac{h}{2\pi}$$

$$\text{or } \Delta x \times \Delta v_x \geq \frac{h}{2\pi m}$$

where Δx is the uncertainty in position and Δpx (or Δvx) is the uncertainty in momentum (or velocity) of the particle.

If the position of the electron is known with high degree of accuracy (Δx is small), then the velocity of the electron will be uncertain [Δ(vx) is large]. On the other hand, if the velocity of the electron is known precisely (Δ(vx) is small), then the position of the electron will be uncertain (Δx will be large). Thus, if we carry out some physical measurements on the electron's position or velocity, the outcome will always depict a fuzzy or blurry picture.

The effect of the Heisenberg Uncertainty Principle is significant only for motion of microscopic objects and is negligible for that of macroscopic objects.

To illustrate this principle, let's take the example of an electron whose position is known at Δx=1 Å= 10^{-10} m, m_e =9,11.10^{-31} Kg

Example

If the uncertainty in the position of a moving particle is 0 then find out Δp.

Example

Calculate the uncertainty in the position of an electron, if the uncertainty in its velocity is 5.7×10^5 ms^{-1}.

Solution:

given

$$\Delta v = 5.7 \times 10^5 ms^{-1} \Delta x = ?$$

according to Heisenberg's uncertainty principle, $\Delta x . \Delta p \geq \frac{h}{2\pi}$

$$\frac{h}{2\pi} = \frac{6.62 \times 10^{-34}}{2 \times 3.14} = 1.054 \times 10^{-34}$$

$$\Delta x . \Delta p \geq 1.054 \times 10^{-34}$$

$$\Delta x. \Delta p \geq 1.054 \times 10^{-34}$$

$$\Delta x. m\Delta v \geq 1.054 \times 10^{-34}$$

$$\Delta x. \geq \frac{1.054 \times 10^{-34}}{9.1 \times 10^{-31} \times 5.7 \times 10^{5}}$$

$$\Delta x. \geq 0.02 \times 10^{-8}\ \mathrm{m}$$

IV.7. Schrodinger Equation for the hydrogen atom

The motion of objects that we come across in our daily life can be well described using classical mechanics, which is based on Newton's laws of motion. In classical mechanics, the physical state of the particle is defined by its position and momentum. If we know both these properties, we can predict the future state of the system based on the force acting on it using classical mechanics. However, according to Heisenberg's uncertainty principle, both these properties cannot be measured simultaneously with absolute accuracy for a microscopic particle such as an electron. Classical mechanics does not consider the dual nature of matter which is significant for microscopic particles. As a consequence, it fails to explain the motion of microscopic particles. Based on Heisenberg's principle and the dual nature of the microscopic particles, a new mechanics called quantum mechanics was developed.

Erwin Schrödinger expressed the wave nature of electrons in terms of a differential equation. This equation determines the change of wave function in space depending on the field of force in which the electron moves. The time-independent Schrödinger equation can be expressed as:

$$\hat{H}\Psi = E\Psi$$

Where $\hat{H}$ is called Hamiltonian operator, Ψ is the wave function and is a function of position co-ordinates of the particle and is denoted as $\Psi(x, y,z)$ E is the energy of the system

$$\hat{H} = \left[\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V\right]$$

the equation above can be written as

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

Multiply by $\frac{-8\pi^2 m}{h^2}$ and rearranging

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\Psi = 0$$

The above Schrödinger wave equation does not contain time as a variable and is referred to as the time-independent Schrödinger wave equation. This equation can be solved only for certain values of E, the total energy. i.e. the energy of the system is quantized. The permitted total energy values are called eigenvalues, and corresponding wave functions represent the atomic orbitals.

IV.7.1. Significance of the Uncertainty Principle

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

A wave function for an electron in an atom is called an **atomic orbital**; this atomic orbital describes a region of space in which there is a high probability of finding the electron. Energy changes within an atom are the result of an electron changing from a wave pattern with one energy to a wave pattern with a different energy (usually accompanied by the absorption or emission of a photon of light). Each electron in an atom is described by four different **quantum numbers**. The first three (n, l, ml) specify the particular orbital of interest, and the fourth (s) specifies how many electrons can occupy that orbital.

IV.8. Quantum numbers

The four different quantum numbers such as principal, azimuthal, magnetic, and spin are used to describe an electron present in the orbitals of an atom. In physics and chemistry, these numbers describe the energy levels and fine structure of the electromagnetic spectrum of an electron particle in an atom. The first three quantum numbers such as principal, azimuthal, and magnetic (n, l, ml) are necessary to study the size shape, size, and orientation of s, p, d, and f orbital and specify the particular orbital but the fourth quantum number specifies how many electrons can occupy that orbital.

IV.8.1. Principal Quantum Number

The electrons inside an atom are arranged in different energy levels called electron shells or orbits.

Each shell is characterized by a quantum number called the principal quantum number.

This is represented by the letter 'n' and 'n' can have values, 1,2,3,4, etc.

The principal quantum number is used to determine the size of an atom and the energy of an electron.

- For the hydrogen atom, the energy is fixed because it contains only one electron.
- For multielectron atoms, the energy of each electron depends mostly on the value of the principal quantum number (n).
- When the value of n increases, the radius or nucleus-electron separation increases. Therefore, the size of the orbital also increases.

How to Find Principal Quantum Number?

The principal quantum number (n) is always an integer having the value from 1 to ∞. The letters K, L, M, … are also used to derive the value of n.

the first level is also known as the K level.

Second is L level, third is M level, fourth is N level, and so on.

The first as the K level is the orbit nearest to the nucleus and the next one is the second or L level, and so on.

shell	**K**	**L**	**M**	**N**	**…**	
Principal Quantum Number (n)	1	2	3	4	…	…

IV.8.2. The subsidiary or azimuthal quantum number (ℓ)

The azimuthal quantum numbers were introduced by Sommerfeld in his atomic structure to derive the angular momentum of an electron in an elliptical orbit.

According to Sommerfield, the electron in any particular energy level could have a circular path or a variety of elliptical paths about the nucleus.

This concept gave rise to the idea of the existence of sub-energy levels in each of the principal energy levels of the atom.

It describes the geometric shape of an orbital or electron wave. The azimuthal quantum number is denoted by the letter ‘ℓ’.

How to Find Azimuthal Quantum Number?

The azimuthal quantum number (ℓ) can have any value from 0 to (n−1) for a given value of n. The total number of different values of l is equal to n.

- **Thus, if n = 1, ℓ = 0 (only one value) s level.**
- **When n=2, ℓ=0 and 1 (2 values or 2 sublevels) s and p level.**
- **if n=3, ℓ=0, 1, and 2 (3 values or 3 sub-levels) s, p, and d level.**
- **When n=4, ℓ=0, 1, 2, and 3 (4 values or 4 sub-levels) s, p,d, and f level.**

quantum number (ℓ)	**0**	**1**	**2**	**3**	**…**
sub -levels	s	**p**	**d**	**f**	**…**

IV.8.3. Magnetic Quantum Number (m)

In a strong magnetic field, a sub-shell is resolved into different orientations in space. These orientations called orbitals have slight differences in energy. This explains the appearance of additional lines in atomic spectra produced when atoms emit light in a magnetic field. Each orbital is designated by a magnetic quantum number which is called a magnetic quantum number “m” and its values depend on the value of 'ℓ'. The values are -'ℓ' through zero to +'ℓ' and thus there are ($2\ell+1$) values.

How to Find Magnetic Quantum Number?

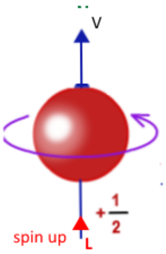
Magnetic quantum is denoted by the symbol ‘m’ or m_ℓ. The total values of m depend on the values of ℓ. For a given value of l, m can have any integral value between '-ℓ' through zero to '+ℓ'.

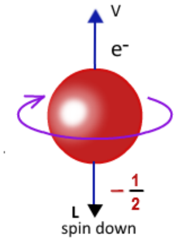
- **Thus, when ℓ=0, m= 0 (only one value or one orbital)**
- **ℓ=1, m= -1, 0, +1 (3 values or 3 orbitals)**
- **ℓ=2, m= -2, -1, 0, +1, +2 (5 values or 5 orbitals)**
- **ℓ=3, m= -3,-2, -1, 0, +1, +2, +3 (7 values or 7 orbitals).**

The three quantum numbers labeling an atomic orbital can be used equally well to label electrons in the orbital. However, a fourth quantum number, the spin quantum number, (*s*) is necessary to describe an electron completely.

IV.8.4. Spin quantum number (*s*)

When the spectral lines of hydrogen, lithium, sodium, and potassium are studied using high-resolution equipment, each line in the spectral series is discovered to be made up of a pair of lines known as a double-line structure. To identify these double-line formations, another quantum number is required. It is referred to as a spin quantum number. The electron in an atom revolves around the nucleus and its axis, with two conceivable rotational orientations (clockwise and anticlockwise). As a result, the spin quantum number has just two possible values: +1/2 or −1/2.





$$\frac{+1}{2}(\uparrow)\ et\ \frac{-1}{2}(\downarrow)$$

IV.9. Shape of Orbitals

There are various shapes and sizes of s, p, d, and f orbitals. When an orbital has a small size, the chance of finding the electron near the nucleus is maximum.

IV.9.1. Shape of s Orbital

For s-orbital, l = 0 and m = 0, it indicates that the s-orbital has only one orientation. Therefore, the electron cloud distribution in s-orbitals is spherically symmetrical. The shape of the s orbital is spherical as shown in Figure IV.16.

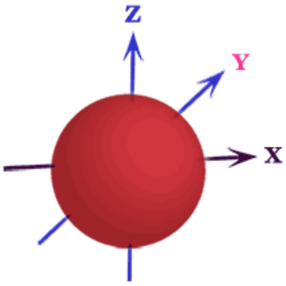


Figure IV.16. The shape of the s orbital

IV.9.2. Shape of p Orbitals

For p-orbital, l = 1 and m = −1, 0, +1. Therefore, the p-orbitals have three orientations represented as px, py, and pz, and the angular distribution for these orbitals shows that the lobes are along the x, y, and z axis, respectively. As seen in Figure IV.17 the 2p orbitals have one nodal plane.

- The dumbbell-shaped p-orbital has two lobes touching each other at the origin.
- These lobes are completely symmetrical along their respective coordinate axis. For example, the two lobes of the p_z orbital are symmetrical along the x-axis.

The two lobes of a p-orbital can be separated by a plane containing the nucleus of an atom.

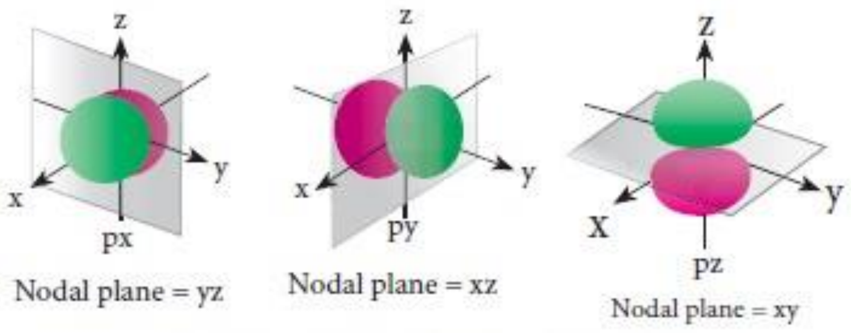


Figure IV.17. Shapes of the p orbitals.

IV.9.3. Shape of d Orbitals

For ‘d’ orbital l = 2, the corresponding m values are -2, -1, 0, +1, +2. The shape of the orbital looks like a 'clover leaf '. The five m values give rise to five d orbitals namely dxy, dyz, dzx, dx2, dz2, and dz2. The 3d orbitals contain two nodal planes as shown in **Figure IV.18.**

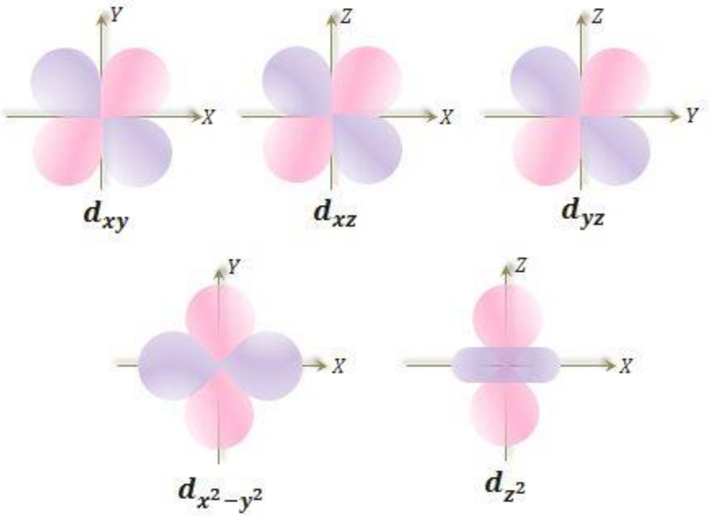


Figure IV.18. Shapes of d orbitals

IV.9.4. Shape of “f” Orbitals

For the 'f ' orbital, $\ell = 3$, and the m values are -3, -2, -1, 0, +1, +2, +3 corresponding to seven f orbitals fz3, fxz2, fyz2, f_{xyz}, fz(x2−y2), f_x(x2−3y2), f_y(3x2−y2), which are shown in **Figure IV.19**. There are 3 nodal planes in the f-orbitals.

The pictorial representation of the f-orbital is very complicated. For f-orbital, the azimuthal quantum number (ℓ) = 3 and magnetic quantum numbers = −3, −2, −1, 0, +1,+2,+3. Therefore, the f-orbital has seven orientations in space.

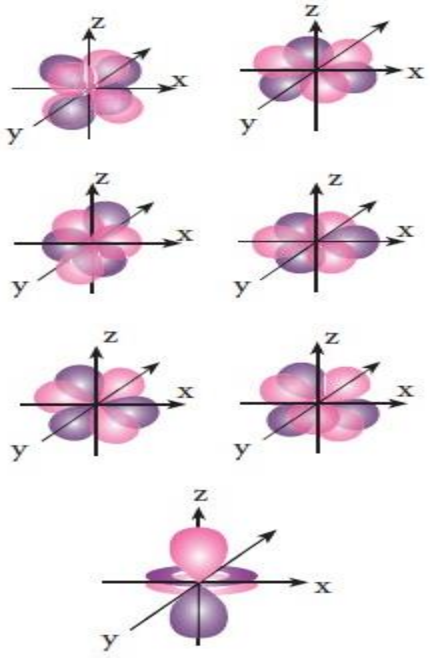


Figure IV.19. Shapes of “f” orbitals

Example 1

What is the total number of orbitals associated with the principal quantum number n=3?

Solution

For n = 3, the possible values of ℓ are 0,1 and 2. Thus, there is one 3s orbital (n = 3, $\ell = 0$ and $m_\ell = 0$); there are three p orbitals (n = 3, $\ell = 1$ and $m_\ell = -1, 0, 1$) there are five 3d orbitals (n = 3, $\ell = 2$, $m_\ell = -2, -1, 0, 1, 2$).

Therefore, the total number of orbitals is 1+3+5 = 9.

Example 2

Using s, p, d, and f notations, describe the orbital with the following quantum numbers

(a) n=2, $\ell = 1$ (b) n = 4, $\ell = 0$ (c) n = 5, $\ell = 3$ (d) n = 3, $\ell = 2$.

IV.10. Filling of Orbitals in Atom

The word Aufbau in German means 'building up'. German scientist Aufbau expresses the building-up principle for the electron configuration process in different electronic orbitals of atoms. According to the Aufbau principle, the electrons are filled up in order of energy.

In the ground state of the atoms, the orbitals are filled in the order of their increasing energies. That is, the electrons first occupy the lowest energy orbital available to them.

Therefore, the orbitals with the lowest energy filled up first, while the highest-energy orbitals filled up in the end. In an atom, the electrons are filled in various orbitals according to the Aufbau principle, Pauli exclusion principle, and Hund's rule.

IV.10.1. Electronic Configuration of Elements in Periodic Table

In chemistry, the arrangement or distribution of electrons in various orbitals or energy levels is known as the electronic configuration or electronic structure of atoms or ions of periodic table elements. The electron is the key to understanding the chemical world, and its electrical arrangement helps determine an element's place in the periodic table. Chemical characteristics like oxidizing and reducing, oxidation number, ionization energy, electron affinity, shielding effect, polarity, acid-base properties, etc. are also derived using the electronic configuration formula.

How do you find the electronic configuration of an element?’KLECHKOWSKI rule)

The order of filling of various orbitals as per the Aufbau principle is given in **Figure IV.20,** which follows the (n+1) rule.

According to the above diagram, the energy levels ordering where electrons are distributed,

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

So

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f…

Sublayers are filled in ascending order of n+l values. For two equal values, the sublayer with the smallest n is filled first.

For example, for 2p and 3s, n+l = 2+1 and n+l = 3+0 respectively, so 2p is filled first (smaller n), and only then 3s.

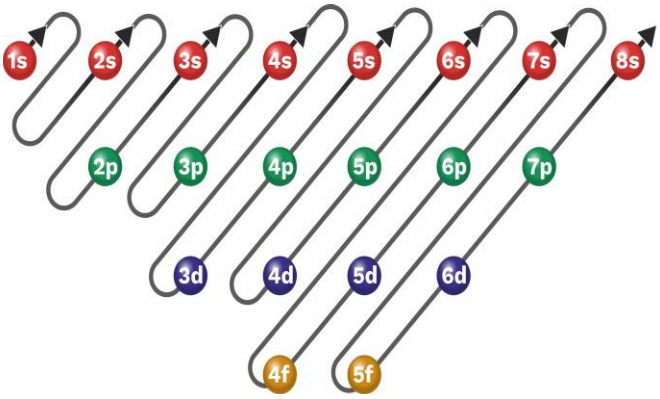


Figure IV.20. The order of filling of various orbitals as per the Aufbau principle

Electrons in Energy Levels

The electronic configuration or arrangement of atoms in different energy levels follows certain rules. The maximum number of electrons in the main energy levels = $2n^2$, where n = principal quantum number.

The maximum number of electrons in sub-shells like s, p, d, and f orbitals = $2(2\ell + 1)$. Where $l = 0, 1, 2, 3$ for s, p, d, f orbitals. Therefore, s, p, d, and f orbitals contain a maximum of 2, 6, 10, and 14 electrons, respectively.

Summary table of the various states of an atom for the first five levels:

Principal quantum number (n)	Azimuthal quantum number (ℓ)	Magnetic quantum number (m)	Number of orbitals	number of electrons in s, p, d and f orbitals	Total number of electrons in the main shell($2xn^2$)
n=1 (K- shell)	0 (1s)	0	1	2	$2 \times 1^2=2$
n=2 (L- shell)	0 (2s)	0	1	2	$2 \times 2^2=8$
	1 (2p)	-1, 0, +1	3	6	
n=3 (M- shell)	0 (3s)	0	1	2	$2 \times 3^2=18$
	1(3p)	-1, 0, +1	3	6	

	2 (3d)	**-2, -1, 0, +1, +2**	**5**	**10**	
n=4 (N- shell)	**0 (4s)**	**0**	**1**	**2**	**2 x 4^2=32**
	1 (4p)	**-1, 0, +1**	**3**	**6**	
	2 (4d)	**-2, -1, 0, +1, +2**	**5**	**10**	
	3 (4f)	**-3,-2,-1,0, +1,+2,+3**	**7**	**14**	

IV.10.2. Hund's rule of maximum multiplicity

According to Hund's rule in chemistry, electrons are filling in the orbital with maximum spin multiplicity. Hence spin pairing occurs only when vacant orbitals of similar energy are not available for occupation.

The electron will tend to form maximum spin. Electrons with similar spin are configured first. In the ground state, when electrons are placed in a multiple sublayer (p, d, f), they occupy the maximum number of orbitals of the same energy, with single electrons having parallel spins (same value of s).

Thus, if three electrons are to be filled in the p-level of any shell, one each will go into each of the three (p_x, p_y, p_z) orbitals. The fourth electron entering the p- level will go to the p_x orbital, which now will have two electrons with opposite spins (as shown above) and said to be paired. The unpaired electrons play an important part in the formation of bonds.

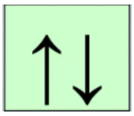
Note

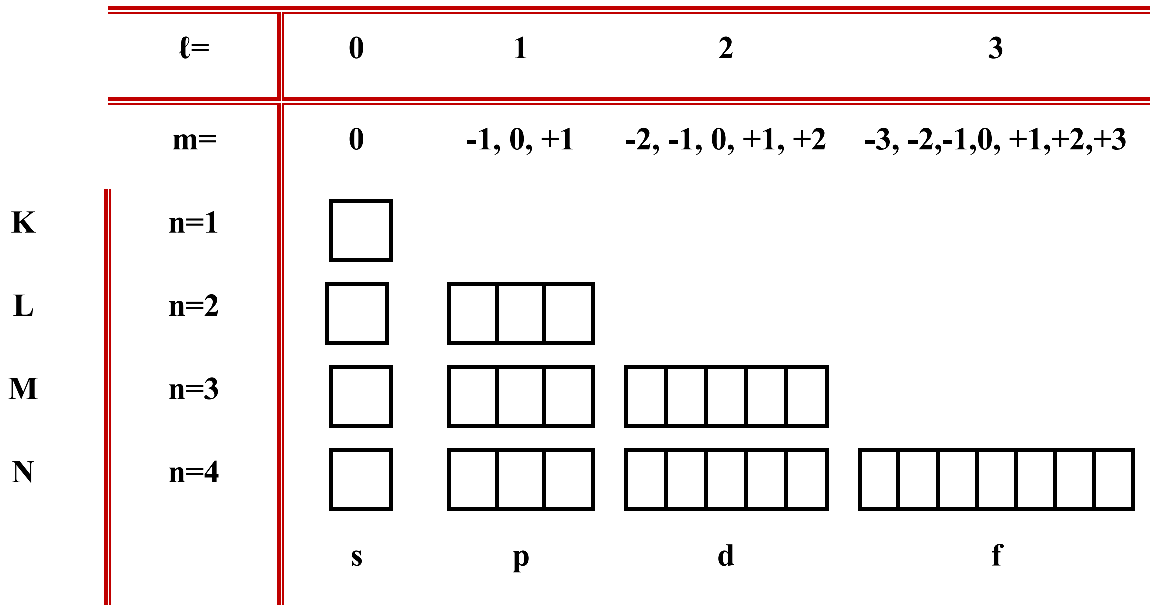
-An orbital is defined by the three numbers n, ℓ, and m. It's convenient to represent orbitals using quantum boxes:

Orbital diagrams

An orbital diagram represents each orbital with a box, with orbitals in the same subshell in connected boxes, electrons are shown as arrows in the boxes, pointing up or down to indicate their spins.

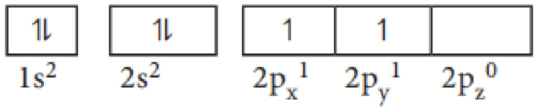
Remember: two electrons in the same orbit must have opposite spins.



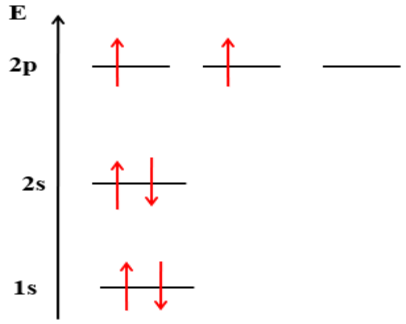


Example: consider the carbon atom, which has six electrons. According to the Aufbau principle, the electronic configuration is $1s^2$, $2s^2$, $2p^2$

It can be represented as below,

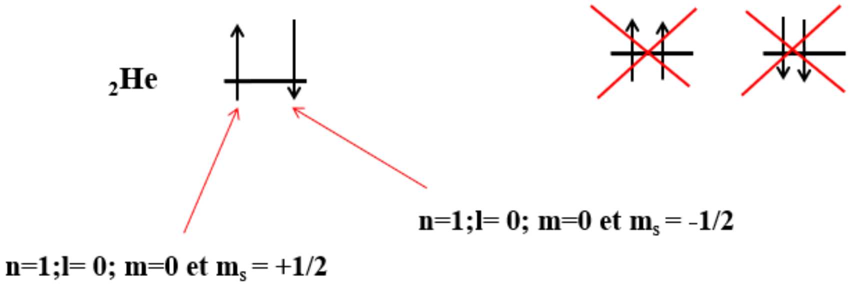


In this case, in order to minimize the electron-electron repulsion, the sixth electron enters the unoccupied $2p_y$ orbital as per Hunds rule. i.e., it does not get paired with the fifth electron already present in the $2P_x$ orbital.

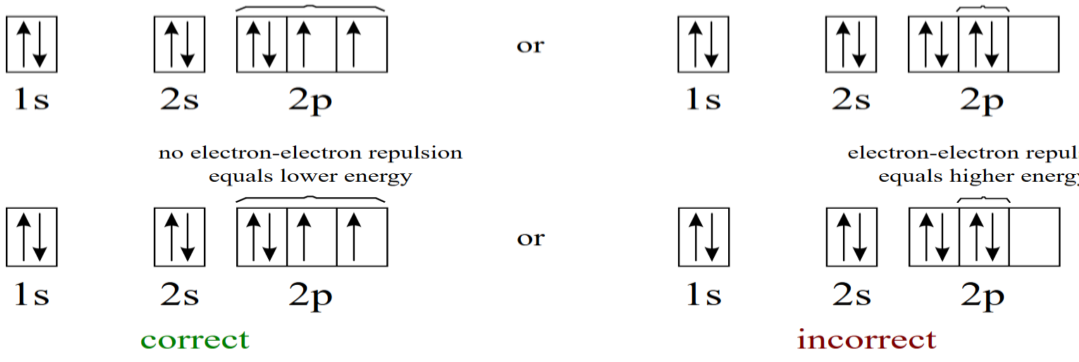


IV.10.3. Pauli Exclusion Principle

The distribution of quantum numbers among the electrons in a given atom is governed by Pauli's Exclusion principle, which states that 'it is impossible for any two electrons in a given atom to have all the four quantum numbers identical' i.e., in an atom, two electrons can have maximum three quantum numbers (n, l, and m) the same and the fourth (s) will definitely be having a different value. Thus, if s = +1/2 for one electron, s should be equal to -1/2 for the other electron.



example: shows the correct and the incorrect way to fill the 2p orbitals.



IV

.10.4. Core electrons

Core electrons are those that populate the inner orbitals. For a given element, they correspond to the configuration of the rare gas that precedes this element in the classification. The configuration of core electrons is symbolized by the rare gas symbol in brackets.

IV.10.5. Valence electrons

Valence electrons populate the orbitals of occupied peripheral layers. The valence configuration is classically noted by aligning the symbols of the sublayers and superscribing the number of electrons in the sublayer. The valence layer represents the layer with the largest n.

IV.10.6. Electron Configuration Exceptions

According to Hund's rule, atoms having half-filled or completely-filled orbitals are comparatively more stable, and hence, more energy is needed to remove an electron from such atoms.

The extraordinary stability of half-filled and completely filled electron configurations can be explained in terms of symmetry and exchange energy. The half-filled and completely filled electron configurations have a symmetrical distribution of electrons and this symmetry leads to stability. Moreover, in such a configuration electron can exchange their positions among themselves to the maximum extent. This exchange leads to stabilization.

In the periodic table elements, the half-filled and filled orbital’s electron configuration formula is relatively more stable than the partially filled orbitals.

Further, it may be noted that chromium and copper have five and ten electrons in 3d orbitals rather than four and nine electrons respectively as expected. Therefore, to acquire more stability one of the 4s electron goes into 3d orbitals so that 3d orbitals get half-filled or completely filled in chromium and copper respectively.

Example

Chromium

Expected configuration: $1s^22s^22p^63s^23p^6\underline{\mathbf{3d^44s^2}}$

Actual configuration: $1s^22s^22p^63s^23p^63\underline{\mathbf{d^54s^1}}$

Electron exchange

Copper

Expected configuration: $1s^22s^22p^63s^23p^6\underline{\mathbf{3d^94s^2}}$

Actual configuration: $1s^22s^22p^63s^23p^6\underline{\mathbf{3d^{10}4s^1}}$

Electron exchange

IV.11. Slater's Rule

In 1930, a scientist J.C. Slater proposed a set of empirical rules to understand the concept of effective charge (Zeff) and to calculate the screening constant or shielding constant (σ) of various electrons present in different orbitals of an atom. A hydrogen atom contains one electron; hence the hydrogen atom has no shielding electron or effect.

He proposed a formula for calculation of effective nuclear charge

$$\mathbf{Z_{eff} = Z - \delta}$$

Where δ is the Slater's screening constant, Z is the nuclear charge Prior to explaining Slater's rules, certain terms like nuclear charge, shielding effect and effective nuclear charge have to be understood.

IV.11.1. What is the nuclear charge?

It is the charge on the nucleus with which it attracts the electron of the atom. Basically, the nuclear charge is said to be equal to the atomic number in an atom. It is denoted by the symbol Z.

IV.11.2. What is the shielding effect (screening effect)?

In multi-electron atoms, when the orbitals fill up, the electrons in the inner orbitals protect the electrons in the outer orbitals from the nucleus.

- In addition to the electrostatic forces of attraction between the nucleus and the electrons, there exists repulsive forces among the electrons.
- The repulsive force between the inner shell electrons and the valence electrons leads to a

decrease in the electrostatic attractive forces acting on the valence electrons by the nucleus.

- Thus, the inner shell electrons act as a shield between the nucleus and the valence electrons. This effect is called the shielding effect.

In learning chemistry, the larger the number of inner or shielding electrons, the lesser the attraction between the nucleus and outer orbitals electrons.

When the number of inner electrons increases, the shielding or screening constant value (σ) also increases.

The shielding effect is defined as a measure of the extent to which the intervening electrons shield the outer electrons from the nuclear charge. It is denoted by the symbol δ.

IV.11.3. What is the effective nuclear charge?

effective nuclear charge means the net positive charge which is the actual charge felt by the outer electrons after taking into account the shielding of the electrons.it is denoted by the symbol $\boldsymbol{Z^{*}\ or\ Z_{eff}}$.

Effective nuclear charge is used because the shielding electrons prevent the attraction of the outer orbital electron of an atom.

When the number of inner electrons increases, the shielding or screening constant increases, but the effective nuclear charge decreases. Therefore, the decrease of effective nuclear charge affects the chemical properties of the elements, atoms, or molecules, and is calculated by Slater’s rule.

IV.11.4. How to Find Shielding Constant?

Slater proposed some empirical set of rules to find the shielding or screening constant (σ) of various electrons present in different orbitals of an atom or ion.

The electrons are arranged in a sequence of groups in order of increasing principal quantum number (n).

In such electron arrangements s and p-orbitals are kept together.

1) **Write the electron configuration for the atom using the following design;**

[1s] [2s, 2p] [3s, 3p] [3d] [4s, 4p] [4d] [4f] [5s, 5p], etc.

Any electrons to the right of the electron of interest contribute nothing towards shielding.

All other electrons in the same group as the electron of interest shield to an extent of 0.35 nuclear charge units irrespective of whether the electrons are in s,p,d or f orbitals.

In case of 1s electron shielding another 1s electron the screening constant value is taken to be 0.30

Slater’s rule for calculating the shielding constant for (ns, np) orbitals is slightly different from (nd, nf) orbitals.

IV.11.4.1. s, p Orbitals

Slater's rules for calculating the screening constant or shielding constant for s, p orbitals of an atom or ion are given below:

1. Electrons lying above the energy level do not screen any electron to any extent. Therefore, the higher energy electrons have no screening effect on the lower energy electrons
2. Electrons of an (ns np) level shield the valence electron in the same group by 0.35 each. It is also true for the electrons of the nd or nf level for electrons in the same group.
3. If the electron of interest is an s or p electron: all electrons belonging to one lower quantum shell or (n−1) shell of the principal quantum number shield to an extent of 0.85 units of nuclear charge.
4. All Electrons belonging to two or more less values (n-2,n-3, n-4 ect.) or still lower quantum energy levels shield the valence electron by 1.0 each.

IV.11.4.1. Shielding Constant for d or f-Orbital Electron

Slater's rule for s or p-electron is quite good for estimating the screening constant of s and p-orbital. However, Slater's rule for d or f-orbital electrons the five and six rules are replaced by new rules for the estimation of screening or shielding effect and effective nuclear charge.

The new rule is all electrons below the nd subshell or nf subshell contribute 1.0 each towards the screening constant.

1. If the electron of interest is a d or f electron: all electrons to the left shield to an extent of 1.00 units of nuclear charge.

Example 1

Slater's Rule for Sodium

For calculating the value shielding constant of inner electrons of the sodium atom, the electron configuration according to Slater's rule, $[1s]^2$ $[2s, 2p]^8$ $[3s]^1$.

Therefore, by using Slater's rule shielding constant and effective nuclear charge for the 3s-electron of a sodium atom, $\sigma = (2 \times 1) + (8 \times 0.85) + (0 \times 0.35) = 8.8$

Hence the effective nuclear charge of sodium, $Z_{eff} = (11 - 8.8) = 2.2$

Example 2

Shielding or Screening Constant of Sodium and Magnesium Ions

Electron configuration of sodium and magnesium ions according to Slater's rule:

Na^+ ion: $[1s]^2$ $[2s, 2p]^8$$Mg^{+2}$ ion: $[1s]^2$ $[2s, 2p]^8$

Screening constant for Na^+ ion,σ (Na^+) = (2 × 0.85) + (7 × 0.35) = 4.15

Similarly, the screening constant for Mg^{+2} ion, σ ($Mg2^+$) = (2 × 0.85) + (7 × 0.35) = 4.15

Therefore, the screening and shielding constants for sodium and magnesium ions are similar but the effective nuclear charge of these two ions is different.

Effective nuclear charge for Na^+ ion = (11 − 4.15) = 6.85

Effective nuclear charge for Mg^{+2} ion = (12 − 4.15) = 7.85

IV.12. Limitations of Slater's Rule

- Slater grouped both s and p orbitals together for calculating the effective charge, which is incorrect. This is because radial probability distribution curves show that s orbitals are more penetrating than p orbitals. so, the s orbitals should shield to a greater extent as compared to the p orbital.
- According to Slater, all the s,p,d, and f electrons present in shell or energy level lower than (n-1) shell will shield the outer n electrons with equal contribution of δ=1.00 each. This is not justified as energetically different orbitals should not contribute equally.
- Slater's rules are less reliable for heavier elements.

CHAPTER V: The Periodic Classification of the Elements

V. Introduction

Millions of chemical compounds exist in nature with different compositions and properties, formed from less than 100 naturally occurring elements.

The discovery of elements is linked with human civilization. In the Stone Age, man used some metals to suit his needs without knowing they were elements. Soon he learnt to extract elements from ores and fashion them into his daily life. Over the years, more and more elements were discovered. In 1789, Lavoisier from France published the first list of chemical elements containing 23 elements after several experimental investigations.

Antoine Lavoisier classified the substances into four groups of elements, namely acid-making elements, gas-like elements, metallic elements, and earthy elements.

V.1. Periodic Classification of Elements

During the 19th century, scientists isolated several elements and the list of known elements increased. Currently, we have 118 known elements. Out of 118 elements, 92 elements with atomic numbers 1 to 92 are found in nature. Every element has its own importance in the environment, some of them are useful while others are harmful. The harmful elements may also be useful in other ways. so, it becomes a necessity to study the chemical and physical properties of each of the elements present around us because every element is related to our life in some or another way. As the number is very large and there is the possibility that more elements will be discovered, so it becomes very difficult to study each of them separately. Scientists have found out there are some similarities in properties among certain elements. This observation has led to the idea of classification of elements based on their properties.

In fact, the Periodic table is the tool that is used to classify the known elements in groups. It helps us to undertake a systematic study of the various elements found in nature without which it would have been impossible for us to study all the elements in the table. With the help of the periodic table, a comparative study of the elements and their compounds can be done. The periodic table also helps us to analyze the periodic trend in various properties such as ionization potential, electron affinity, electronegativity etc.

Several attempts were made to classify the elements. However, classification based on the atomic weights led to the construction of a proper form of the periodic table.

V.1.1. Dobereiner's Triads, 1829

In 1817, J. W. Döbereiner (Johann Wolfgang Dobereiner, a German chemist) was the first scientist to classified some elements such as chloride, bromide and iodine with similar chemical properties in the order of increasing atomic masses. These groups were called triads.

In triads, the atomic weight of the middle element nearly equal to the arithmetic mean of the atomic weights of the remaining two elements. However, only a limited number of elements can be grouped as triads. This concept cannot be extended to some triads which have nearly the same atomic masses such as [Fe, Co, Ni], [Ru, Rh, Pd], and [Os, Ir, Pt].

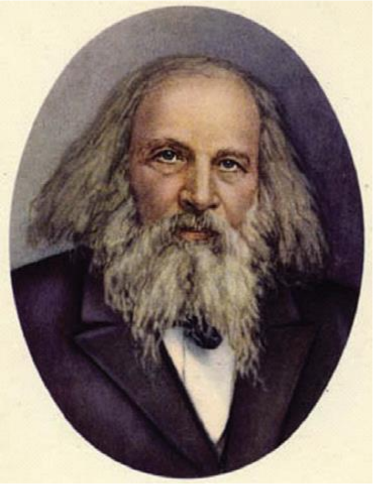
In 1862, A. E. B. de Chancourtois reported a correlation between the properties of the elements and their atomic weights. He arranged the elements in the increasing atomic weights along the helix on the surface of this cylinder. One complete turn of a helix corresponds to an atomic weight increase of 16. Elements which lie on the 16 equidistant vertical lines drawn on the surface of cylinder shows similar properties. This was the first reasonable attempt towards the creation of periodic table. However, it did not attract much attention.

In 1864, J. Newland made an attempt to classify the elements and proposed the law of octaves. On arranging the elements in the increasing order of atomic weights, he observed that the properties of every eighth element are similar to the properties of the first element. This law holds good for lighter elements up to calcium.

V.1.2. Mendeleef's Classification (Periodic Table)

In 1868, Lothar Meyer had developed a table of the elements that closely resembles the modern periodic table. He plotted the physical properties such as atomic volume, melting point and boiling point against atomic weight and observed a periodical pattern.

In 1871, a Russian Chemist, Dmitri Mendeleev, gave a more useful and comprehensive scheme for the classification of elements.



Mendelee started by arranging the 70 known elements at that time in several vertical columns in ascending order of their atomic masses and found that elements having similar chemical properties appeared at regular intervals. Thus, Mendeleev constructed the first periodic table based on the periodic law.

Mendeleev left some gaps in his table for elements, which had not yet been discovered, and by considering their positions in the periodic table, he predicted properties of these elements. For example, germanium was not known at that time, but Mendeleev was confident that this element must exist so he predicted its properties. A few years later, germanium was indeed discovered and a remarkable agreement was found with Mendeleev's predictions.

❖ Anomalies of Mendeleev’s Periodic Table

i. Mendeleev could not assign a correct position to Hydrogen in the periodic table.

ii. The position of isotopes of all elements was not certain according to Mendeleev’s periodic table.

iii. Atomic masses did not increase regularly in going from one element to the next. So, it was not possible to predict how many elements could be discovered between two elements.

The Pt and Ag, which have similar properties, were placed in group VIII and group IB, respectively.

V.1.3. Moseley's Work

In 1913, Henry Moseley studied the characteristic X-rays spectra of several elements by bombarding them with high energy electrons and observed a linear correlation between atomic number and the frequency of X-rays emitted.

Based on his work, the modern periodic law was developed which states that “the physical and chemical properties of the elements are periodic functions of their atomic numbers.

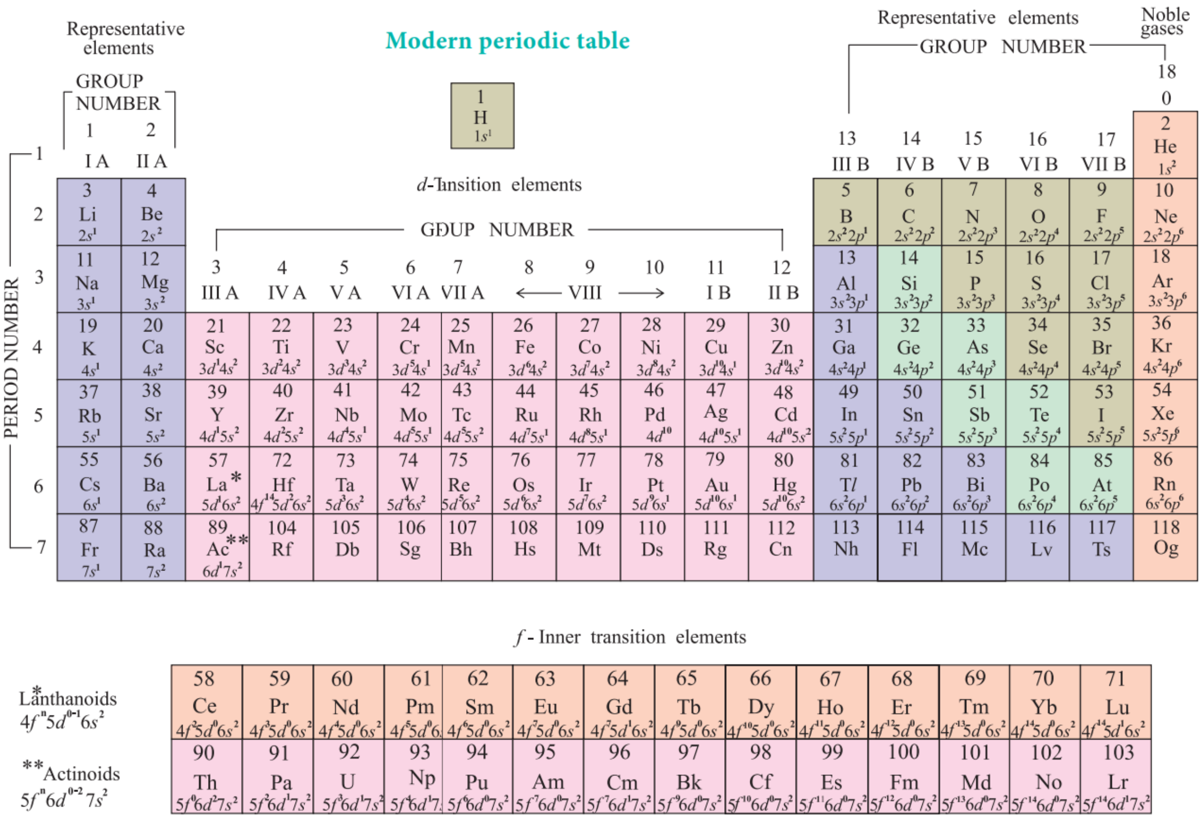
” Based on this law, the elements were arranged in order of their increasing atomic numbers.

This mode of arrangement reveals an important truth that the elements with similar properties recur after regular intervals. The repetition of physical and chemical properties at regular intervals is called periodicity.

V.2. Modern Periodic Table

The modern law for the periodic table of elements aims to remove the defects of Mendeleev’s scientific classification.

In the modern periodic table chart, all the elements are arranged which contains 18 vertical columns and 7 horizontal rows. The vertical columns are called groups, and the horizontal rows are called periods. Groups are numbered 1 to 18 in accordance with the IUPAC recommendation, which replaces the old numbering scheme IA to VIIA, IB to VIIB, and VIII.



Modern periodic table

Representative elements — GROUP NUMBER 1, 2

d-Transition elements — GROUP NUMBER 3–12

Representative elements — GROUP NUMBER 13–17

Noble gases 18

PERIOD NUMBER

PERIOD NUMBER	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	I A	II A	III A	IV A	V A	VI A	VII A	← VIII	VIII	VIII →	I B	II B	III B	IV B	V B	VI B	VII B	0
1	1 H $1s^1$																	2 He $1s^2$
2	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^22p^1$	6 C $2s^22p^2$	7 N $2s^22p^3$	8 O $2s^22p^4$	9 F $2s^22p^5$	10 Ne $2s^22p^6$
3	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^23p^1$	14 Si $3s^23p^2$	15 P $3s^23p^3$	16 S $3s^23p^4$	17 Cl $3s^23p^5$	18 Ar $3s^23p^6$
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^14s^2$	22 Ti $3d^24s^2$	23 V $3d^34s^2$	24 Cr $3d^54s^1$	25 Mn $3d^54s^2$	26 Fe $3d^64s^2$	27 Co $3d^74s^2$	28 Ni $3d^84s^2$	29 Cu $3d^{10}4s^1$	30 Zn $3d^{10}4s^2$	31 Ga $4s^24p^1$	32 Ge $4s^24p^2$	33 As $4s^24p^3$	34 Se $4s^24p^4$	35 Br $4s^24p^5$	36 Kr $4s^24p^6$
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^15s^2$	40 Zr $4d^25s^2$	41 Nb $4d^45s^1$	42 Mo $4d^55s^1$	43 Tc $4d^55s^2$	44 Ru $4d^75s^1$	45 Rh $4d^85s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10}5s^1$	48 Cd $4d^{10}5s^2$	49 In $5s^25p^1$	50 Sn $5s^25p^2$	51 Sb $5s^25p^3$	52 Te $5s^25p^4$	53 I $5s^25p^5$	54 Xe $5s^25p^6$
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La* $5d^16s^2$	72 Hf $4f^{14}5d^26s^2$	73 Ta $5d^36s^2$	74 W $5d^46s^2$	75 Re $5d^56s^2$	76 Os $5d^66s^2$	77 Ir $5d^76s^2$	78 Pt $5d^96s^1$	79 Au $5d^{10}6s^1$	80 Hg $5d^{10}6s^2$	81 T*l* $6s^26p^1$	82 Pb $6s^26p^2$	83 Bi $6s^26p^3$	84 Po $6s^26p^4$	85 At $6s^26p^5$	86 Rn $6s^26p^6$
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac** $6d^17s^2$	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

f - Inner transition elements

*Lanthanoids $4f^n5d^{0-1}6s^2$	58 Ce $4f^25d^06s^2$	59 Pr $4f^35d^06s^2$	60 Nd $4f^45d^06s^2$	61 Pm $4f^55d^06$	62 Sm $4f^65d^06s^2$	63 Eu $4f^75d^06s^2$	64 Gd $4f^75d^16s^2$	65 Tb $4f^95d^06s^2$	66 Dy $4f^{10}5d^06s^2$	67 Ho $4f^{11}5d^06s^2$	68 Er $4f^{12}5d^06s^2$	69 Tm $4f^{13}5d^06s^2$	70 Yb $4f^{14}5d^06s^2$	71 Lu $4f^{14}5d^16s^2$
**Actinoids $5f^n6d^{0-2}7s^2$	90 Th $5f^06d^27s^2$	91 Pa $5f^26d^17s^2$	92 U $5f^36d^17s^2$	93 Np $5f^46d^17$	94 Pu $5f^66d^07s^2$	95 Am $5f^76d^07s^2$	96 Cm $5f^76d^17s^2$	97 Bk $5f^96d^07s^2$	98 Cf $5f^{10}6d^07s^2$	99 Es $5f^{11}6d^07s^2$	100 Fm $5f^{12}6d^07s^2$	101 Md $5f^{13}6d^07s^2$	102 No $5f^{14}6d^07s^2$	103 Lr $5f^{14}6d^17s^2$

V.2.1. Periods in Periodic Table of Elements

The periods on the periodic table are the horizontal rows used to arrange the chemical elements. The long form or modern form of the periodic table contains seven (7) periods for the accommodation of elements.

Each period starts with the element having general outer electronic configuration ns1 and ends with np6. Here ‘n’ corresponds to the period number (principal quantum number) and the principal quantum number (n) = 1 indicates that there is only one main energy level for the elements in this period.

First Period

The first period starts with the filling of valence electrons in 1s orbital, which can accommodate only two electrons. Therefore, this period has two chemical elements beginning with hydrogen and ending with inert gas helium.

Second Period

The second period starts with the filling of valence electrons in the 2s orbital followed by three 2p orbitals (2×1 + 3×2) with eight elements beginning with the alkali metal lithium and ending with the inert gas neon.

Third Period

The third period starts with filling valence electrons in the 3s orbital followed by 3p orbitals. Therefore, this period has (2×1 + 3×2) = 8 chemical elements beginning with another alkali metal sodium ending with the inert gas argon.

Fourth Period

The fourth period There are three sub-shells (4s, 4p, and 3d) for the elements in this period. Therefore, this period has (2×1 + 3×2 + 5×2) = 18 chemical elements beginning with an alkali metal potassium and ending with an inert gas krypton.

Fifth Period

There are also three sub-shells (5s, 5p, and 4d) for the elements in this period. Therefore, this period has (2×1 + 3×2 + 5×2) = 18 chemical elements beginning with the alkali metal rubidium and ending with inert gas xenon. It contains eight typical elements and ten transition metals

Sixth Period

in the sixth period There are four sub-shells (6s, 6p, 5d, and 4f) for the elements in this period. Therefore, this period has (2×1 + 3×2 + 5×2 + 7×2) = 32 chemical elements

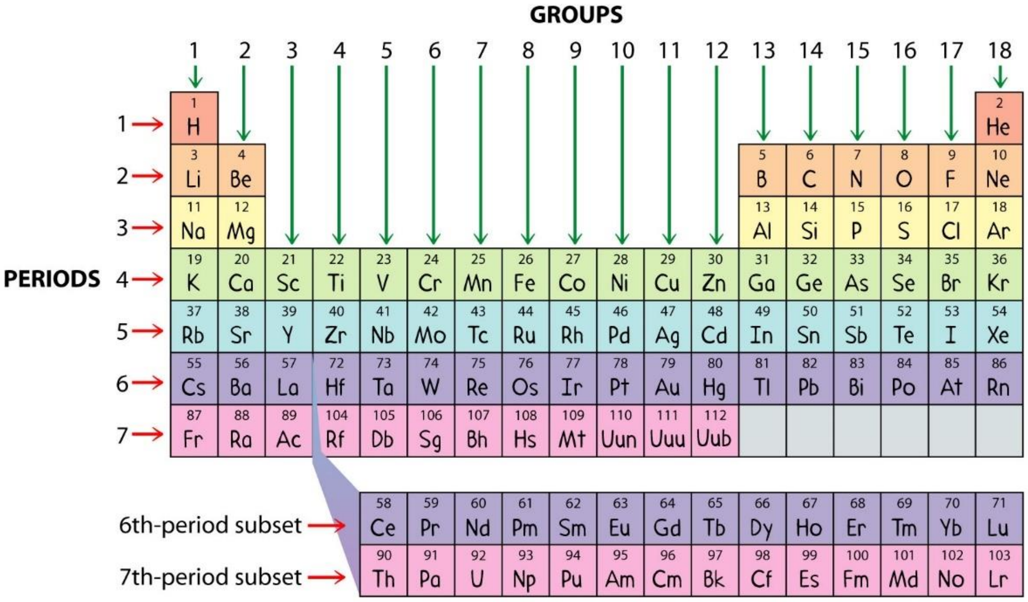
begins with Cerium (Z=58) and ending with an inert gas radon.

The sixth period contains eight typical elements, ten transition metals, and fourteen lanthanides or rare earth elements. The lanthanides (lanthanum to ytterbium) are placed in the lower position of the periodic table.

Seventh Period

There are also four sub-shells (7s, 7p, 6d, and 5f) for the elements in this period. Therefore, this period has (2×1 + 3×2 + 5×2 + 7×2) = 32 chemical elements beginning with the radioactive francium and ending with oganesson.

of the elements in this period are radioactive. The actinides (actinium to nobelium) are placed in the lower position of the periodic table.



V.2.2. Groups in the Periodic Table of Elements

The vertical columns are called groups for the periodic table elements. The modern periodic table contains eighteen (18) groups divided into two subgroups, A and B, representing the state of the external electrons, where chemical elements are arranged. Elements of a group have similar electronic configurations in the outer shell.

The indices I, II, III, ... indicate the number of electrons on the outer layer, called valence electrons.

V.2.2.1. Subgroups A

Subgroup A contains the elements whose outer layer is **ns np**.

The subgroups A constitute the blocks s and p which have the following electronic configuration:

Block s: ns^1 or ns^2

p block: ns^2np^x , $1 \le x \le 6$

The subgroups A are summarized in the following table

Table 1: Subgroup A (electronic configuration of the outer layer)

columns	1	2	13	14	15	16	17	18
subgroup	I_A	II_A	III_A	IV_A	V_A	VI_A	VII_A	$VIII_A$
Outer layer	ns^1	ns^2	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
Nbr of é valences	1	2	3	4	5	6	7	8

V.2.2.2. Subgroups B

contains the atoms which possess a d state. The elements of the block d or f whose sublayer d is incompletely filled are transition metals;$(n-1)d^xns^y$ with $1\leq x\leq 10, 1\leq y\leq 2$.

The subgroups B are summarized in the following table

Table 2: subgroup B (electronic configuration of the outer layer)

columns	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
subgroup	**IIIB**	**IVB**	**VB**	**VIB**	**VIIB**	**VIIIB**			**IB**	**IIB**
Outer layer	$ns^2(n-1)d^1$	$ns^2(n-1)d^2$	$ns^2(n-1)d^3$	$ns^1(n-1)d^5$	$ns^2(n-1)d^5$	$ns^2(n-1)d^6$	$ns^2(n-1)d^7$	$ns^2(n-1)d^8$	$ns^1(n-1)d^{10}$	ns2$(n-1)d^{10}$
Nbr of é valences	3	4	5	6	7	8	9	10	1	2

V.2.3. Blocks of Periodic Table Elements

The modern periodic law is based on the atomic number and valence shell electron arrangement of elements. In chemistry, according to the valence shell electron arrangement of elements, the different types of metals and non-metals are organized to form s, p, d, and f-block of the periodic table.

s-Block Elements

The elements of group 1 and group 2 are called s-block elements, since the last valence electron enters the ns orbit. They are also called representative elements.

The valence shell electron configuration of s-block elements is $ns^{1\rightarrow2}$. Here n = principal quantum number, or the number of periods.

The elements of group 1 (except hydrogen) are metals, and the elements of group 2 are called alkaline earth metals.

p-Block Elements

The elements of groups 13 to 18 are called p-block elements or representative elements, and the valence shell electron configuration of such elements, $2s^2\ 2p^{1\rightarrow6}$, where n = number of periods. They include boron, carbon, nitrogen, oxygen, fluorine families in addition to noble gases (Except helium).

The p-block is home to the biggest variety of elements and is the only block that contains all three types of elements: metals, nonmetals, and metalloids.

d-Block Elements

The name d-block on the periodic table is given due to the presence of progressively filled -d-orbital in the valence shell electronic structure.

The elements including group 3 to group 12, are called d-block elements or transition elements.

Therefore, they are found in the center of the periodic table between s and p-block with valence shell electronic configuration, $4s^{0\rightarrow2}$, $3d^{1\rightarrow10}$.

Their properties are intermediate to those of s block and p block elements.

3d-block elements scandium, titanium, vanadium, chromium, iron, cobalt, nickel, copper, and zinc.

f-Block Elements

The f-block elements on the periodic table are divided into two series, 4 for lanthanides ($4f^{1-14}$, $5d^{0-1}$, $6s^2$) and 5 for actinides ($5f^{0-14}$, $6d^{0-2}$, $7s^2$).

They are placed at the bottom of the periodic table. They are also called as inner Transition elements. These elements are metallic in nature and have high melting points. Their compounds are mostly colored. The f-block contains many missing elements discovered or synthesized by the nuclear reaction of radioactive isotopes.

In the following schema, we present the division of the periodic table by blocks

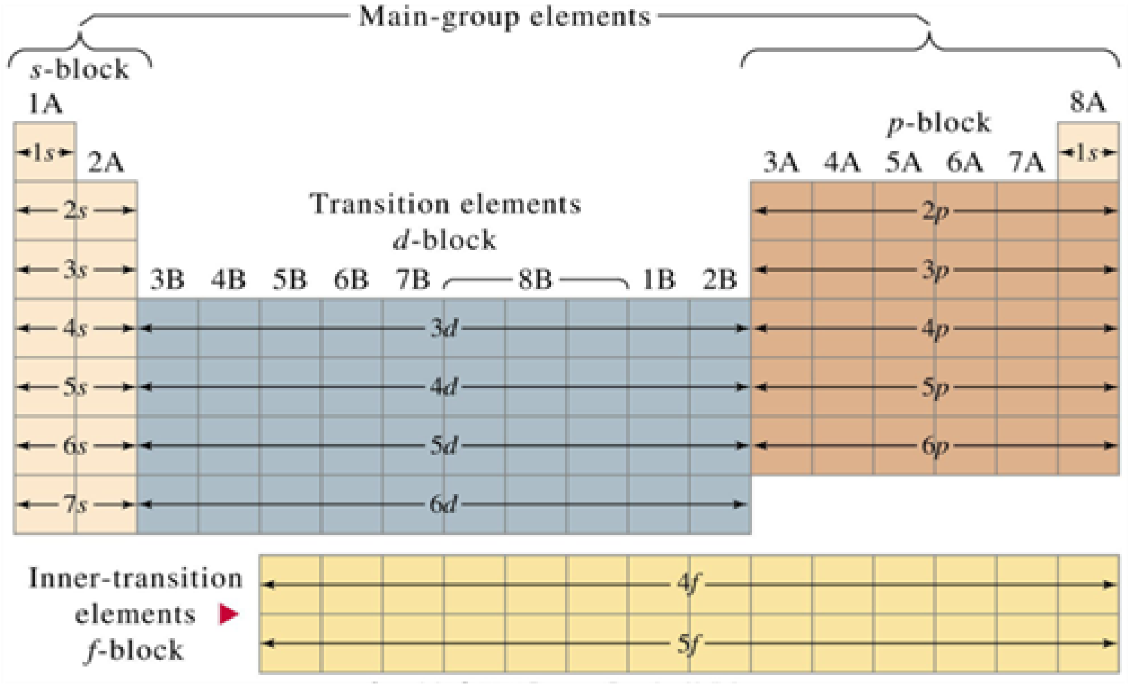


Figure V.1. s, p, d, and f blocks in the periodic table

V.2.4. Families of the Periodic Table

In the periodic classification, the elements that have common characteristics are grouped by family and are located in the same column of the periodic table. The periodic table is then divided into three main regions: metals, metalloids, and non-metals. The elements of the same region have common properties.

What are the Families of Nonmetals?

Except for hydrogen, nonmetals are located on the right side of the periodic table. Nonmetals include some elements in Groups 13–16 and all the elements in Groups 17 and 18. Families of nonmetals include the noble gases and the halogens.

- **Position of hydrogen in the periodic table**

Hydrogen is the lightest, smallest and first element of the periodic table. Its electronic configuration (1s1) is the simplest of all the elements. It occupies a unique position in the periodic table. It behaves like alkali metals as well as halogens in its properties.

- **Position of Rare Gases**

The elements Helium, Neon, Argon, Krypton, Xenon, and Radon belonging to group 18 in the periodic table and which are located on the extreme right side of the periodic table are called Noble gases or rare gases. Their outermost shells contain 8 electrons except He which contains only 2 electrons.

They are monatomic gases and do not react with other substances easily, due to completely filled subshells. Hence, they are called as inert gases. They are found in very small quantities.

- **halogens**

The word halogen comes from the Greek meaning salt-forming. French chemists discovered that the majority of halogen ions will form salts when combined with metals.

The elements in Group 17 form a family called the halogens. Halogens are members of Group 17, which is also referred to as 7A. The halogens are the most reactive nonmetals. They are very reactive because each atom has seven valence electrons. If it gains one electron, a halogen atom becomes stable.

It is the only group in the Periodic Table that contains all of the states of matter at room temperature. Fluorine, F_2, and chlorine, Cl_2 are gases, while Bromine, Br_2, is a liquid, and iodine, I_2, and astatine, At_2, are both solids.

Some examples of common uses of halogens are described below.

- A compound containing the fluoride ion, F^-, is added to many toothpastes and water supplies. Fluoride helps prevent tooth decay.
- A compound containing the iodide ion, I^-, is added to table salt to make iodized salt. You need iodine in your diet to help you stay healthy.
- A compound containing chlorine is added to swimming pools and drinking water supplies. Chlorine can kill bacteria

What Are the Families of Metals?

Many elements are classified as metals. Recall that metals can conduct heat and electricity. Most metals can be stretched and shaped into flat sheets or pulled into wires. Families of metals include the alkali metals, the alkaline-earth metals, and the transition metals.

- **alkali metals**

The elements in Group 1 (except for hydrogen, which has unique properties) form a family called the alkali metals. Because their atoms have only one valence electron, the alkali metals are very reactive. The alkali metals include: lithium, sodium, potassium, rubidium, cesium, and francium. The valence electron can be easily removed to form a cation such as Na^+ or K^+.

Alkali metals are among the most reactive metals. This is due in part to their larger atomic radii and low ionization energies. They get their name from ancient Arabic (al qali) because "scientists" of the time found that the ashes of the vegetation they were burning contained a large amount of sodium and potassium. In Arabic, al qali means ashes.

Although most metals tend to be very hard, alkali metals have a soft texture, are silvery in color, and can be easily cut. They also have low boiling and melting points and are less dense than most elements.

They are found combined with other elements as compounds. For example, the alkali metal sodium is found in the salt sodium chloride, NaCl. Sodium chloride is more commonly known as table salt.

- **alkaline earth metals**

The elements in Group 2 form a family called the

alkaline-earth metals. They get their name because early "scientists" found that all of the alkaline earth metals were found in the earth's crust. alkaline earth metals include Beryllium, Magnesium, Calcium, Barium, Strontium, and Radium are soft, silver metals that are less metallic in character than the Group 1 alkali metals.

The atoms of alkaline-earth metals have two valence electrons. Alkaline-earth metals form cations with 2+ charges, such as Mg^{2+} and Ca^{2+}. The alkaline-earth metals combine with other elements to form compounds. For example, two magnesium compounds—milk of magnesia and Epsom salts—are commonly used to treat minor medical problems. In addition, many calcium compounds are important to living things. Some make up the hard shells of many sea animals. Calcium compounds also make your bones and teeth strong.

➢ The transition metals

An element located in Groups 3-12 (also known as the Group B elements) is a transition metal. Transition metals are the middle block of the periodic table and there are the larger block of elements.

Their two outermost shells are incomplete.

Since these elements represent a transition (change) from the most electropositive element to the most electronegative element, they are named as transition elements. Transition elements differ from the main group elements (group A elements) in that they tend to be hard and have high densities.

Their important characteristics are as follows:

(a) All these elements are metals and have high melting and boiling points and can show various oxidation states when forming chemical bonds.

(b) They are good conductors of heat and electricity.

(c) Some of these elements get attracted towards magnets.

(d)They often form colored compounds that are highly stable and most of these elements are used as catalysts.

(e) They exhibit variable valencies.

➢ Metalloids

Some elements, especially lower members of groups, III A, IVA and VA have properties of both metals as well as non-metals. These elements are called semi-metals or metalloids.

Metalloids are the elements that show mixed properties of both metals and non-metals. They are present along the diagonal line starting from group 13 (Boron) and going down to group 16 (Polonium).

➢ Inner Transition Elements

In the inner transition elements, there are two series of elements. 1) Lanthanoids (previously called lanthanides) 2) Actinoids (previously called actinides)

1) Lanthanoids (previously called lanthanides)

The Lanthanoid series consists of fourteen elements from Cerium ($_{58}$Ce) to Lutetium ($_{71}$Lu) following Lanthanum ($_{57}$La). These elements are characterized by the preferential filling of 4f orbitals,

2) Actinoids (previously called actinides)

In 1923 Neils Bohr postulated the existence of an actinide series analogous to the lanthanide series.

Similarly, actinoids consist of 14 elements from Thorium ($_{90}$Th) to Lawrencium ($_{103}$Lr) following Actinium ($_{89}$Ac). These elements are characterized by the preferential filling of 5f orbital.

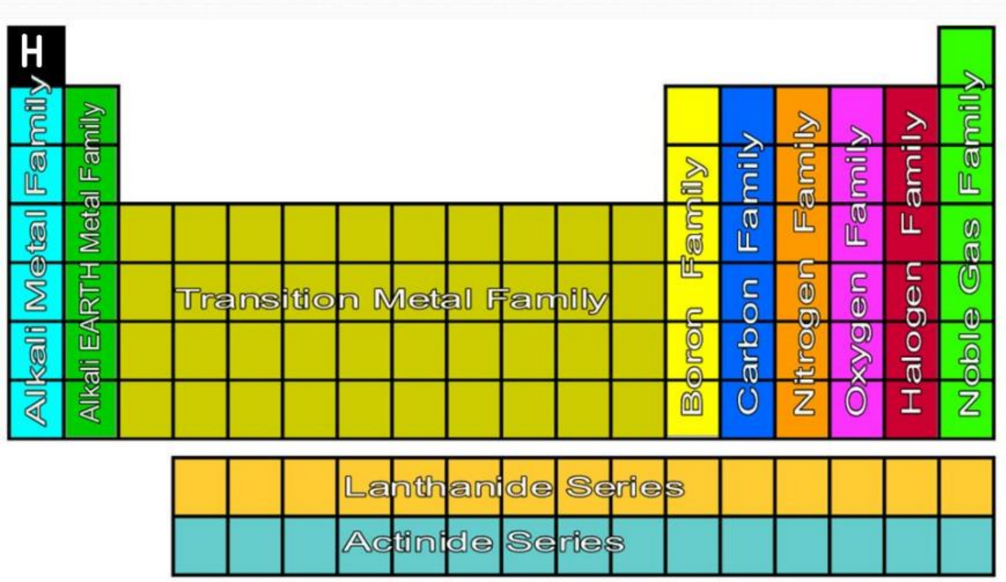


Figure V.2. The distribution of the Families of the groups in the periodic table

V.3. Atomic characteristics and periodic Table Trends of Elements

V.3.1. Atomic radius (covalent radius) r_c

The covalent radius of a molecule is half the distance between the nuclei of two identical atoms linked by a single covalent bond. Expressed in picometers, the measurement of the atomic radius is based on experience.

So, covalent radius for A−A

$$r_A = \frac{d_{A-A}}{2}$$

If the covalent bond is formed between two different elements, then

$$d_{A-B} = r_A + r_B - 0.09(\chi_A - \chi_B)$$

Whereχ_A and χ_B are electronegativities of A and B.

V.3.2. Ionic Radius

It is defined as the distance from the center of the nucleus of the ion up to which it exerts its influence on the electron cloud of the ion. The ionic radius of a univalent crystal can be calculated using Pauling's method from the interionic distance between the nuclei of the cation and anion. Pauling assumed that ions present in a crystal lattice are perfect spheres, and they are in contact with each other; therefore,

$d = r_C^+ + r_A^-$

Where d is the distance between the center of the nucleus of cation C^+ and anion A^-, and r_C^+, rA^- are the radius of the cation and anion, respectively.

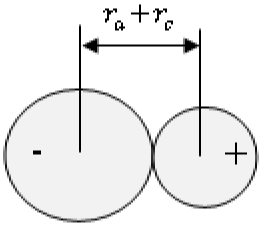
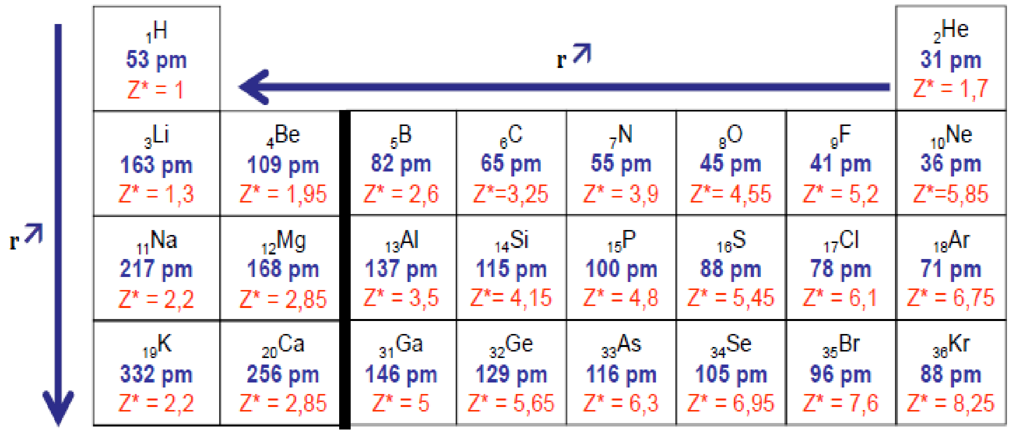


Figure V.3. Ionic radius: r_a: anion radius and r_c: cation radius

- **Variation of the Atomic Radius in the Periodic Table**

Moving left to right in a period, the atomic radii of elements decrease because the number of protons or nuclear charge in the atom increases.

On going down in a group, the atomic radii of elements increase down the group due to the addition of new electrons to higher energy levels.



$_1$H 53 pm Z* = 1							$_2$He 31 pm Z* = 1,7
$_3$Li 163 pm Z* = 1,3	$_4$Be 109 pm Z* = 1,95	$_5$B 82 pm Z* = 2,6	$_6$C 65 pm Z*=3,25	$_7$N 55 pm Z* = 3,9	$_8$O 45 pm Z*= 4,55	$_9$F 41 pm Z* = 5,2	$_{10}$Ne 36 pm Z*=5,85
$_{11}$Na 217 pm Z* = 2,2	$_{12}$Mg 168 pm Z* = 2,85	$_{13}$Al 137 pm Z* = 3,5	$_{14}$Si 115 pm Z*= 4,15	$_{15}$P 100 pm Z* = 4,8	$_{16}$S 88 pm Z* = 5,45	$_{17}$Cl 78 pm Z* = 6,1	$_{18}$Ar 71 pm Z* = 6,75
$_{19}$K 332 pm Z* = 2,2	$_{20}$Ca 256 pm Z* = 2,85	$_{31}$Ga 146 pm Z* = 5	$_{32}$Ge 129 pm Z* = 5,65	$_{33}$As 116 pm Z* = 6,3	$_{34}$Se 105 pm Z* = 6,95	$_{35}$Br 96 pm Z* = 7,6	$_{36}$Kr 88 pm Z* = 8,25

Figure V.4. The evolution of the atomic radius in the periodic table.

V.3.3. Ionization Energy (EI)

Ionization energy (I or IE), also called ionization potential, is the least amount of energy required to remove the most loosely bound electron or the outermost electron from an isolated gaseous atom of an element in its lowest energy state or ground state to produce a cation.

It is generally represented by IE or IP and expressed in terms of either kilojoules per mole (kJ/mol) or electron Volts per atom.

The following equation can represent ionization energy:

$M(g) + IE \rightarrow M^+(g) + e^-$

From the above equation, M = an atom of the periodic table of elements, M^+= cation form due to ionization, and e^-= electron removed from the M atom.

IE is positive for neutral atoms, and ionization is an endothermic process.

The ionization energy is given by the relation:

$$\boldsymbol{E_{I_1} = E_{M^+} - E_M}$$

- **First, Second, and Third Ionization Energies**

The electrons are removed in stages one after the other from an atom or ions. Therefore, the values of successive ionization energies of an element differ one from another. The successive ionization energies can be represented as first, second, third, fourth, etc.

- **First ionization energy:** The amount of energy required for the removal of the first electron from a gaseous atom is called its first ionization energy (IE_1).
  $M(g) + IE_1 \longrightarrow M^+(g) + e^-$
- **Second ionization energy:** The energy required for the removal of the second electron from a unipositive cation is called the second ionization energy (IE_2).
  $M^+(g) + IE_2 \longrightarrow M^{+2}(g) + e^-$
- **Third and fourth ionization energies:** Similarly, we have to define the terms third, and fourth ionization energies of periodic table elements.
  $M^{+2}(g) + IE_2 \longrightarrow M^{+3}(g) + e^-$
  $M^{+3}(g) + IE_2 \longrightarrow M^{+4}(g) + e^-$

Successive Ionization Energies Values

If a second electron is to be removed from the same element, the energy required will be higher than that required for the removal of the first electron because it is more difficult to remove an electron from a positively charged species than from a neutral atom.

Similarly, the third ionization enthalpy will be higher than the second, and so on.

$$M \xrightarrow[-e^-]{IE_1} M^+ \xrightarrow[-e^-]{IE_2} M^{2+} \xrightarrow[-e^-]{IE_3} M^{3+} \xrightarrow[-e^-]{IE_4} M^{4+}$$

$\mathrm{IE_1, IE_2, IE_3}$ and $\mathrm{IE_4}$ are successive ionization energies

The values of successive ionization energies decrease in the following order:

$$\mathrm{IE_4 > IE_3 > IE_2 > IE_1}$$

Factors Affecting Ionization Energy

The magnitude of the ionization energy of the periodic table elements depends on the following factors,

- Charge of the nucleus
- Atomic radius
- Half-filled and filled orbitals

- Shielding effect of electrons

Variation of Ionization Energy in the Periodic Table

The ionization energy of an element depends on its electronic configuration. Ionization potentials of noble gases are found to be maximum, and those of alkali metals are found to be minimum. The high values of noble gases are due to completely filled electronic configurations in their outermost shells, and the low values of alkali metals are due to their large size and a single electron in the outermost shell.

The value of ionization energy generally increases in moving from left to right in a period because when we move from left to right nuclear charge of the atoms of the elements also increases.

As we moving down top to bottom in a group, the outer electrons, which are to be removed, are farther from the nucleus, so the ionization energy generally decreases due to increased atomic radii of elements.

Consequently, the removal of electrons becomes easier down the group.

The screening or shielding effect is also used to explain the ionization energy variation of elements along a group of the periodic table. Therefore, in many cases, ionization energy from the top to bottom increases due to shielding electrons or effective nuclear charges.

Ionization Energy of Second-Period Elements

Due to the presence of a fully-filled and half-filled orbital of beryllium and nitrogen, the ionization energy of beryllium and nitrogen is slightly higher than the neighboring elements boron and oxygen.

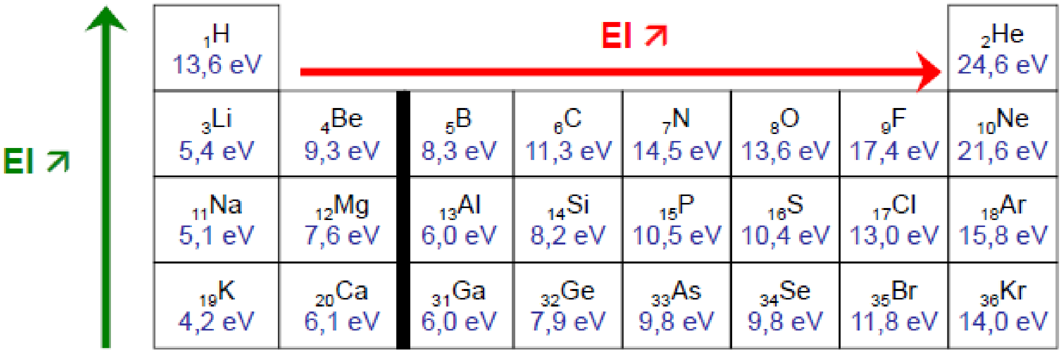
Therefore, the ionization potential trends of second-period elements maintain the following order:

Li < B < Be < C < O < N < F < Ne

Exceptions to the Ionization Energy Trend

A few exceptions in the value of the ionization energy trends in the periodic table are explained based on the half-filled and fully-filled orbitals.

- Group-15 elements (nitrogen and phosphorus) in the periodic table have a higher ionization potential than the group-16 elements (oxygen and sulfur).
- Similarly, group-2 elements (beryllium and magnesium) have higher than the group-13 elements (boron and aluminum) in the periodic table.



$_1$H 13,6 eV							$_2$He 24,6 eV
$_3$Li 5,4 eV	$_4$Be 9,3 eV	$_5$B 8,3 eV	$_6$C 11,3 eV	$_7$N 14,5 eV	$_8$O 13,6 eV	$_9$F 17,4 eV	$_{10}$Ne 21,6 eV
$_{11}$Na 5,1 eV	$_{12}$Mg 7,6 eV	$_{13}$Al 6,0 eV	$_{14}$Si 8,2 eV	$_{15}$P 10,5 eV	$_{16}$S 10,4 eV	$_{17}$Cl 13,0 eV	$_{18}$Ar 15,8 eV
$_{19}$K 4,2 eV	$_{20}$Ca 6,1 eV	$_{31}$Ga 6,0 eV	$_{32}$Ge 7,9 eV	$_{33}$As 9,8 eV	$_{34}$Se 9,8 eV	$_{35}$Br 11,8 eV	$_{36}$Kr 14,0 eV

Figure V.5. The evolution of the ionization energy EI (in eV) in the periodic table

V.3.4. Electron Affinity of Elements in Periodic Table A or EA

In modern terminology, electron affinity is known as the electron gain enthalpy. Electron gain enthalpy defines the amount of energy released when an isolated gaseous atom in its lowest energy level (ground state) accepts an electron to form a monovalent gaseous anion.

$Atom(g) + Electron \ \longrightarrow Anion\ (g) + energy$

Example: $Cl\ (g) + é\ \longrightarrow Cl^-\ (g) + EA$

In electron affinity, the energy is released with the addition of one or more electrons in an atom or anion.

The electron affinity is an exothermic reaction with a negative sign.

The values of electron gain enthalpy are expressed either in electron volts per atom or kilojoules per mole of atoms.

The Electron Affinity is expressed by the following correlation: $E_A = E_{(X)} - E_{(X^-)}$

Factors influencing the magnitude of electron affinity

The electron affinity trend in the periodic table is influenced by the following factors,

- Atomic radius
- Effective nuclear charge
- Electronic structure or configuration

❖ **Electron affinity group trend**

When we move down a group in the periodic table, the size of atoms generally increases with increasing atomic number. The magnitude of electron affinity generally decreases on moving down the group.

- **Electron affinity periodic trend**

EA values generally increase on moving left to right in a period of the periodic table.

Electron affinity exceptions

There are many exceptions to general periodic trends.

Electron affinity of lithium and beryllium

The atomic number and electronic configuration of lithium and beryllium are,

Li: $1s^2\ 2s^1$

Be: $1s^2\ 2s^2$

Lithium has an incompletely filled 2s subshell while beryllium has a filled subshell. Therefore, lithium has an affinity to receive electrons in 2s sub-shell, but for beryllium, a still higher energy 2p level is needed. Hence, beryllium resists gaining extra electrons in the higher energy 2p orbital.

Electron affinity of nitrogen and phosphorus

The electron configurations of nitrogen and phosphorus are,

${}_7N$: $1s^2\ 2s^2\ 2p^3$

${}_{15}P$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

Nitrogen is small size atom compared to phosphorus. When a nitrogen atom adds an extra electron to the stable half-filled 2p subshell, some amount of energy is required for this addition. Hence, the electron affinity of nitrogen is negative.

On the other hand, due to the bigger size of phosphorus compared to nitrogen small amount of energy is released when an electron is added to the stable half-filled 3p subshell.

Electron affinities of halogens

Halogens (elements of group 17) can take up an electron to acquire the stable noble gas configuration. Their values for electron gain enthalpy are thus very high.

From the electron gain enthalpy data of halogens, it is clear that, contrary to expectation, the electron gain enthalpy of fluorine is lower than that of chlorine. This is because the fluorine atom has a very compact electronic shell due to its small size. The compactness of the fluorine shell results in electron repulsion whenever an electron is introduced into its 2p-orbital. This is why its electron gain enthalpy is less than the expected value. In Cl atom, 3p-orbitals are not as compact as the 2p-orbitals in the fluorine atom. The incoming electron is more readily accepted by the chlorine atom because of weaker electron-electron repulsion. The electron gain enthalpy of chlorine is, therefore, higher than that of fluorine.

Electron affinity of noble gases

In the case of noble gases or inert gases, like helium, neon, argon, krypton, xenon, and radon the outer s-and p-orbitals are completely filled. No more electrons can be accommodated in these orbitals. Noble gases, therefore, show no tendency to accept electrons. Their electron gain enthalpies are zero.

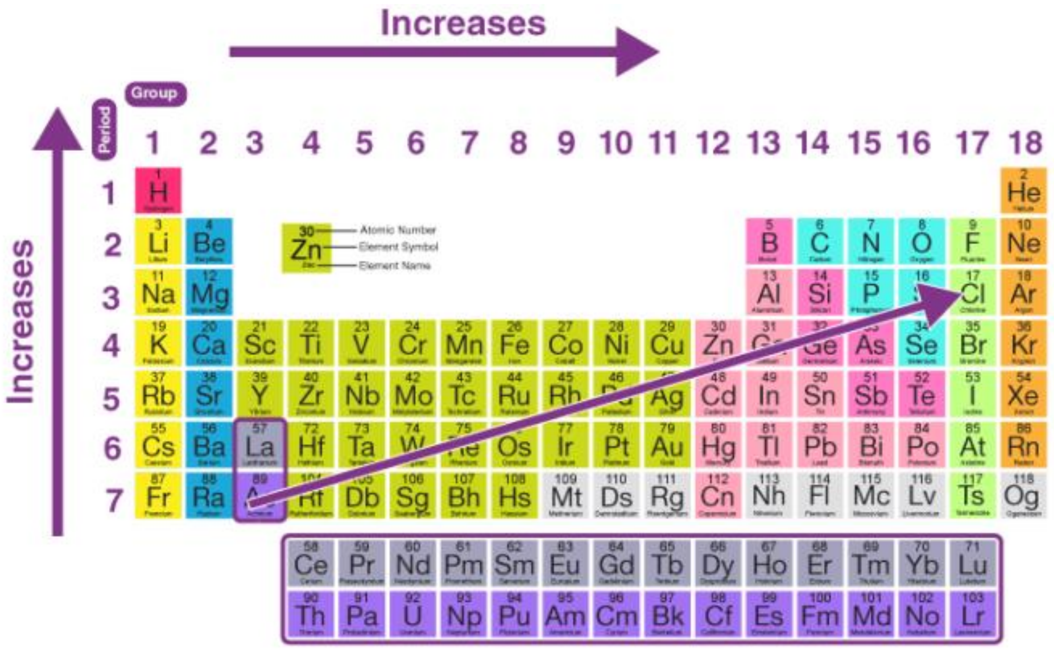


Figure V.6. The evolution of the Electron affinity in the periodic table

V.3.5. Electronegativity χ

Electronegativity is defined as the ability of an atom in a molecule to attract the shared pair of electrons toward itself to achieve stability. electronegativity plays an important role in chemical bonding.

The main factors on which electronegativity depends are effective nuclear charge and atomic radius. The greater the effective nuclear charge greater the electronegativity. The smaller the atomic radius greater the electronegativity.

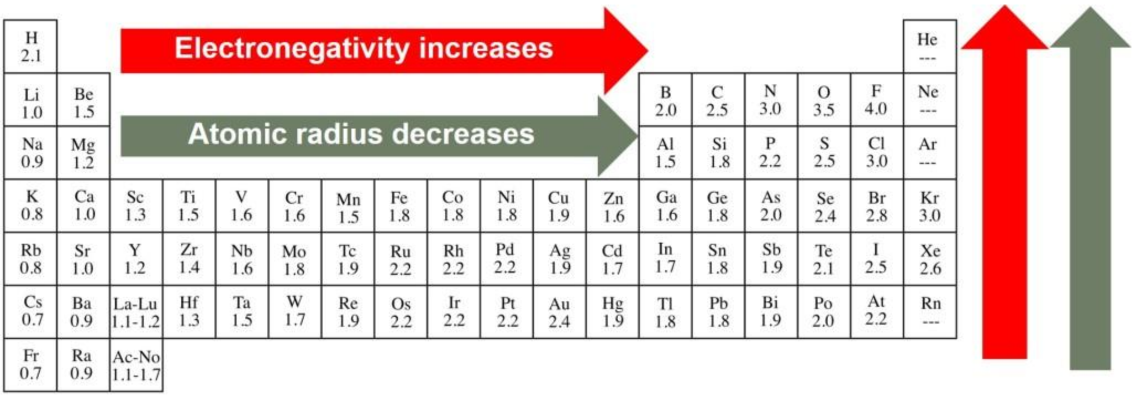
The trends for electronegativity in the periodic table are that electronegativity increases as you go across a period, and increases as you go up a group,

with fluorine being the most electronegative atom. Noble gases are given an electronegativity rating of 0 due to their inherent stability, which keeps them from forming bonds with other atoms.

V.3.5.1. Periodic Trends in Electronegativity

In a period, electronegativity increases in moving from left to right. This is due to the reason that the nuclear charge increases whereas atomic radius decreases as we move from left to right in a period. Halogens have the highest value of electronegativity in their respective periods.

In a group, electronegativity decreases on moving down the group. This is due to the effect of the increased atomic radius. Among halogens fluorine has the highest electronegativity. In fact, fluorine is the most electronegative element and is given a value of 4.0 (Pauling's scale) whereas cesium is the least electronegative element (E.N. = 0.7) because of its largest size and maximum screening effect. In other words, cesium is the most electropositive element and hence is the most metallic element in the periodic table.



H 2.1																	He ---
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne ---
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.2	S 2.5	Cl 3.0	Ar ---
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6
Cs 0.7	Ba 0.9	La-Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn ---
Fr 0.7	Ra 0.9	Ac-No 1.1-1.7															

V.3.5.2. Electronegativity scales.

The electronegativity scale is an arbitrary scale. They are based on various types of experimental data like bond energy, dipole moment, ionization potential, and electron affinity. There are various numerical scales for rating electronegativity, the most commonly used scales are

a. Pauling scale (1932)

It is based on the dissociation energies of the bonds of simple diatomic molecules: E_{A-A}, E_{B-B}, and E_{A-B}.

Consider a bond A-B between two dissimilar atoms A and B of a molecule AB. Let the bond energies of A-A, B-B, and A-B bonds be represented as E_{A-A}, E_{B-B}, and E_{A-B} respectively. The difference in electronegativity between elements B and A is given by:

$$|\chi_1 - \chi_B| = 0.102\sqrt{E_{1-B}\sqrt{E_{A-A}E_{B-B}}} \quad at\ eV$$

0.102 coefficient that allows energies values in Kg/mol to be used and converted to eV/mol.

Disadvantages of the Pauling scale

The disadvantage of Pauling's scale is that bond energies are not known with any degree of accuracy for many solid elements.

b. Millikan scale.

In 1934, Mulliken suggested an alternative approach to electronegativity based on ionization energy and electron affinity of an atom. According to this method electronegativity could be regarded as the average of the ionization energy and electron affinity of an atom, by the relationship:

$$Electronegativity(\chi) = \frac{(\mathrm{E}I + \mathrm{E}A)}{2}$$

Mulliken used ionization energy and electron affinity values measured in electron volts.

The values of ionization energy and electron affinity are measured in kJ mol^{-1} and 1eV =96.48 kJ mol^{-1}.

Disadvantage

Although Mulliken's scale is less empirical than the Pauling Scale, yet it suffers from a serious disadvantage in that electron affinities with the exception of a few elements are not reliably known.

c. Allred and Rochow

given by: $\boldsymbol{\chi} = \frac{e^2 Z_{eff}}{r_{cov}^2}$with

Z_{eff}: effective charge of the nucleus, e: elementary charge, r_{cov}: covalent radius of the element.

note: Noble gases do not have electronegativity because their valence layer is saturated.

V.4. Calculates the energy of poly electronics by Slater's rule

V.4.1. Calculation of ionization energies

Consider atom X, which is subject to initial ionization: X(g)→ X^+(g) + e^-

The ionization energy is expressed by the following correlation:$\mathbf{E_{I_1} = E_{M^+} - E_M}$

The total energy of an atom is calculated by the sum of the individual energies of all its electrons.

Example

Quantify the ionization energy necessary for extracting the outermost electron from a neutral potassium atom.

solution

$19\mathrm{K}: [1S^2][2S^2; 2P^6][3S^2; 3P^6][4S^1]$

The outermost electron is in the 4s orbital.

Apply Slater’s Rules:

- For **Group 4** (the electron in the 4s orbital):
  - Each electron in Group 4 contributes 0.35 to shielding.

  - There are no other electrons in Group 4 (since the 4s orbital has only 1 electron).
  - So the shielding contribution from Group 4 is 0.
- For **Group 3** (electrons in the 3s and 3p orbitals):
  - Each electron in Group 3 contributes 0.85 to shielding.
  - There are 8 electrons in Group 3 (6 in 3p and 2 in 3s).
  - So the total shielding from Group 3 is 8×0.85=6.8.
- For **Group 2** (electrons in the 2s and 2p orbitals):
  - Each electron in Group 2 contributes 1.00 to shielding.
  - There are 8 electrons in Group 2.
  - So the total shielding from Group 2 is 8×1.00=8.0.
- For **Group 1** (electrons in the 1s orbital):
  - Each electron in Group 1 contributes 1.00 to shielding.
  - There are 2 electrons in Group 1.
  - So the total shielding from Group 1 is 2×1.00=2.0.

Calculate the effective nuclear charge (Z_{eff}): The effective nuclear charge felt by the outermost electron is given by:

$Z_{eff} = Z-\sum\sigma$; where Z is the nuclear charge (atomic number) and σ\sigma is the total shielding constant.

- The atomic number Z of potassium is 19.
- The total shielding σ is the sum of the shielding contributions: $\sigma=6.8 + 8.0 + 2.0 = 16.8$

So, the effective nuclear charge is:

$Z_{eff}=19-16.8= 2.2$

$19K^{+}: [1S^{2}][2S^{2}; 2P^{6}][3S^{2}; 3P^{6}]$

The outermost electron is in the 3p orbital.

Apply Slater's Rules:

- For **Group 3** (electrons in the 3s and 3p orbitals):
  - Each electron in Group 3 contributes 0.35 to shielding.
  - There are 7 electrons in Group.
  - So the total shielding from Group 3 is 7×0.35= 2.45.
- For **Group 2** (electrons in the 2s and 2p orbitals):
  - Each electron in Group 2 contributes 0.85 to shielding.
  - There are 8 electrons in Group 2.
  - So the total shielding from Group 2 is 8×0.85= 6.8.

- For **Group 1** (electrons in the 1s orbital):
    - Each electron in Group 1 contributes 1.00 to shielding.
    - There are 2 electrons in Group 1.
    - So, the total shielding from Group 1 is 2×1.00=2.0.

Calculate the effective nuclear charge (Z_{eff}): The effective nuclear charge felt by the outermost electron is given by:

$Z_{eff}=Z-\sum\sigma = Z$ Where Z is the nuclear charge (atomic number) and σ is the total shielding constant.

- The atomic number Z of potassium is 19.
- The total shielding σ is the sum of the shielding contributions: σ=2.45+6.8 + 2.0 = 11.25.

So, the effective nuclear charge is:

$Z_{eff}=19-11.25= 7.75$

$E_K = 2E_1 + 8E_2 + 8E_3 + 1E_4$

$E_{K^+} = 2E'_1 + 8E'_2 + 8E'_3$

The ionization energy is expressed by the following correlation: $\mathbf{E_{I_1} = E_{M^+} - E_M}$

$\mathbf{E_{I_1} = E_{K^+} - E_K}$

$\mathbf{E_{I_1}} = \cancel{2E'_1} + \cancel{8E'_2} + \cancel{8E'_3} - \cancel{2E_1} - \cancel{8E_2} - \cancel{8E_3} - 1E_4$

$\mathbf{E_{I_1}} = -1E_4$

Use the Bohr model formula for ionization energy: $E_I = -13.6\frac{Z_{eff}^2}{n^2}$

n=4

$$E_4 = -13.6\frac{Z_{eff}^2}{n^2} = -13.6\frac{(2.2)^2}{(4)^2} = -4.114 \text{ eV}$$

$\mathbf{E_I = 4.114\ eV}$

V.4.2. Calculation of Electron Affinity

Example: Quantify the ionization energy necessary for extracting the outermost electron from a neutral chlorine atom.

Solution

$17Cl: [1S^2][2S^2; 2P^6][3S^2; 3P^5]$

The outermost electron is in the 3p orbital.

Apply Slater's Rules:

- For **Group 3** (the electron in the 3p orbital):
    - Each electron in Group 3 contributes 0.35 to shielding.

  - There are 7 electrons in Group 3.
  - So the total shielding from Group 3 is 6×0.35= 2.1.
- For **Group 2** (electrons in the 2s and 2p orbitals):
  - Each electron in Group 2 contributes 0.85 to shielding.
  - There are 8 electrons in Group 2.
  - So the total shielding from Group 2 is 8×0.85 = 6.8.
- For **Group 1** (electrons in the 1s orbital):
  - Each electron in Group 1 contributes 1.00 to shielding.
  - There are 2 electrons in Group 1.
  - So the total shielding from Group 1 is 2×1.00=2.0.

Calculate the effective nuclear charge (Zeff): The effective nuclear charge felt by the outermost electron is given by:

Zeff = $Z-\sum\sigma$; where Z is the nuclear charge (atomic number) and σ\sigma is the total shielding constant.

- The atomic number Z of chlorine is 17.
- The total shielding σ is the sum of the shielding contributions: $\sigma=2.1+6.8+2.0=10.9$

So, the effective nuclear charge is: Zeff=17−10.9= 6.1

$17Cl^-: [1S^2][2S^2; 2P^6][3S^2; 3P^6]$

The outermost electron is in the 3p orbital.

Apply Slater's Rules:

- For **Group 3** (electrons in the 3s and 3p orbitals):
  - Each electron in Group 3 contributes 0.35 to shielding.
  - There are 8 electrons in the Group.
  - So the total shielding from Group 3 is 7×0.35= 2.45.
- For **Group 2** (electrons in the 2s and 2p orbitals):
  - Each electron in Group 2 contributes 0.85 to shielding.
  - There are 8 electrons in Group 2.
  - So the total shielding from Group 2 is 8×0.85= 6.8.
- For **Group 1** (electrons in the 1s orbital):
  - Each electron in Group 1 contributes 1.00 to shielding.
  - There are 2 electrons in Group 1.
  - So the total shielding from Group 1 is 2×1.00=2.0.

Calculate the effective nuclear charge (Zeff): The effective nuclear charge felt by the outermost electron is given by:

Zeff =Z−∑σ = Z; Where Z is the nuclear charge (atomic number) and σ\sigma is the total shielding constant.

- The atomic number Z of chlorine is 17.
- The total shielding σ is the sum of the shielding contributions: σ= 2.45 + 6.8 + 2.0 = 11.25.

So, the effective nuclear charge is: Zeff=17−11.25= 5.75

$E_{Cl} = 2E_1 + 8E_2 + 7E_3$

$E_{Cl^-} = 2E'_1 + 8E'_2 + 8E'_3$

The Electron Affinity is expressed by the following correlation: $E_A = E_{(X)} - E_{(X^-)}$

$E_A = E_{(Cl)} - E_{(Cl^-)}$

$E_A = \cancel{2E_1} + \cancel{8E_2} + 7E_3 \cancel{- 2E'_1 - 8E'_2} - 8E'_3$

$E_A = 7E_3 - 8E'_3$

Use the Bohr model formula: $E_I = -13.6\frac{Z_{eff}^2}{n^2}$

n=3

$$\mathbf{E_3 = -13.6\frac{Z_{eff}^2}{n^2} = -13.6\frac{(6.1)^2}{(3)^2} = -56.23\ eV}$$

$$\mathbf{E'_3 = -13.6\frac{Z_{eff}^2}{n^2} = -13.6\frac{(5.75)^2}{(3)^2} = -49.96\ eV}$$

$E_A = 7(\mathbf{-56.23}) - 8(\mathbf{-49.96}) = 6{,}07\ eV$

$E_A = 6{,}07\ eV$

V.4.3. Calculation of ionic radii

example

calculate the ionic radii of K^+ and Cl^- ions in KCl crystal. the internuclear distance between K^+ and Cl^- ions are found to be 3.14 Å.

solution

r(K+) +r(Cl-) =d(K+-Cl-) =3.14 Å (1)

K^+ and Cl^- ions have Ar (Z=18) type configurations. The effective nuclear charge for K+ and Cl- can be calculated as follows.

$K^+: [1S^2][2S^2; 2P^6][3S^2; 3P^6]$

$Z_{eff}(K^+) = Z - \sum \sigma$

$Z_{eff}(K^+)$ =7.75

$Z_{\mathrm{eff}}(\mathrm{Cl}^-) = 5.75$

$$\frac{r(K^+)}{r(\mathrm{Cl}^-)} = \frac{Z_{\mathrm{eff}}(\mathrm{Cl}^-)}{Z_{\mathrm{eff}}(K^+)} = \frac{5.75}{7.75} = 0.74$$

$r(K^+) = 0.74\, r(\mathrm{Cl}^-)$ (2)

substitute (2) in (1)

$$0.74\, r(\mathrm{Cl}^-) + r(\mathrm{Cl}^-) = 3.14\ \text{Å} \qquad (3)$$

$$1.74\, r(\mathrm{Cl}^-) = 3.14\ \text{Å}$$

$$r(\mathrm{Cl}^-) = \frac{3.14\ \text{Å}}{1.74} = 1.81\ \text{Å}$$

from (2)

$$r(K^+) = 0.74\, r(\mathrm{Cl}^-)$$

$$= 0.74 \times 1.81$$

$$= 1.33\ \text{Å}$$

$$r(K^+) = 1.33\ \text{Å}$$

$$r(\mathrm{Cl}^-) = 1.81\text{Å}$$

CHAPTER VI Chemical Bonding

VI. Introduction

The bonding situation in covalently bonded molecules was described as a sharing of valence electrons. The valence electrons involved belong to neither of the atoms involved completely. Nowadays, chemical bonding is mainly explained by the application of wave mechanics and described either by the valence bond (VB) or molecular orbital (MO) theory.

A logical explanation for chemical bonding was provided by Kossel and Lewis in 1916. Their approach to chemical bonding is based on the inertness of the noble gases which have little or no tendency to combine with other atoms. They proposed that the noble gases are stable due to their completely filled outer shell electronic configuration.

A chemical bond is defined as a mutual electrical attraction between the nuclei and valence electrons of different atoms that binds the atoms together, which leads to the formation of chemical substances containing two or more atoms. The bond is a result of the electrostatic attraction between opposite charges, such as electrons or nuclei or dipole attraction.

There are very few atoms that exist as individual particles in nature. Most atoms are bonded to other atoms to form compounds.

Lewis structures are used to simply describe how valence electrons are arranged in molecules and how they are involved in chemical bonds. Basically, dots are used to visualize the number of valence electrons, whereas the elemental symbol represents the nuclei. As a basic rule, electrons should be ruled. Paired electrons are sometimes also represented by a line, which can be interpreted as a single covalent bond. An element with a single electron represents a radical. Electron pairs not contributing to any bonds are called lone pairs.

Double and triple bonds can also be symbolized using Lewis structures.

VI.1. Types of Chemical Bonds

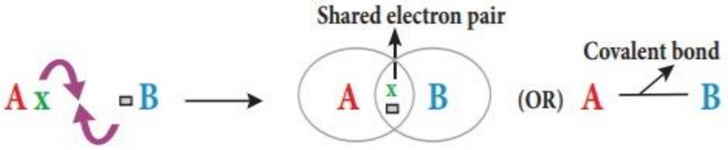
All chemical bonds involve the valence electrons of the atoms, but the latter intervene in different ways, giving rise to several types of bonds. Chemical bonds can be classified based on the nature of the interaction between the bonded atoms. the major types of chemical bonding in chemistry or chemical science are Ionic, covalent, metallic, and hydrogen bonds. Generally, metals react with nonmetals to form ionic compounds, and covalent bonds are present in the compounds formed by nonmetals.

VI.1.1 covalent bonding

Covalent bond or covalent bonding is defined as the sharing of one or more electron pairs between two combining atoms similar or dissimilar atoms. Each atom of periodic table elements contributes one electron to form an electron pair in this type of chemical bonding.

If two atoms share just one pair of electrons a single covalent bond is formed as in the case of the hydrogen molecule. If two or three electron pairs are shared between the two combining atoms, then the covalent bond is called a double bond or a triple bond, respectively.

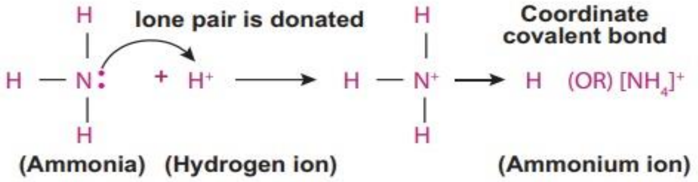
The compounds like hydrogen (H_2), chlorine (Cl_2), oxygen (O_2), water (H_2O), and hydrocarbons (methane, ethane, propane) are formed by covalent chemical bonding.



VI.1.2 Dative bond or coordinate covalent bond

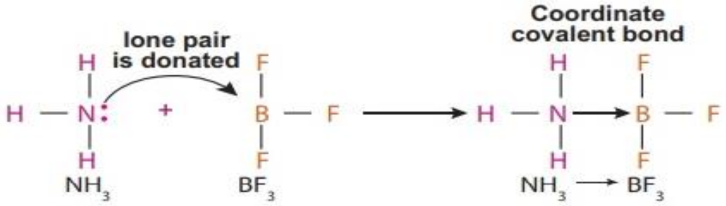
In the formation of a normal covalent bond each of the two bonded atoms contributes one electron to form the bond. However, in some compounds, the formation of a covalent bond between two atoms takes place by the sharing of two electrons, both of which come from only one of the combining atoms. This bond is called a Coordinate covalent bond or Dative bond.

Mostly the lone pair of electrons from an atom in a molecule may be involved in the dative bonding. The atom that provides the electron pair is called the donor atom while the other atom which accepts the electron pair is called the acceptor atom. The Coordinate covalent bond is represented by an arrow (→) which points from the donor to the acceptor atom.



Example: Formation of a coordinate covalent bond between $NH_3 \rightarrow BF_3$ molecules

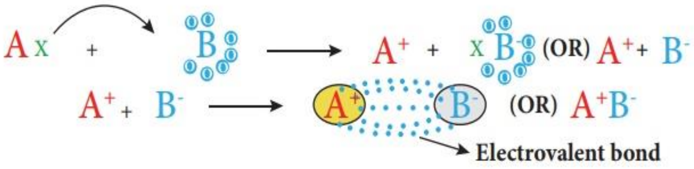
In some cases, the donated pair of electrons comes from a molecule as a whole, which is already formed to another acceptor molecule. Here, the molecule ammonia (NH_3) gives a lone pair of electrons to the Boron trifluoride (BF_3) molecule, which is electron-deficient. Thus, a Coordinate covalent bond is formed between NH_3(donor molecule) and BF_3 (acceptor molecule) and is represented by $NH_3 \rightarrow BF_3$.



VI.1.3 Ionic bonding

When the electronegativity difference between the two combining atoms is large, the least electronegative atom completely transfers one or more 'from an electropositive metal) of its valence electrons to the other combining atom (an electronegative non-metal atom) so that both atoms can attain the nearest inert gas electronic configuration. The complete transfer of electrons leads to the formation of a cation and an anion. Both these ions are held together by the electrostatic attractive force which is known as an ionic bond that results between cations and anions.

In purely ionic bonding atoms completely give up electrons to other atoms. Ionic bonding generally involves metals and nonmetals



Formation of Ionic Bonding

Every halogen atom has seven electrons in its outermost orbital. Therefore, the halogen atom gains one electron by chemical bonding to attain the stable electronic configuration of the next noble gas molecule.

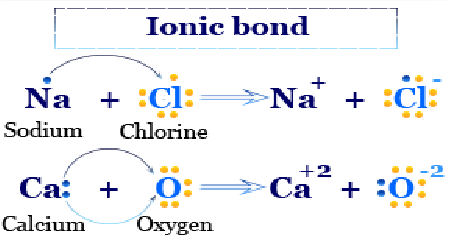
On the other hand, alkali metal with very low ionization energy has one electron in the outermost orbitals. Therefore, alkali metal tries to lose this electron for the formation of chemical bonding to form a stable noble gas electronic configuration.

Ionic Bonding in Sodium Chloride

Formation of NaCl, the sodium atom loses one electron to form a positively charged Na^+ ion. But the chlorine atom gains one electron to form a negatively charged Cl^- ion.

These two oppositely charged ions are associated or bonded together by electrostatic attraction to form a sodium chloride crystalline solid.

Crystallographic studies of sodium chloride show that there is no discrete sodium chloride molecule in nature. Hence in sodium chloride crystal lattice, each potassium ion is surrounded by six chlorine atoms or vice versa.



VI.1.4 Metallic bond

A metallic bond is most commonly described as a type of chemical bond where the metal atom donates its valence electrons to a ‘pool’ of electrons that surrounds the network of metal atoms. Electrons are not anymore identified with one particular atom but are seen as delocalized over a wide range. This is a very strong type of chemical bond. Electrical and thermal conductivity as well as malleability of metals can be explained using this model.

VI.2. Lewis diagram

The Lewis structure (Lewis dot structure) is a pictorial representation of covalent bonding between the combining atoms. In this structure, the shared valence electrons are represented as a pair of dots between the combining atoms, and the unshared electrons of the atoms are defined as a pair of dots (lone pairs) on the respective individual atoms.

The Lewis dot symbol is very useful when learning about chemical bonding and chemical reactions.

It consists of the symbol of an element and one dot for each valence electron in an atom of the element. The dots are placed on the four sides of the symbol—

top, bottom, left, and right —and each side can accommodate up to two electrons.

VI.2.1. Lewis structure of atoms

The valence electrons (outer shell electrons) of an element are represented as small dots around the symbol of the element. The valence electrons are denoted as single dots around the four sides of the atomic symbol.

Example: the electronic configuration of nitrogen is $1s^2$, $2s^2$, $2p^3$. It has 5 electrons in its outer shell (valence shell). The Lewis structure of nitrogen is as follows.

The only exception to this is helium which has only two electrons in its valence shell which is represented as a pair of dots (duet).

VI.2.2. Lewis structure of molecular compounds and ions

The Lewis dot structure for a given compound can be written by following the steps given below.

1. Draw the skeletal structure of the molecule. In general, the most electronegative atom is placed at the center.

2. Calculate the total number of valence electrons of all the atoms in the molecule. In the case of polyatomic ions, the charge on the ion should also be considered during the calculation of the total number of valence electrons. In the case of anions, the number of negative charges should be added to the number of valence electrons. For positive ions, the total number of positive charges should be subtracted from the total number of valence electron

3. Draw a single bond between the atoms in the skeletal structure of the molecule. Each bond will account for two valence electrons (a bond pair).

4. Distribute the remaining valence electrons as pairs (lone pair), giving octet (only duet for hydrogen) to the atoms in the molecule. The distribution of lone pairs starts with the most electronegative atoms followed by other atoms.

5. Verify whether all the atoms satisfy the octet rule (for hydrogen duet). If not, use the lone pairs of electrons to form additional bonds to satisfy the octet rule.

Example 1

Write the Lewis structure of nitrogen trifluoride (NF_3).

Step 1: N is less electronegative than F, put N in center

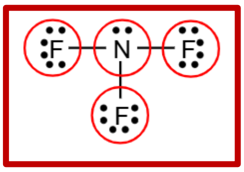
Step 2: Count valence electrons N : 5 ($2s^2\ 2p^3$) and F : 7 ($2s^2\ 2p^5$)

5 + (3 x 7) = 26 valence electrons

Step 3: Draw single bonds between N and F atoms and complete octets on N and F atoms.

Step 4: Check, are of the e^- in the structure is equal to the number of valence e^-.

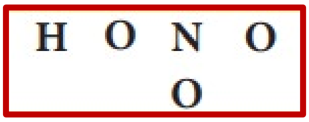
3 single bonds (3x2) + 10 lone pairs (10x2) = 26 valence electrons



Example 2

Let us draw the Lewis structure for nitric acid.

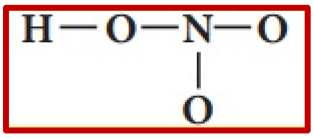
1. Skeletal structure



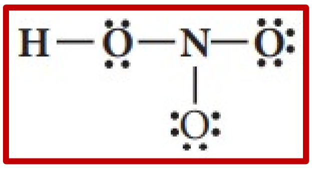
2. Total number of valence electrons in HNO_3

= [1 × 1(hydrogen)] + [1 × 5(nitrogen)] + [3× 6(oxygen)] = 1+ 5 + 18 = 24

3. Draw single bonds between atoms. Four bonds can be drawn as shown in the figure for HNO_3 which accounts for eight electrons (4 bond pairs).

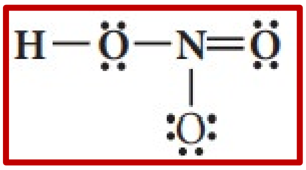


4. Distribute the remaining sixteen (24 - 8= 16) electrons as eight lone pairs starting from the most electronegative atom, the oxygen. Six lone pairs are distributed to the two terminal oxygens (three each) to satisfy their octet and two pairs are distributed to the oxygen that is connected to hydrogen to satisfy its octet.



5. Verify whether all the atoms have octet configuration. In the above distribution, the nitrogen has one pair short for octet. Therefore, move one of the lone pair from the terminal oxygen to form another bond with nitrogen.

The Lewis structure of nitric acid is given as



VI.2.3. Formal charge

Sometimes there is more than one acceptable Lewis structure for a given species. In such cases, we can often select the most plausible Lewis structure by using formal charges.

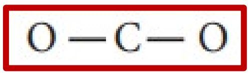
An atom's formal charge is the electrical charge difference between the valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis structure.

Let us draw the Lewis structure for carbon dioxide.

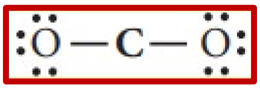
1. Skeletal structure

2. Total number of valence electrons in CO2 = [1 x 4(carbon)] + [2 x 6(oxygen)] = 4+ 12 = 16

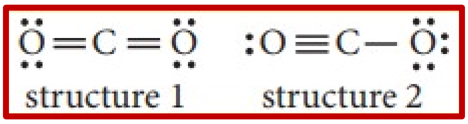
3. Draw single bonds between atoms. Two bonds can be drawn as shown in the figure for CO2 which accounts for four electrons (2 bond pairs).



4. Distribute the remaining twelve electrons (16 - 4= 12) as six lone pairs starting from most electronegative atom, the oxygen. To satisfy their octet, six lone pairs are distributed to the two terminal oxygens (three each).



5. Verify whether all the atoms have an octet configuration. In the above distribution, the central carbon has two pairs short for octet. Therefore, to satisfy the octet rule two lone pairs from one oxygen or one pair from each oxygen can be moved to form multiple bonds, leading to the formation of two possible structures for carbon dioxide as shown below


structure 1 structure 2

Similarly, the Lewis structure for many molecules drawn using the above steps gives more than one acceptable structure. Let us consider the above mentioned two structures of carbon dioxide. Which of the above forms represents the best distribution of electrons in the molecule? To find an answer, we need to know the formal charge of each atom in the Lewis structures. The formal charge of an atom in a molecule is the electrical charge difference between the valence electron in an isolated atom and the number of electrons assigned to that atom in the Lewis structure.

$$\textbf{Formal charge of an atom} = \boldsymbol{N_V - \left(N_l + \frac{N_b}{2}\right)}$$

Where,

N_V: Number of valence electrons of an atom in its isolated state.

N_l: Number of electrons present as lone pairs around the atom in the Lewis structure

N_b: Number of electrons present in bonds around the atom (bond pairs) in the Lewis structure]

After calculating the formal charges, the best representation of Lewis structure can be selected by using the following guidelines.

1. A structure in which all formal charges are zero preferred over the one with charges.

2. A structure with small formal charges is preferred over the one with higher formal charges.

3. A structure in which negative formal charges are placed on the most electronegative atom is preferred.

In the case of CO_2 structures, structure one is preferred over structure 2 as it has zero formal charges for all atoms.

Formal charge guidelines

- **A Lewis structure with no formal charges is generally better than one with formal charges.**
- **Small formal charges are generally better than large formal charges.**
- **Negative formal charges should be on the more electronegative atom(s).**

VI.2.4. Octet rule

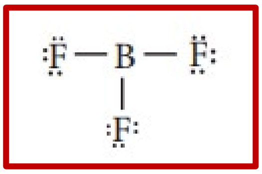
The idea of Kossel Lewis approach to chemical bonds lead to the octet rule, which states that "the atoms transfer or share electrons so that all atoms involved in chemical bonding obtain 8 electrons in their outer shell (valence shell)".

a. Exceptions to the Octet Rule

The octet rule is useful for writing Lewis structures for molecules with second-period elements as central atoms. In some molecules, the central atoms have fewer than eight electrons around them, while some others have more than eight electrons. The exception to the octet rule can be categorized into the following three types.

1. Molecules with electron-deficient central atoms

Fewer than 8: H at most only 2 electrons (one bond) BeH_2, only 4 valence electrons around Be (only 2 bonds), boron compounds only 6 valence electrons (three bonds).



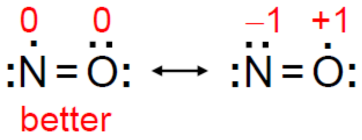
Molecules such as BCl_3, $BeCl_2$, etc... also have incomplete octets.

2. Molecules containing odd electrons

Some molecules contain an odd number of electrons. Among them are nitric oxide (NO) and nitrogen dioxide (NO_2): the octet rule clearly cannot be satisfied for all the atoms in any of these molecules.

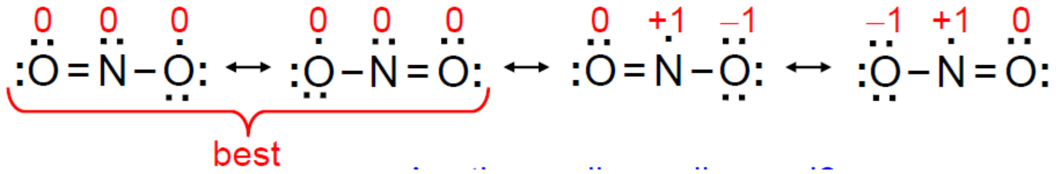
Example: NO (nitrogen monoxide or nitric oxide)

$$NO \Longrightarrow (1\times 5)+(1\times 6)=11\ valence\ é$$



Example: NO_2 (nitrogen dioxide)

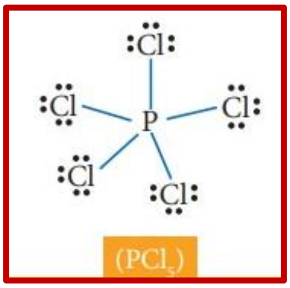
$$NO_2 \Longrightarrow (1\times 5)+(2\times 6)=17\ valence\ é$$

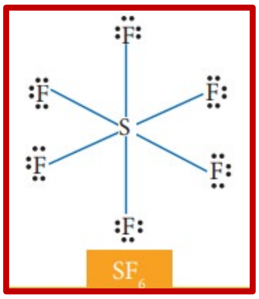


3. Molecules with expanded valence shells

<u>Expanded valence (more than 8):</u> can only happen if the central element had d- orbitals which means it is from the 3rd period or greater and can thus be surrounded by more than four valence pairs in certain compounds. The number of bonds depends on the balance between the ability of the nucleus to attract electrons and the repulsion between the pairs. Some of the more elements are fluorine oxygen, chlorine, and noble gases.

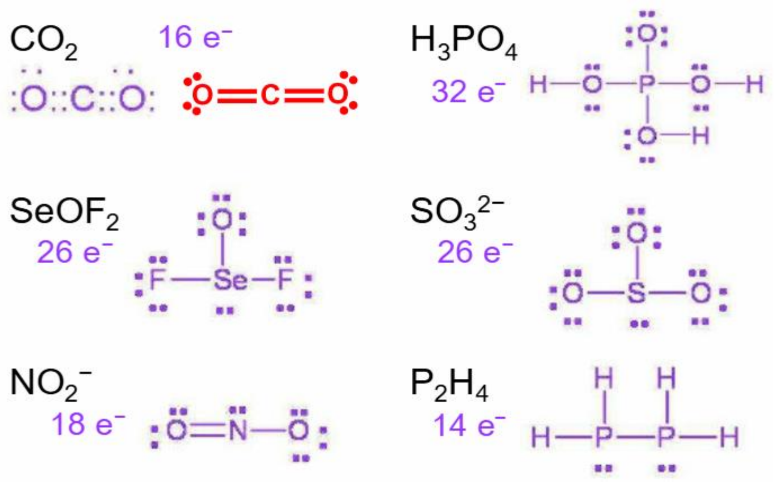
In molecules such as sulphur hexafluoride (SF_6), and phosphorous pentachloride (PCl_5) the central atom has more than eight valence electrons around them. Here the central atom can accommodate additional electron pairs by using outer vacant d orbitals. In SF_6 the central atom sulphur is surrounded by six bonding pair of electrons or twelve electrons.





Example: Draw the Lewis structure of the following

$$CO_2, SO_3^{2-}, NO_2^{-}, P_2H_4, H_3PO_4, SeOF_2$$



Application

Draw Lewis structures for the following compounds:

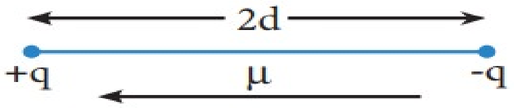
HBr, H_2S, CH_4, ICl, PH_3, N_2H_4, $COBr_2$

VI.3. Dipole moment:

The polarity of a covalent bond can be measured in terms of dipole moment, which is defined as

$$\mu = q \times 2d$$

Where μ is the dipole moment, q is the charge, and 2d is the distance between the two charges. The dipole moment is a vector, and the direction of the dipole moment vector points from the negative charge to the positive charge.



Representation of Dipole

Unit of Dipole Moment

The charge of an electron = 4.8×10^{-10} esu, and the distance between the center is of order 10^{-8} cm.

Hence the calculated dipole moment order, = $10^{-10} \times 10^{-} = 10^{-18}$esu= 1 Debye

- **∴ 1 Debye = 10^{-18} esu cm = 3.336×10^{-30} coulomb meter**

VI.3.1. Dipole Moment and Percentage Ionic Character

Dipole moment data is used to calculate the percentage ionic character of covalent or ionic heteronuclear diatomic molecules. Let us consider a molecule AB having the observed dipole moment = μ_{obs} and the bond length l cm.

- **If the shared pair lies at the midpoint of the atoms, the bond would be a purely covalent bond, and the percentage ionic character is zero.**
- **But if the bond is 100 percent ionic and B is more electronegative than A. Therefore, A carries a unit positive charge, and B carries a unit negative charge.**

VI.3.2. Percentage Ionic Character Formula

In that case, the μ of AB would be, $\mu_{ionic} = e \times l = 4.8 \times 10^{-18}$ esu cm. But the μ of AB is neither zero nor μ_{ionic}.

$$\text{\% of Ionic Character of the bond} = \frac{\mu_{obs}}{\mu_{ionic}} \times 100 = \frac{\mu_{obs}}{4.8 \times 10^{-10} \times 1} \times 100$$

Where, μ_{obs} = observed dipole moment

μ_{ionic} = theoretical dipole momentent

1= bond length

VI.4. Valence Shell Electron Pair Repulsion (VSEPR) theory

Lewis's concept of the structure of molecules deals with the relative position of atoms in the molecules and the sharing of electron pairs between them. However, we cannot predict the molecule's shape using the Lewis concept. Lewis's theory in combination with VSEPR theory will be useful in predicting the shape of molecules.

the theory of VSEPR was suggested by Sidwich and Powell in 1940, it was further improved by Gillespie and Nyholm in 1957. The abbreviation VSEPR stands for “valence- shell, electron-pair repulsion” referring to the repulsion between pairs of valence electrons of the atoms in a molecule. The VSEPR) rules are a set of rules used to predict the shape of a molecule.

The basic principle is that valence electrons around the center atom repel each other and therefore will form an arrangement in which they are situated furthest from each other. Also, lone pairs are included in this electrostatic repulsion. In VSEPR theory, double and triple bonds are treated in the same way as single bonds. And polyatomic ions are treated similarly to molecules. The resulting geometry depends on the number of bonding and nonbonding electron pairs.

a. **Steps in the prediction of geometry**

- **Determine the central atom.**
- **Draw the electron dot structure and bar diagram**
- **Find the arrangement of electron pairs**
- **Determine the geometry based on bonding pairs.**

VSEPR theory applies to molecules or ions of type: $\mathbf{AX_nE_m}$

the letter A represents the central atom in a molecule and the atoms bonded to the central atom by the letter X, E represents the unshared electron pair, n represents the number of atoms bonded and m represents the number of the unshared electron pair.

VI.4.1. Applications of VSEPR theory

VI.4.1.1. $\mathbf{AX_n}$ type with simple bond

- ♣ **Molecules with the central atom with an incomplete octet**

In the case of a 2 é pair, the possible shape to keep them at the maximum distance is to arrange them at an angle of 180. This gives a **linear shape**.

Molecules with only 3 bonding pairs on the central atom will have a **Triangular (Trigonal) planar shape** with bond angles of 120°.

VI.4.1.2. AXn type with multiple bonds

- **Molecules with the central atom surrounded by four bonding pairs**

If the central atom is placed at the center of a sphere, than each of the four pairs of electrons will occupy a position to be as apart as possible.

This will result in the electron pairs being at the corners of a regular tetrahedron, therefore these molecules are said to have a TETRAHEDRAL shape. The bond angle between each bond will be 109.5°

VI.4.1.3. Molecules of AX_nE_m types.

- **Molecules with the central atom surrounded by 2 bonding pairs and 2 non-bonding pairs**

The four pairs of electrons will be arranged tetrahedrally but since only 2 pairs are bonding electrons, the surrounding atoms are at 2 corners of the tetrahedron.

As a result, these molecules will have a BENT or V-shape.

The repulsion between the non-bonding pairs will result in a bond angle of 104.5°.

For each pair of non-bonding electrons, the bond angle decreases by 2.5°

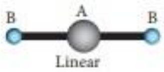
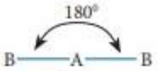
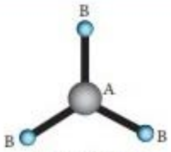
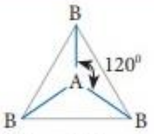
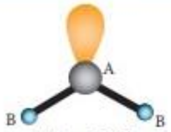
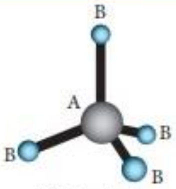
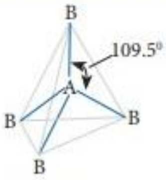
- **Molecules with the central atom surrounded by 3 bonding pairs and 1 non-bonding pair**

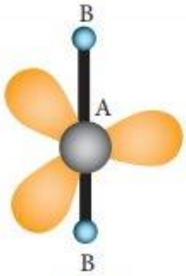
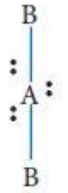
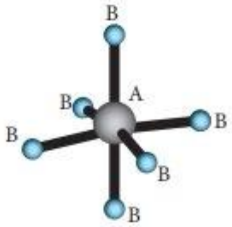
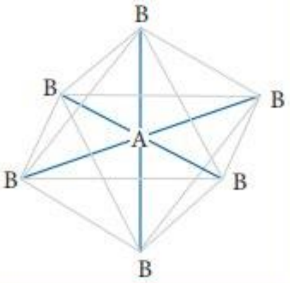
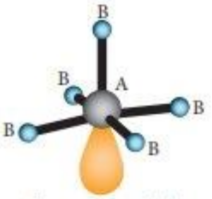
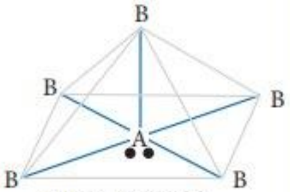
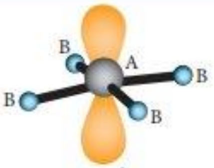
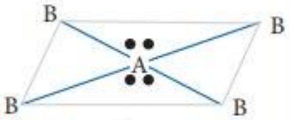
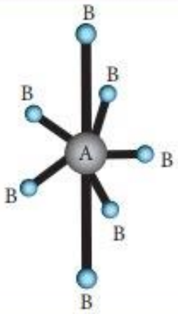
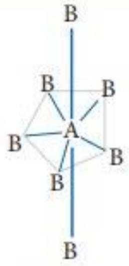
Four pairs of electrons will always arrange themselves tetrahedrally around the central atom. The shape of the molecule is determined by the arrangement of the atoms, not the electrons. As a result, such molecules will have a TRIANGULAR (TRIGONAL) PYRAMIDAL shape.

Due to the repulsion, a non-bonding electron pair requires more spaces than a bonding pair, the angles in these molecules are 107°, not 109° as in the tetrahedral molecules.

The following Table illustrates the shapes of molecules predicted by VSEPR theory. Consider a molecule AXnEm where A is the central atom and **n** represents the number of atoms of X covalently bonded to the central atom A. The lone pairs present in the atoms are denoted as E.

Table 1. Shapes of molecules predicted by VSEPR theory.

Number of electron Pairs	Molecule	No.of bond pairs	No.of. lone pairs	Shape	Molecular geometry	Examples
2	AB_2	2	-	 Linear	 Linear	$BeCl_2$, $HgCl_2$, CO_2, CS_2, HCN, BeF_2
3	AB_3	3	-	 Trigonal planar	 Trigonal planar	BF_3, BCl_3, NO_3^-, BF_3, CO_3^{2-}
	AB_2L	2	1	 Bent or V - Shape	 Bent or V - Shape	HCHO, SO_2, O_3, $PbCl_2$, $SnBr_2$
4	AB_4	4	-	 Tetrahedral	 Tetrahedral	CH_4, CCl_4, CCl_2F_2, SO_4^{2-},ClO_4^-, NH_4^+

Number of electron Pairs	Molecule	No.of bond pairs	No.of. lone pairs	Shape	Molecular geometry	Examples
	AB_2L_3	2	3	 Linear	 Linear	XeF_2, I_3^-, IF_2^-
6	AB_6	6	-	 Octathedral		SF_6, IOF_5,
	AB_5L	5	1	 Square pyramidal	 Square pyramidal	BrF_5, IF_5, TeF_5^-, $XeOF_4$,
	AB_4L_2	4	2	 Square planar	 Square Planar	XeF_4, ICl_4^-
7	AB_7	7	-		 pentagonal bi-pyramidal	IF_7

VI.5. Chemical bonding in the quantum model

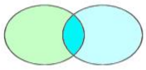
When two atomic orbitals overlap linearly along the axis, the resultant bond is called a sigma (σ) bond. This overlap is also called 'head-on overlap' or 'axial overlap'. Overlap involving an s orbital (s-s and s-p overlaps) will always result in a sigma bond as the s orbital is spherical. Overlap between two p orbitals along the molecular axis will also result in sigma bond formation. When we consider the x-axis as the molecular axis, the px-px overlap will result in σ-bond.

VI.5.1. Formation and nature of bonds (Orbital Overlap)

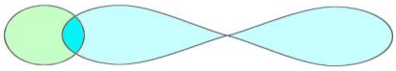
VI.5.1.1. s-s overlap. σ-bond

When two atomic orbitals overlap linearly along the axis, the resultant bond is called a sigma (σ) bond. This overlap is also called 'head-on overlap' or 'axial overlap'. Overlap involves an s orbital (s-s and s-p overlaps) and will always result in a sigma bond as the s orbital is spherical. Overlap between two p orbitals along the molecular axis will also result in sigma bond formation. When we consider the x-axis as the molecular axis, the px-px overlap will result in σ-bond. It is a stronger bond and cylindrically symmetrical.

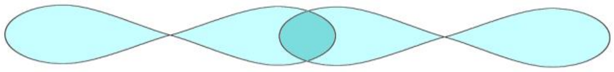
Depending on the type of orbital's overlapping, the σ-bond is divided into the following types: **1)** $\sigma_{s\text{-}s}$-bond, **2)** $\sigma_{p\text{-}p}$-bond, **3)** $\sigma_{s\text{-}p}$-bond



s-s head-to-head overlap



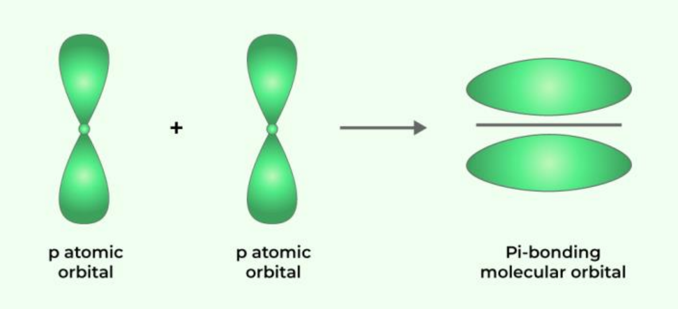
s-p head-to-head overlap



p-p head-to-head overlap

VI.5.1.2. p-p overlap. π-bond

When two atomic orbitals overlap sideways, the resultant covalent bond is called a pi (π) bond. When we consider the x-axis as a molecular axis, the py-py and pz-pz overlaps will result in the formation of a π-bond. When we consider the x-axis as a molecular axis, the py-py and pz-pz overlaps will result in the formation of a π-bond. When we consider the x-axis as molecular axis, the py-py and pz-pz overlaps will result in the formation of a π-bond.



Example: Formation of hydrogen (H_2) Molecule

The electronic configuration of the hydrogen atom is **$1s^1$**

During the formation of the H_2 molecule, the 1s orbitals of two hydrogen atoms containing one unpaired electron with opposite spin overlap with each other along the internuclear axis. This overlap is called s-s overlap. Such axial overlap results in the formation of a σ-covalent bond.

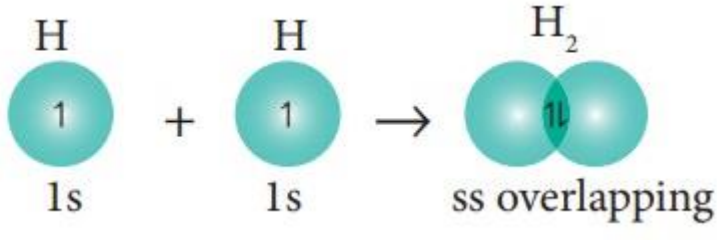


Figure.VI.1. formation of hydrogen molecule

Example: Formation of fluorine molecule (F_2):

Valence shell electronic configuration of fluorine atom: **$2s^22p_x^2$, $2p_y^2$, $2p_z^1$**

When the half-filled p_z orbitals of two fluorines overlap along the z-axis, a σ-covalent bond is formed between them.

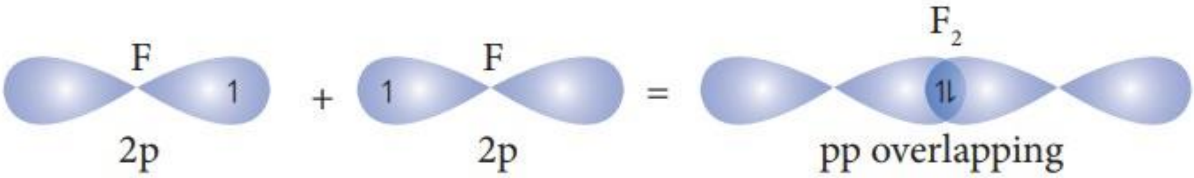


Figure.VI.2. formation of F_2 molecule

Example: Formation of HF molecule:

The electronic configuration of the hydrogen atom is **$1s^1$**

Valence shell electronic configuration of fluorine atom: **$2s^22p_x^2$, $2p_y^2$, $2p_z^1$**

When a half-filled **1s** orbital of hydrogen linearly overlaps with a half-filled **2pz** orbital of fluorine, a σ-covalent bond is formed between hydrogen and fluorine.

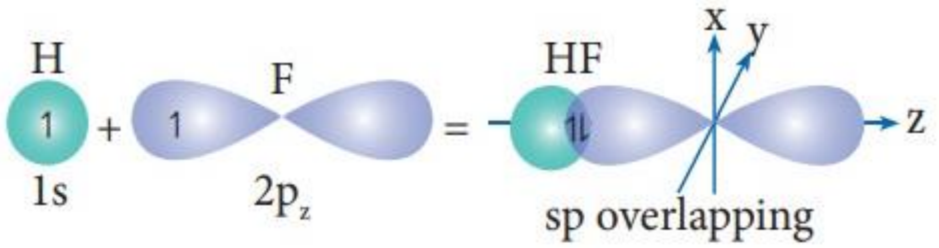
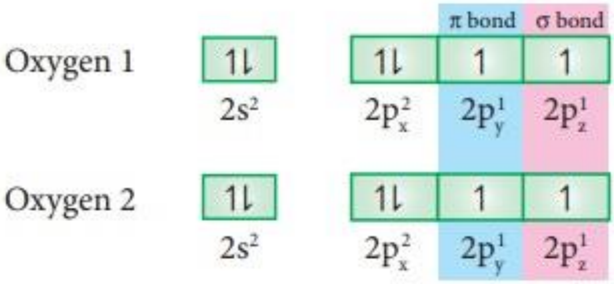


Figure.VI.3. formation of HF molecule

Example: Formation of oxygen molecule (O_2):

Valence shell electronic configuration of oxygen atom: $\mathbf{2s^2\ 2p_x^2,\ 2p_y^1,\ 2p_z^1}$



When the half-filled p_z orbitals of two oxygen overlap along the z-axis (considering the molecular axis as the z-axis), a σ-covalent bond is formed between them. The other two half-filled p_y orbitals of two oxygen atoms overlap laterally (sideways) to form an π-covalent bond between the oxygen atoms. Thus, in an oxygen molecule, two oxygen atoms are connected by two covalent bonds (double bond). The other two pairs of electrons present in the 2s and $2p_x$ orbital are not involved in bonding and remain as lone pairs on the respective oxygen.

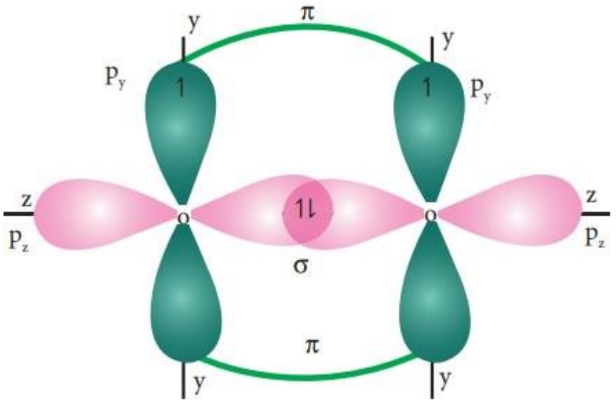


Figure.VI.4. formation of π bond in the O_2 molecule

VI.6. Molecular Orbital Theory (T.O.M)

Lewis concept and valence bond theory qualitatively explain chemical bonding and molecular structure. Both approaches are inadequate to describe some of the observed properties of molecules. For example, these theories predict that oxygen is diamagnetic. However, it was observed that oxygen in liquid form was attracted towards the poles of strong magnets, indicating that oxygen is paramagnetic. As both these theories treated the bond formation in terms of electron pairs and hence they fail to explain the bonding nature of paramagnetic molecules.

F. Hund and Robert. S. Mulliken developed a bonding theory called molecular orbital theory which explains the magnetic behavior of molecules.

The salient features of this theory are:

The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.

The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.

While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei, depending upon the number of atoms in the molecule. Thus, an atomic orbital is monocentric while a molecular orbital is polycentric.

The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is known as a bonding molecular orbital while the other is called an antibonding molecular orbital.

The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.

Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is provided by a molecular orbital.

The molecular orbitals, like atomic orbitals, are called in accordance with the Aufbau principle, obeying Pauli's exclusion principle and Hund's rule.

VI.7. Linear combination of atomic orbitals (LCAO method)

The wave functions for the molecular orbitals can be obtained by solving the Schrödinger wave equation for the molecule. Since solving the Schrödinger equation is too complex, approximation methods are used to obtain the wave function for molecular orbitals. The most common method is the linear combination of atomic orbitals (LCAO).

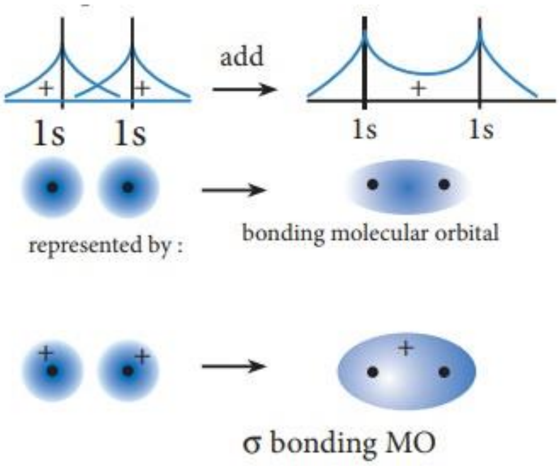
We know that the atomic orbitals are represented by the wave function Ψ. Let us consider two atomic orbitals represented by the wave functions ψ_A and ψ_B with comparable energy, combined to form two molecular orbitals. One is a bonding molecular orbital($\psi_{bonding}$) and the other is an antibonding molecular orbital($\psi_{antibonding}$). The wave functions for these two molecular orbitals can be obtained by the linear combination of the atomic orbitals ψ_A and ψ_B as below.

$\psi_{bonding} = \psi_A + \psi_B$

$\psi_{antibonding} = \psi_A - \psi_B$

The formation of bonding molecular orbital can be considered as the result of constructive interference of the atomic orbitals and the formation of anti-bonding molecular orbital can be the result of the destructive interference of the atomic orbitals. The formation of the two molecular orbitals from two 1s orbitals is shown below.

Constructive interaction: The two 1s orbitals are in phase and have the same sign.



Destructive interaction the two 1s Orbitals are out phase

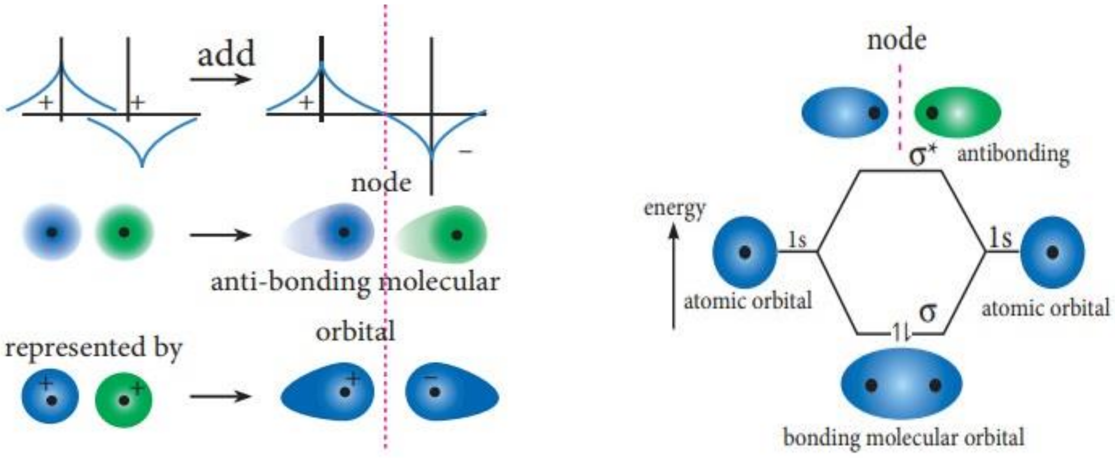


Figure.VI.5. linear combination of atomic orbitals

VI.7.1. Energy level diagram for molecular orbitals

A brief outline of this theory is given below:

- **(i)** In a molecule, electrons are present in new orbitals called molecular orbitals.
- **(ii)** Molecular orbitals are formed by the combination of atomic orbitals of equal energies (in the case of homonuclear molecules) or of comparable energies (in the case of heteronuclear molecules).
- **(iii)** The number of molecular orbitals formed is equal to the number of atomic orbitals undergoing combination.
- **(iv)** Two atomic orbitals can combine to form two molecular orbitals. One of these two molecular orbitals one has a lower energy and the other has a higher energy. The molecular orbital with lower energy is called a bonding molecular orbital and the other with higher energy is called anti bonding molecular orbital.
- **(v)** The shapes of molecular orbitals depend upon the shapes of combining atomic orbitals.
- **(vi)** The bonding molecular orbitals are represented by σ (sigma),π (pi),δ (delta), and the antibonding molecular orbitals are represented by σ*, π*, δ*.
- **(vii)** The molecular orbitals are filled in the increasing order of their energies, starting with orbital of least energy. (Aufbau principle).
- **(viii)** A molecular orbital can accommodate only two electrons and these two electrons must have opposite spins. (Paul's exclusion principle).
- **(ix)** While filling molecular orbitals of equal energy, the pairing of electrons does not take place until all such molecular orbitals are singly filled with electrons having parallel spins. (Hund's rule).

In the case of homonuclear diatomic molecules, the combination of two 1s atomic orbitals of participating atoms gives rise to two new molecular orbitals designated as σ_{1s} and σ^*_{1s}. In the same manner, the 2s and three 2p-orbitals of each atom, i.e., eight atomic orbitals, can give rise to eight new molecular orbitals, viz.,

σ_{2s}, σ^*_{2s}, π_{2px}, π^*_{2px}, π_{2py}, π^*_{2py}, σ_{2pz}, σ^*_{2pz}.

VI.7.2. Atomic Structure and Chemical Bonding

Energy levels of these molecular orbitals have been determined experimentally by spectroscopic studies. The order of increasing energy in the case of the diatomic homonuclear molecules of the first and second periods of the periodic table is as given below:

$\boldsymbol{\sigma_{1s}<\sigma^*_{1s}<\sigma_{2s}<\sigma^*_{2s}<\pi_{2px} = \pi_{2py}<\sigma_{2pz}<\pi^*_{2px}=\pi^*_{2py}<\sigma^*_{2pz}}$

This order of energies of various molecular orbitals is valid for molecules or ions like H_2, H_2^+, He2+, He_2 (hypothetical), Li_2, Be_2 (hypothetical), B_2, C_2, and N_2 molecules. However, experimental evidence for oxygen and heavier diatomic molecules has shown that the above sequence of energy levels of MOs is not correct. In the case of these elements, the order of energy levels of s_{2pz} P_{2px}, and P_{2py} is reversed i.e., $s2p_z$ has lesser energy than P_{2px} or P_{2py}.

VI.7.3. Bond Order

The stability of a molecule or an ion can also be determined from another parameter called bond order. Bond order is defined as one-half the difference between the number of electrons present in the bonding and the antibonding orbitals.

$$\boldsymbol{bond\ order = \frac{N_b - N_a}{2}}$$

Where,

N_b = Total number of electrons present in the bonding molecular orbitals

N_a = Total number of electrons present in the antibonding molecular orbitals and

The resulting molecule or ion will be stable if Nb> Na i.e., if the bond order is positive. The resulting molecule or ion will be unstable if Nb<Na i.e., if the bond order is negative or zero. A bond order of zero value indicates that the molecule doesn't exist.

The stability of a molecule or an ion is directly proportional to bond order. Thus, a molecule with bond order 3 (e.g., N_2) is more stable (i.e., has a higher bond dissociation energy) than a molecule with bond order 2 (e.g., O_2) or 1 (e.g., Li_2).

Nature of bond in terms of bond order: A chemical bond can be single, double, or triple but cannot be a fraction, on the other hand, bond order can be a fraction.

VI.7.4. magnetic properties

Diamagnetic and paramagnetic nature of the molecule: If all the electrons in the molecule are paired then the substance is diamagnetic in nature.

On the other hand, if the molecule has unpaired electron(s) it is paramagnetic in nature.

VI.7.5. Bonding in some Homonuclear di-atomic molecules:

The filling of molecular orbitals is governed by the following principles.

1. **Aufbau principle**
2. **Pauli's exclusion principle and Hund's rule of maximum multiplicity. Now, let us consider some examples of homonuclear diatomic molecules.**

Example 1: Molecular orbital diagram of hydrogen molecule (H_2)

It is formed by the combination of two hydrogen atoms. Each hydrogen atom in the ground state has one electron in 1s orbital. Therefore, in all, there are two electrons in the hydrogen molecule that are present in the lowermost σ_{1s} molecular orbital. According to Pauli's exclusion principle, these two electrons should have opposite spins.

The molecular orbital electronic configuration of the hydrogen molecule is $(\sigma 1s)^2$.

The molecular orbital energy level diagram of the H_2 molecule is given in Fig.

$$\boldsymbol{bond\ order} = \frac{\boldsymbol{N_b - N_a}}{\mathbf{2}} = \frac{\mathbf{2-0}}{\mathbf{2}} = \mathbf{1}$$

Nature of bond: This means that a single covalent bond bonds the two hydrogen atoms in a molecule of hydrogen.

Diamagnetic character: Since no unpaired electron is present in the hydrogen molecule, it is diamagnetic in nature

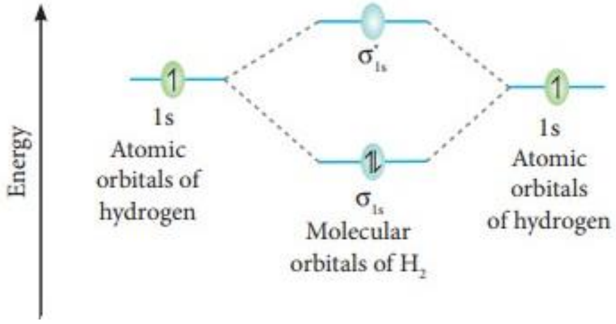


Figure.VI.6. MO diagram for H_2 molecule

Example 2: Molecular orbital diagram of Lithium molecule (Li2)

The electronic configuration of the **Lithium** atom is $1s^2\,2s^1$.

The electronic configuration of the **Lithium** molecule is σ^2_{1s}, σ^{*2}_{1s}, σ^2_{2s}.

The molecular orbital energy level diagram of the Li_2 molecule is given in Fig.

$$\boldsymbol{bond\ order} = \frac{\boldsymbol{N_b - N_a}}{\mathbf{2}} = \frac{\mathbf{2-0}}{\mathbf{2}} = \mathbf{1}$$

Nature of bond: This means that a single covalent bond bonds the two Lithium atoms in a molecule of Lithium.

Diamagnetic character: Since no unpaired electron is present in the Lithium molecule, it is diamagnetic in nature

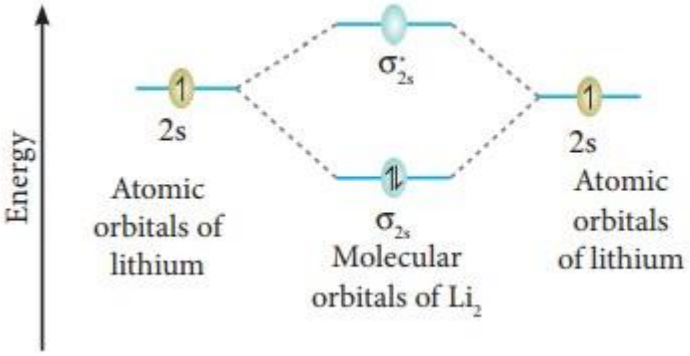


Figure.VI.7. MO diagram for Li2 molecule

Example 3: Molecular orbital diagram of Boron molecule (B2)

The electronic configuration of the **Boron** atom is $1s^2\,2s^2\,2p^1$.

The electronic configuration of the **Boron** molecule is σ^2_{1s}, σ^{*2}_{1s}, σ^2_{2s}, σ^{*2}_{2s}, π^1_{2py}, π^1_{2pz}.

The molecular orbital energy level diagram of the B_2 molecule is given in Fig.

$$\boldsymbol{bond\ order} = \frac{\boldsymbol{N_b - N_a}}{\boldsymbol{2}} = \frac{\boldsymbol{6-4}}{\boldsymbol{2}} = \boldsymbol{1}$$

Nature of bond: This means that a single covalent bond bonds the two **Boron** atoms in a molecule of Lithium.

Diamagnetic character: The molecule has two unpaired electrons hence it is paramagnetic in nature

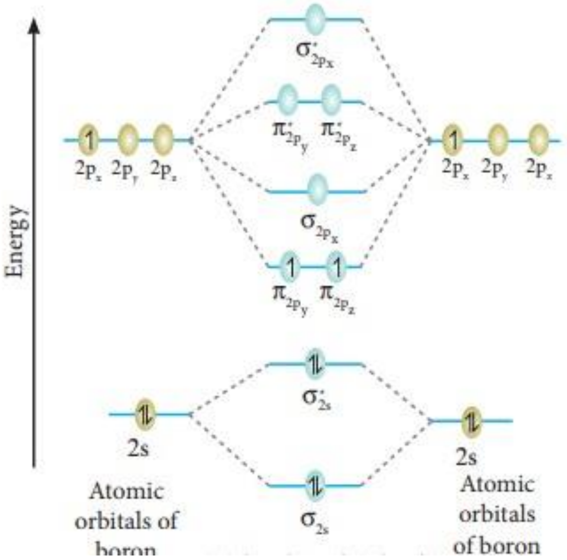


Figure.VI.8. MO diagram for B_2 molecule

Example 4: Molecular orbital diagram of Nitrogen molecule (N2)

The electronic configuration of the **Nitrogen** atom is $1s^2\,2s^2\,2p^3$.

The electronic configuration of the **Nitrogen** molecule is σ^2_{1s}, σ^{*2}_{1s}, σ^2_{2s}, σ^{*2}_{2s}, π^2_{2py}, π^2_{2pz}, σ^2_{2px}.

The molecular orbital energy level diagram of the N_2 molecule is given in Fig.

$$\boldsymbol{bond\ order = \frac{N_b - N_a}{2} = \frac{10-4}{2} = 3}$$

Diamagnetic character: The molecule has no unpaired electrons hence it is diamagnetic in nature**.**

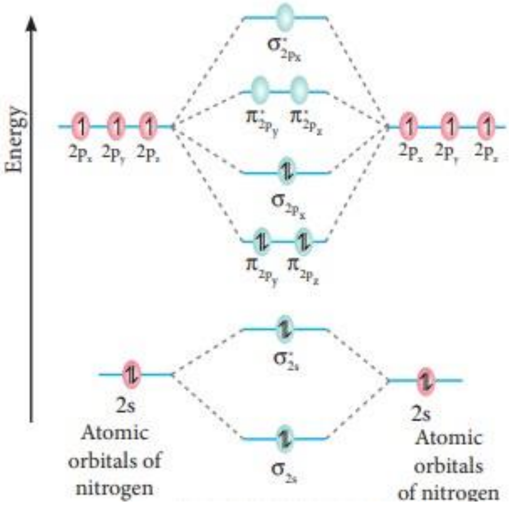


Figure.VI.9. MO diagram for N_2 molecule

Example 5: Molecular orbital diagram of Oxygen molecule (O2)

The electronic configuration of oxygen (Z = 8) in the ground state is $1s^2 2s^2 2p^4$. Each oxygen atom has 8 electrons, hence, in the O_2 molecule, there are 16 electrons. Therefore, the electronic configuration of O_2 is as follows.

$\sigma^2{}_{1s}$, $\sigma^{*2}{}_{1s}$, $\sigma^2{}_{2s}$, $\sigma^{*2}{}_{2s}$, $\sigma^2{}_{2px}$, $\pi^2{}_{2py}$, $\pi^2{}_{2pz}$, $\pi^{1*}{}_{2py}$, $\pi^{1*}{}_{2pz}$.

The molecular orbital energy level diagram of the O_2 molecule is given in Fig.

$$\boldsymbol{bond\ order = \frac{N_b - N_a}{2} = \frac{10-6}{2} = 2}$$

The molecule has two unpaired electrons hence it is paramagnetic**.**

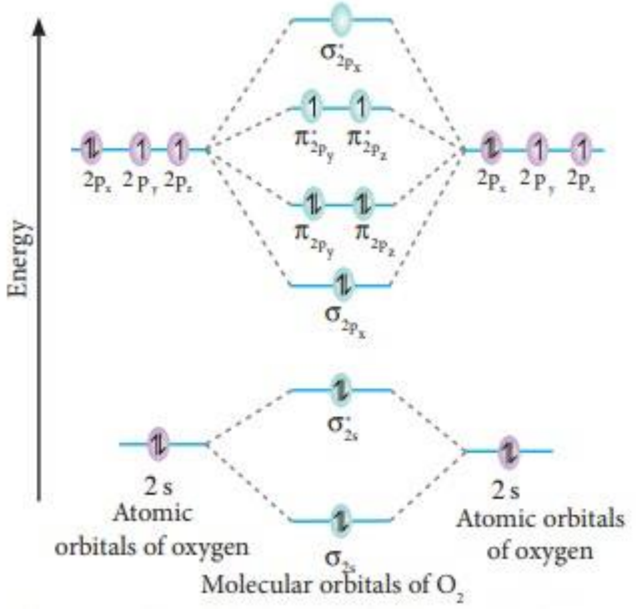


Figure.VI.10. MO diagram for O_2 molecule

VI.7.6. Molecular orbital for Heteronuclear Diatomic Molecules

Diatomic molecules with two non-identical atoms are called heteronuclear diatomic molecules. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi B > \chi A$), the net result is a "skewed" molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in **Figure.VI.11.**

The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B.

The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

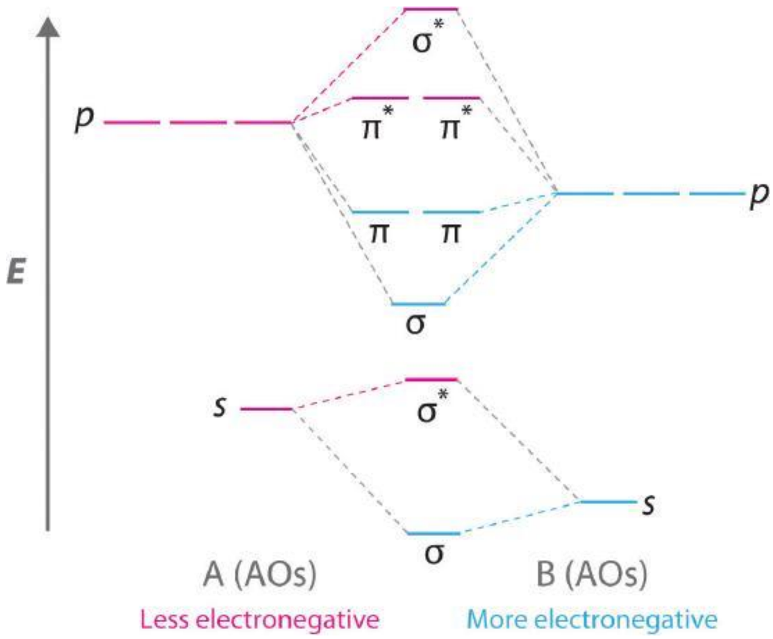


Figure.VI.11. Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic

Molecule AB, where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

examples include CO and NO. Molecular orbital diagrams for these molecules have one more layer of complexity, but they also explain many bond and molecular properties we will encounter later in the course.

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a “skewed” molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in **Figure.VI.11.** The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

Example 1 Molecular orbital diagram of carbon monoxide (CO)

Let’s consider CO as an example. The atomic orbitals in a carbon atom do not have the same energies as those in an oxygen atom, so how do we place these atomic orbitals relative to each other in a MO diagram? We can use their ionization energies to guide us, where the carbon atom's IE1 = 1087 kJ/mol and the oxygen atom's IE1 = 1314 kJ/mol tells us that the oxygen atom's atomic orbitals are lower in energy than those of carbon's.

The electronic configuration of the **carbon** atom is $1s^2 2s^2 2p^2$.

The electronic configuration of the **Oxygen** atom is $1s^2 2s^2 2p^4$.

The electronic configuration of the **CO** molecule is $\sigma^2_{1s}, \sigma^{*2}_{1s}, \sigma^2_{2s}, \sigma^{*2}_{2s}, \pi^2_{2py}, \pi^2_{2pz}, \sigma^2_{2px}$.

The molecular orbital energy level diagram of the **CO** molecule is given in Fig.

$$\boldsymbol{bond\ order = \frac{N_b - N_a}{2} = \frac{10-4}{2} = 3}$$

Diamagnetic character: The molecule has no unpaired electron hence it is diamagnetic in nature**.**

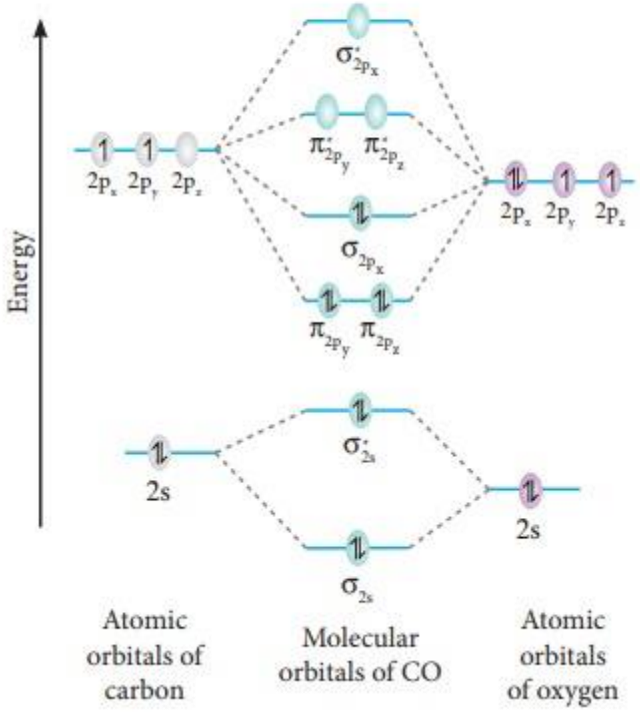


Figure.VI.12. MO diagram for CO molecule

Example Molecular orbital diagram of Nitric oxide (NO)

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory.

The electronic configuration of the **Nitrogen** atom is $1s^2 2s^2 2p^3$.

The electronic configuration of the **Oxygen** atom is $1s^2 2s^2 2p^4$.

The electronic configuration of the **NO** molecule is $\sigma^2_{1s}, \sigma^{*2}_{1s}, \sigma^2_{2s}, \sigma^{*2}_{2s}, \pi^2_{2py}, \pi^2_{2pz}, \sigma^2_{2px}; \pi^{*1}_{2py}$. The molecular orbital energy level diagram of the **NO** molecule is given in Fig.

$$\boldsymbol{bond\ order = \frac{N_b - N_a}{2} = \frac{10-5}{2} = 2.5}$$

Diamagnetic character: The molecule has one unpaired electron hence it is paramagnetic in nature**.**

The predicted bond order for NO is therefore (8-3) ÷ 2 = 2 1/2. Experimental data, showing an N–O bond length of 115 pm and N–O bond energy of 631 kJ/mol, are consistent with this description. These values lie between those of the N2 and O2 molecules, which have triple and double bonds, respectively. As we stated earlier, molecular orbital theory can therefore explain the bonding in molecules with an odd number of electrons, such as NO, whereas Lewis electron structures cannot.

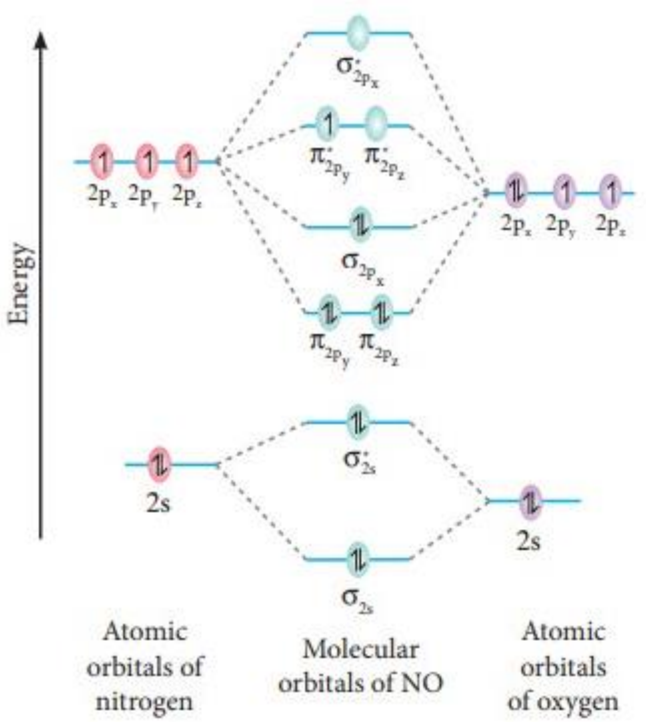


Figure.VI.13. MO diagram for NO molecule

VI.8. Theory of hybridization of atomic orbitals

VI.8.1. Hybridisation

Bonding in simple molecules such as hydrogen and fluorine can easily be explained based on the overlap of the respective atomic orbitals of the combining atoms. However, the observed properties of polyatomic molecules such as methane, ammonia, beryllium chloride, etc... cannot be explained based on a simple overlap of atomic orbitals. For example, it was experimentally proved that methane has a tetrahedral structure and the four C-H bonds are equivalent. This fact cannot be explained based on the overlap of atomic orbitals of hydrogen (1s) and the atomic orbitals of carbon with different energies ($2s^2\ 2p_x^2\ 2p_y\ 2p_z$).

To explain these observed facts, Linus Pauling (1931) proposed that the valence atomic orbitals in the molecules are different from those in isolated atoms and he introduced the concept of hybridization. Hybridization is the concept of intermixing the orbitals of an atom having nearly the same energy to give exactly equivalent orbitals with the same energy, identical shapes, and symmetrical orientations in space.

The new equivalent orbitals formed are known as the hybrid orbitals or hybridized orbitals. Hybrid orbitals have properties entirely different from the properties of the original orbitals from which they have been obtained.

The intermixing of two or more pure atomic orbitals of an atom with almost the same energy to give the same number of identical and degenerate new orbital types is known as hybridization.

The new orbitals formed are known as hybrid orbitals.

During hybridization, the atomic orbital with different characteristics is mixed with each other.

In an AXn molecule, hybridization generally concerns the O.A. of the central atom A.

Salient Features Regarding Hybridization

1. Orbitals involved in hybridization should have nearly the same energy.
2. The orbitals of one and the same atom participate in hybridization.
3. The number of hybrid orbitals formed is equal to the number of hybridizing orbitals.
4. The hybrid orbitals are all equivalent in shape and energy.
5. A hybrid orbital that is taking part in bond formation must contain one electron in it.
6. Due to the electronic repulsions between the hybrid orbitals, they tend to remain at the maximum distance apart.
7. The head-on overlap of atomic orbitals gives sigma (σ) bonds.
8. The sidewise or lateral overlap of atomic orbitals gives pi (π) bonds.

VI.8.2. Types of Hybridization

The hybridization generally relates to the O.A. s, p; according to the number and the nature of the O.A. which are hybridized, several types of hybridizations are distinguished

Sp, Sp^2, Sp^3, Sp^3d, sp^3d^2, sp^3d^3

VI.8.2.1. sp Hybridisation:

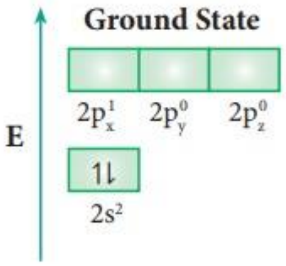
intermixing of one “s” and one “p” orbital of almost equal to give two identical and degenerate hybrid orbital is called “sp” hybridization.

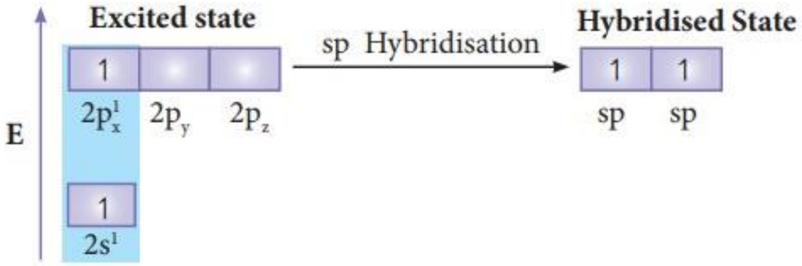
These sp hybrid orbital are arranged linearly at by making of 180° angle.

They possess 50% “s” and 50% “p” character.

Example: $BeCl_2$

Let us consider the bond formation in beryllium chloride. The valence shell electronic configuration of beryllium in the ground state is shown in the figure.





In $BeCl_2$ both the Be-Cl bonds are equivalent and it was observed that the molecule is linear. VB theory explains this observed behavior by sp hybridization. One of the paired electrons in the 2s orbital gets excited to 2p orbital and the electronic configuration at the excited state is shown.

Now, the 2s and 2p orbitals hybridize and produce two equivalent sp hybridized orbitals which have 50 % s-character and 50 % p-character. These sp hybridized orbitals are oriented in opposite directions as shown in the figure.

Overlap with orbital of chlorine

Each of the sp hybridized orbitals linearly overlaps with pz orbital of the chlorine to form a covalent bond between Be and Cl as shown in the Figure.

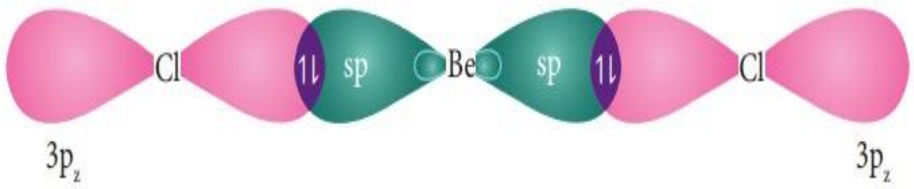


Figure.VI.14. sp hybridization: $BeCl_2$

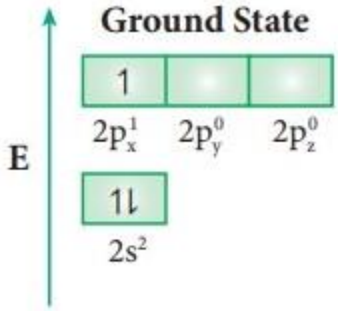
VI.8.2.2. sp^2 Hybridisation:

The intermixing of one “s” and two “p” orbitals of almost equal energy to give three identical and degenerate hybrid orbitals is known as “sp^2” hybridization.

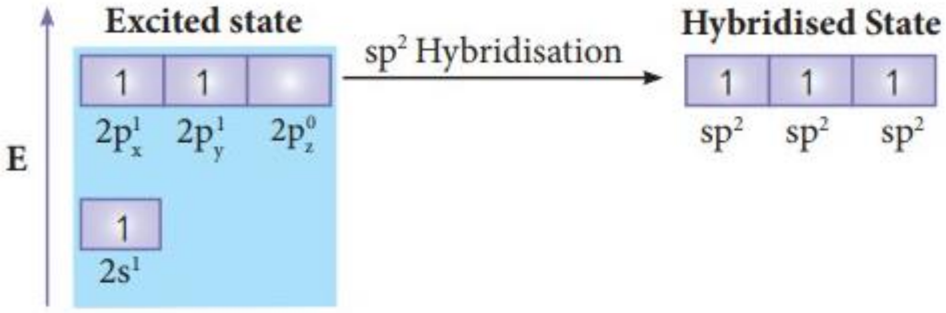
The three sp2 hybrid orbitals are oriented in trigonal planar symmetry at an angle of 120° to each other. The sp2 hybrid orbital has 33.3% “s” character and 66.6% “p” character.

Example of molecule BF_3

Consider the boron trifluoride molecule. The valence shell electronic configuration of the boron atom is $[He]2s^2 2p^1$.



In the ground state boron has only one unpaired electron in the valence shell. In order to form three covalent bonds with fluorine atoms, three unpaired electrons are required. To achieve this, one of the paired electrons in the 2s orbital is promoted to the 2py orbital in the excited state. In boron, the s orbital and two p orbitals (p_x and p_y) in the valence shell hybridise, to generate three equivalent sp^2 orbitals as shown in the Figure. These three orbitals lie in the same xy plane and the angle between any two orbitals is equal to 120º



Overlap with 2pz orbitals of fluorine:

The three sp^2 hybridised orbitals of boron now overlap with the 2pz orbitals of fluorine (3 atoms). This overlap takes place along the axis as shown below.

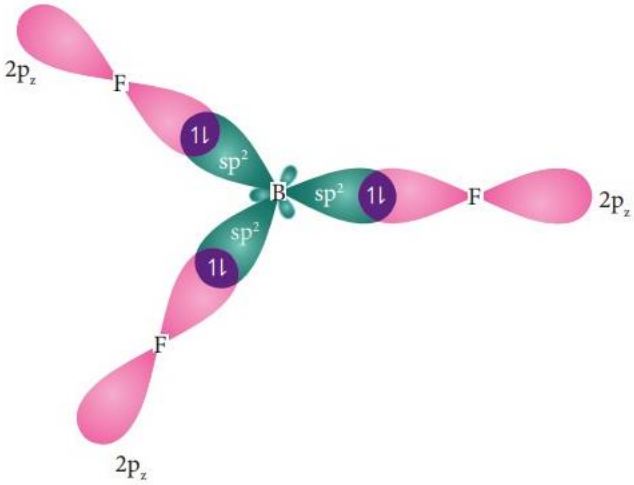


Figure.VI.15. sp^2 hybridisation of molecule BF$_3$

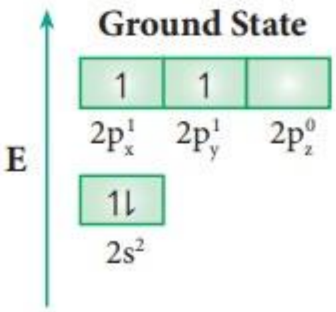
VI.8.2.3. sp^3 Hybridisation

in sp^3 hybridization, one « s » and three « p » p orbitals of almost equal energy intermix to give four identical and degenerate hybrid orbitals.

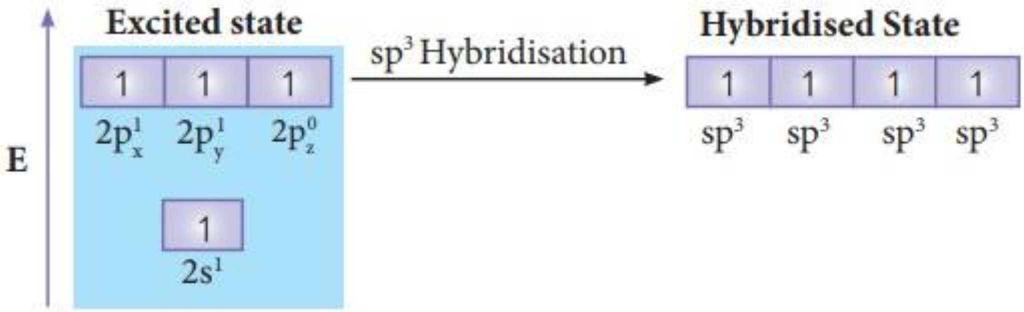
These four sp^3 hybrid orbitals are oriented in tetrahedral symmetry with 109°angle with each other. The sp^3 hybrid orbitals have 25% “s” and 75% “p” character.

Example of the molecule CH$_4$:

sp^3 hybridisation can be explained by considering methane as an example. In a methane molecule, the central carbon atom is bound to four hydrogen atoms. The ground state valence shell electronic configuration of carbon is [He]2s^2 2p$_x^1$ 2p$_y^1$ 2p$_z^0$.



In order to form four covalent bonds with the four hydrogen atoms, one of the paired electrons in the 2s orbital of carbon is promoted to its 2p$_z$ orbital in the excited state. The one 2s orbital and the three 2p orbitals of carbon mix to give four equivalent sp^3 hybridised orbitals. The angle between any two sp^3 hybridised orbitals is 109°,28.



Overlap with 1s orbitals of hydrogen:

The 1s orbitals of the four hydrogen atoms overlap linearly with the four sp3 hybridised orbitals of carbon to form four C-H σ-bonds in the methane molecule, as shown below.

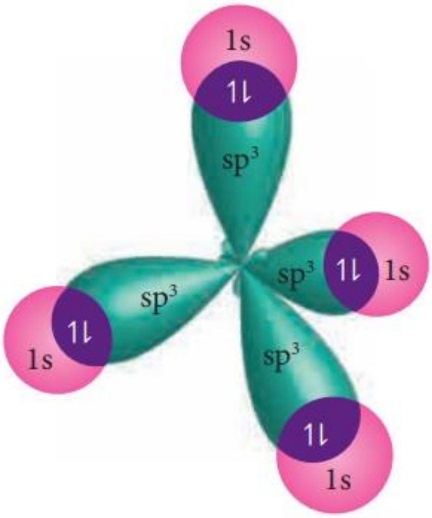


Figure.VI.16. sp^3 Hybridisation CH_4

VI.8.2.4. sp^3d Hybridisation:

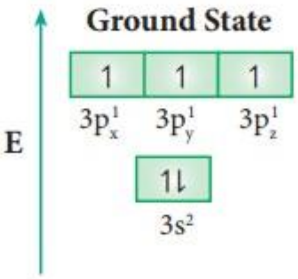
In sp^3d hybridization, one ‘s’, three ‘p’, and one ‘d’ orbital’s of almost equal energy intermix to give five identical and degenerate hybrid orbitals, which are arranged in trigonal bipyramidal symmetry.

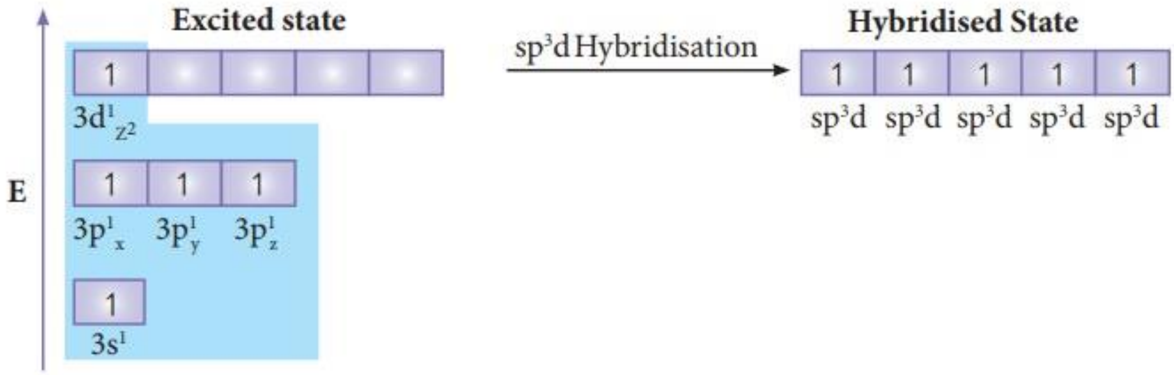
Among them, three are arranged in a trigonal plane and the remaining two orbitals are present above and below the trigonal at right angles.

The sp^3d hybrid orbitals have 20% ‘s’, 60% ‘p’, and 20% d’characters.

Example

In molecules such as PCl_5, the central atom of phosphorus is covalently bound to five chlorine atoms. Here the atomic orbitals of phosphorous undergo sp^3d hybridisation which involves its one 3s orbital, three 3p orbitals, and one vacant 3d orbital (d_{z2}). The ground state electronic configuration of phosphorous is $[Ne]3s^2\ 3p^1{}_x3p_y{}^13p_z{}^1$ as shown below.





One of the paired electrons in the 3s orbital of phosphorous is promoted to one of its vacant 3d orbital ($d_z{}^2$) in the excite state. One 3s orbital, three 3p orbitals and one $3d_z{}^2$ orbital of phosphorus atom mixes to give five equivalent sp3d hybridised orbitals. The orbital geometry of sp$^3{}_d$ hybridised orbitals is trigonal bi-pyramidal.

Overlap with $3p_z$ orbitals of chlorine:

The $3p_z$ orbitals of the five chlorine atoms linearly overlap along the axis with the five sp^{3}d hybridised orbitals of phosphorous to form the five P-Cl σ-bonds, as shown below.

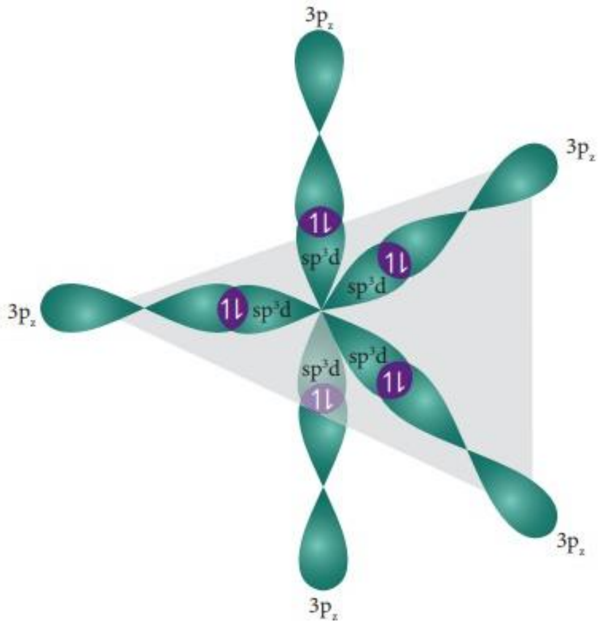


Figure.VI.17. sp^{3}d Hybridisation PCl_5

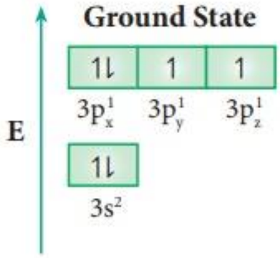
VI.8.2.5. sp^3d^2 Hybridisation:

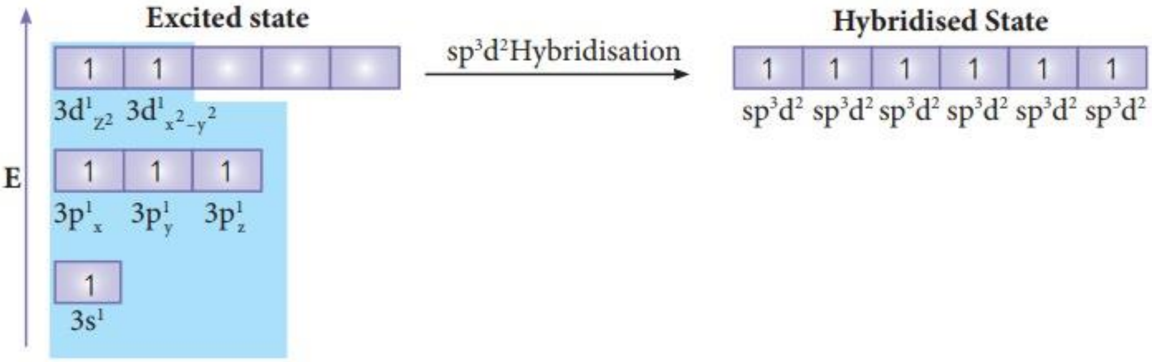
Intermixing of one ‘s’, three ‘p’, and two ‘d’ orbitals of almost the same energy by giving six identical and degenerate hybrid orbitals is called sp^3d^2 hybridisation.

These six sp3d2 orbitals are arranged in octahedral symmetry by making 90° angles to each other. This arrangement can be visualized as four orbitals arranged in a square plane, and the remaining two are oriented above and below this plane perpendicularly.

Example

In sulfur hexafluoride (SF_6) the central atom sulfur extends its octet to undergo sp^3d^2 hybridisation to generate six sp^3d^2 hybridised orbitals which accounts for six equivalent S-F bonds. The ground state electronic configuration of sulfur is[Ne]$3s^2$ $3p_x^1$ $3p_y^1$ $3p_z^1$.





One electron each from the 3s orbital and 3p orbital of sulfur is promoted to its two vacant 3d orbitals (d_{z2} and d_{x2-y2}) in the excited state. A total of six valence orbitals from sulfur (one 3s orbital, three 3p orbitals, and two 3d orbitals) mixes to give six equivalent sp^3d^2 hybridized orbitals. The orbital geometry is octahedral as shown in the figure.

Overlap with 2pz orbitals of fluorine:

The six sp^3d^2 hybridized orbitals of sulfur overlap linearly with the $2p_z$ orbitals of six fluorine atoms to form the six S-F bonds in the sulfur hexafluoride molecule.

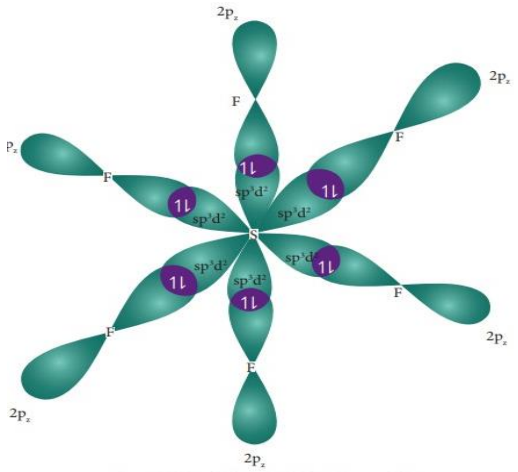


Figure.VI.18. sp^3d^2 Hybridisation SF_6

VI.8.2.6. sp^3d^3 Hybridisation:

in sp^3d^3 hybridisation, one ‘s’, three ‘p’, and three ‘d’ orbitals of almost the same energy intermix to give seven sp^3d^3 hybrid orbitals, which are oriented in pentagonal bipyramidal symmetry.

five among the sp^3d^3 orbitals are arranged in a pentagonal plane by making 72° of angles. the remaining are arranged perpendicularly above and below this pentagonal plane.

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