Atoms, Atomic Theory &Periodicity

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Objectives

At the end of this, we will be able to-

- **Know about the structure of atom and the elements of periodic table**
- **Explain all the atomic models or postulations along with the related principles**
- **Apply the knowledge of electronic configurations and periodicity to ascertain the properties of a specific element.**

Contents

- **Atomic particles**
- **Atomic number, mass number, isotopes**
- **Atomic models/postulations**
- **Electromagnetic radiation**
- **Photoelectric effect**
- **Atomic orbitals**
- **Electronic configurations of atoms Aufbau principles, Pauli exclusion principle, Hund's rule**
- **Periodic table**
- **Periodic properties of elements**

Atoms & Laws of Chemical Combination

Matter is made up of atoms, and therefore an understanding of the structure of atom is very important.

John Dalton revived the concept of atom in the beginning of nineteenth century in terms of his atomic theory which successfully explained the laws of chemical combination.

Law of Conservation of Mass

French chemist, Antoine Lavoisier in 1789, studied this law. This law states that "In all physical and chemical changes, the total mass of the reactants is equal to that of the products" or "Mass can neither be created nor destroyed."

Law of Constant Composition or Definite Proportions

French chemist, J.L. Proust in 1799, discovered this law. It states that "A chemical compound is always found to be made up of the same elements combined together in the same fixed proportion by mass".

For example, a sample of pure water from various sources or any country is always made up of only hydrogen and oxygen. These elements are always in the same fixed ratio of 1:8 by mass.

Law of Multiple Proportions

When two elements combine to form two or more chemical compounds, then the masses of one of the elements which combined with a fixed mass of the other, bear a simple ratio to one another. For eg, Carbon combines with oxygen to form two compounds namely carbon dioxide and carbon monoxide.

Law of Reciprocal Proportion

This law was put forward by Richter in 1792. It states that "The ratio of masses of 2 elements, A and B which combines separately with a fixed mass of the third element C is either the same or some multiple of the ratio of the masses in which A and B combine directly with each other".

Gay Lussac's Law of Gaseous Volume

When gases react together, they always do so in volumes which bear a simple ratio to one another and to the volume of the products, if these are also gases. This holds true provided all measurements of volumes are done under similar conditions of temperature and pressure.

Fundamental Particles of Atom

In 1897 J.J. Thomson discovered electron as a constituent of atom. He determined that an electron had a negative charge and had very little mass as compared to that of the atom.

Since an atom was found to be electrically neutral it was inferred that some source of positive charge must be present in the atom. This soon led to the experimental discovery of the proton, which is a positively charged subatomic particle. Proton was found approximately 1840 times heavier than an electron.

Further experiments revealed that the atomic masses were more than that expected from the presence of just protons and electrons in the atom. For example, the mass of helium atom was expected to be double that of hydrogen atom but was actually found to be almost four times the mass of hydrogen atom. This suggested the presence of neutral particles with mass comparable to that of protons in the atom. Sir James Chadwick in 1932 discovered this neutral particle and called it neutron subsequently.

Fundamental particles of atom and their characteristics

Particle	Symbol	Mass/ kg	Actual Charge / C	Relative charge
Electron	e	$9.109\ 389 \times 10^{-31}$	$-1.602\ 177 \times 10^{-19}$	-1
Proton	p	$1.672\ 623 \times 10^{-27}$	$1.602\ 177 \times 10^{-19}$	$+1$
Neutron	n	$1.674\ 928 \times 10^{-27}$	0	0

Atomic Number, Mass Number, Isotopes & Isobars

All atoms can be identified by the number of protons and neutrons they contain.

The atomic number (Z) is the number of protons in the nucleus of each atom of an element. In, a neutral atom the number of protons is equal to the number of electrons, so the atomic number also indicates the number of electrons present in the atom. The chemical identity of an atom can be determined solely from its atomic number.

$$^A_Z X$$

Atomic number and Mass number of an atom of an element (X)

The mass number (A) is the total number of neutrons and, protons present in the nucleus of an atom of an element. Except for the most common form of hydrogen, which has one proton and no neutrons, all atomic nuclei contains both protons and neutrons. The number of neutrons in an atom is equal to the difference between the mass number and the atomic number, or (A - Z).

Note that the atomic number, number of neutrons, and mass number all must be positive integers (whole numbers).

Isotopes of hydrogen

$$^1_1 H \qquad ^2_1 H \qquad ^3_1 H$$

hydrogen   deuterium   tritium
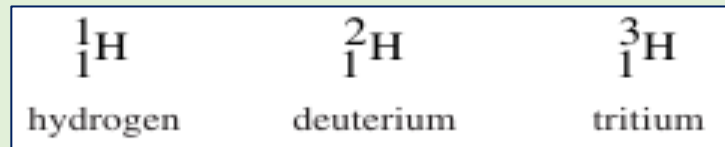
Isotopes of Uranium

$$^{235}_{92} U \qquad ^{238}_{92} U$$
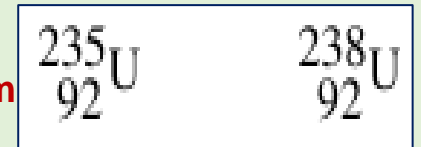
Atoms of a given element do not all have the same mass. Most elements have two or more **isotopes**, atoms that have the same atomic number but different mass numbers. For example, there are three isotopes of hydrogen. One, simply known as hydrogen, has one proton and no neutrons. The deuterium isotope contains one proton and one neutron, and tritium has one proton and two neutrons.

Isobars are atoms of different chemical elements with equal atomic mass values, whereas isotones are atoms of different chemical elements with an equal number of neutrons in the atomic nucleus.

$$^{40}_{16}S, \ ^{40}_{17}Cl, \ ^{40}_{18}Ar, \ ^{40}_{19}K, \text{ and } ^{40}_{20}Ca.$$ Isobars

$$^{36}_{16}S, \ ^{37}_{17}Cl, \ ^{38}_{18}Ar, \ ^{39}_{19}K, \text{ and } ^{40}_{20}Ca$$ Isotones

Atomic Structure- Earlier Models
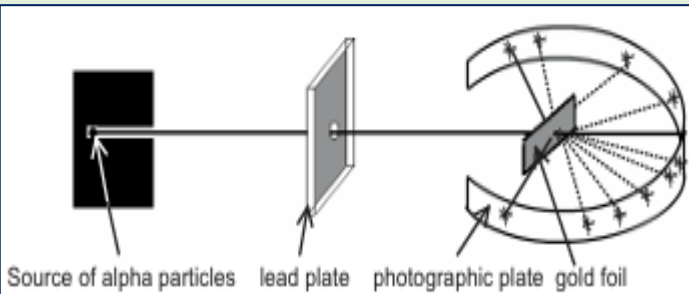
Thomson's Model

On the basis of his experiments on discharge tubes, Thomson proposed that atoms could be considered as a large positively charged body with a number of small negatively charged electrons scattered throughout it. This model was called as plum pudding model of the atom or watermelon model. The electrons represent the plums in the pudding made of positive charge.
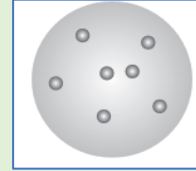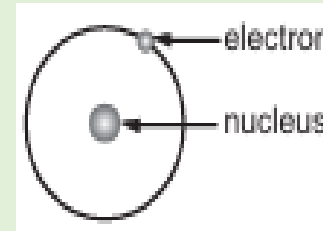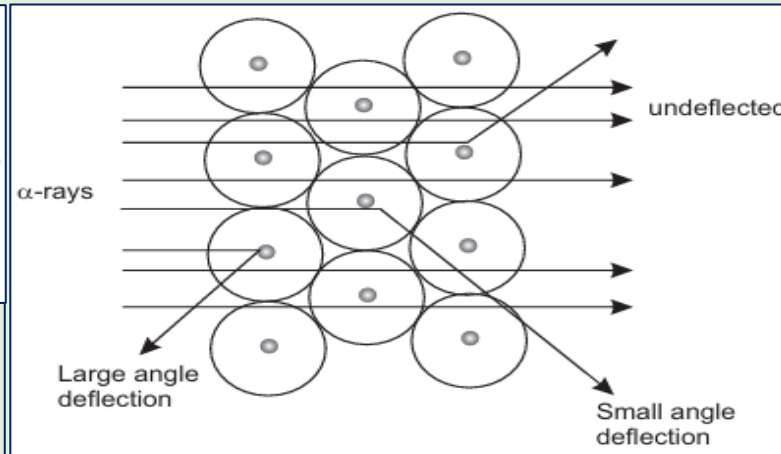

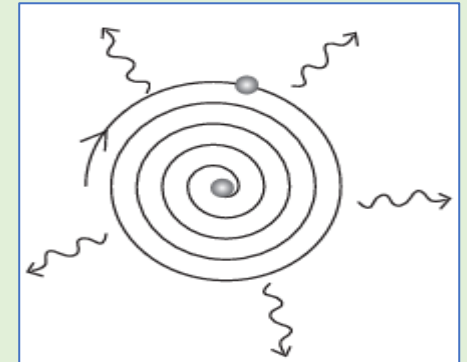Representation of Thomson's plum-pudding model

Rutherford's Model

Ernest Rutherford performed an experiment called 'Gold Foil Experiment' or 'á ray scattering experiment' to test the structure of an atom as proposed by Thomson.

Source of alpha particles   lead plate   photographic plate   gold foil
Schematic representation of Rutherford's α-ray scattering experiment

α-rays
undeflected
Large angle deflection
Small angle deflection

electron
nucleus
Representation of Rutherford's model

Failure of Rutherford's model

- The atom contained some dense and positively charged region located at the center, called as nucleus.
- The positive charge of the atom and most of its mass was contained in the nucleus.
- The rest of the atom would be empty space which contained the much smaller and negatively charged electrons.

Rutherford's model failed to explain the stability of the atom.
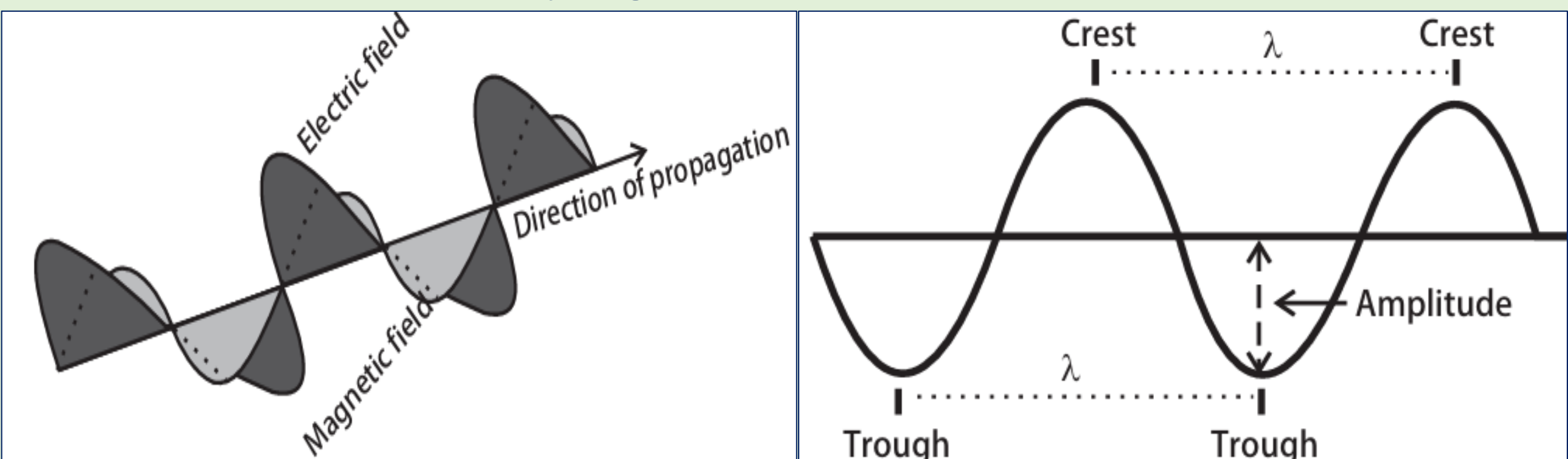
Electromagnetic Radiations

Electromagnetic radiation is a kind of energy, which is transmitted through space in the form of electric and magnetic fields. These do not require any medium to propagate.

Visible light, radiant heat, radio waves, X-rays and gamma radiation are some of the examples of electromagnetic radiations.

According to the Maxwell's theory, an electromagnetic radiation can be visualized as oscillating electric and magnetic fields.

These travel as waves in the planes perpendicular to each other and also to the direction of propagation.

These radiations travel with the velocity of light (3.0×108 m s^{-1}).

Electromagnetic Radiations

Amplitude: This refers to the maximum height to which the wave oscillates. It equals the height of the crests or depth of the troughs.

Wavelength: It is the linear distance between two consecutive wave-crests or wave- troughs as shown. It is represented by a Greek letter lambda (λ) and is expressed in terms of m, cm, nm or Angstrom (1Å = 10^{-10} m).

Frequency: It is defined as the number of wave crests or wave troughs that pass through a given point per second. It is represented by a Greek letter ν and is expressed in terms of s^{-1}. It is also called as Hz (Hertz).

Wave number: It equals the number of waves per unit length. It is denoted as $\bar{\nu}$ and is equal to the reciprocal of the wavelength. The SI unit of $\bar{\nu}$ is m^{-1}. It is also expressed as cm^{-1}. $\bar{\nu} = \dfrac{1}{\lambda}$

Velocity: It is defined as the linear distance travelled by the wave in one second. The velocity in meters per second can be obtained by multiplying frequency in Hertz (s^{-1}) with wavelength in meters. c = ν λ or $\nu = \dfrac{c}{\lambda}$ **The velocity of a radiation depends on the medium. In vacuum the velocity is equal to 3.00×10^8 m s^{-1}.**

Although the wave model of light explains many aspects of its behavior, this model cannot explain several phenomena

Blackbody radiation: The emission of light from hot objects (They appear black before heating.)
Photoelectric effect: The emission of electrons from metal surfaces on which light shines.
Emission spectra: The emission of light from electronically excited gas atoms.

Max Planck (1858–1947) explained it by assuming that energy comes in discrete "chunks" of some minimum size called quanta (the plural of quantum meaning "fixed amount"). Thus, The electromagnetic radiations also show the characteristics of particles, called as quanta. These quanta are actually bundles of energy. A quantum of visible light is called a photon. The energy of the quantum (or photon) is proportional to the frequency of the radiation. The two are related as E = hν, h is Planck's constant, 6.626×10^{-34} Js^{-1}. The energy of the quantum can also be related to the wavelength or wave number as

$$E = h\dfrac{c}{\lambda} \text{ or } E = hc\bar{\nu}$$

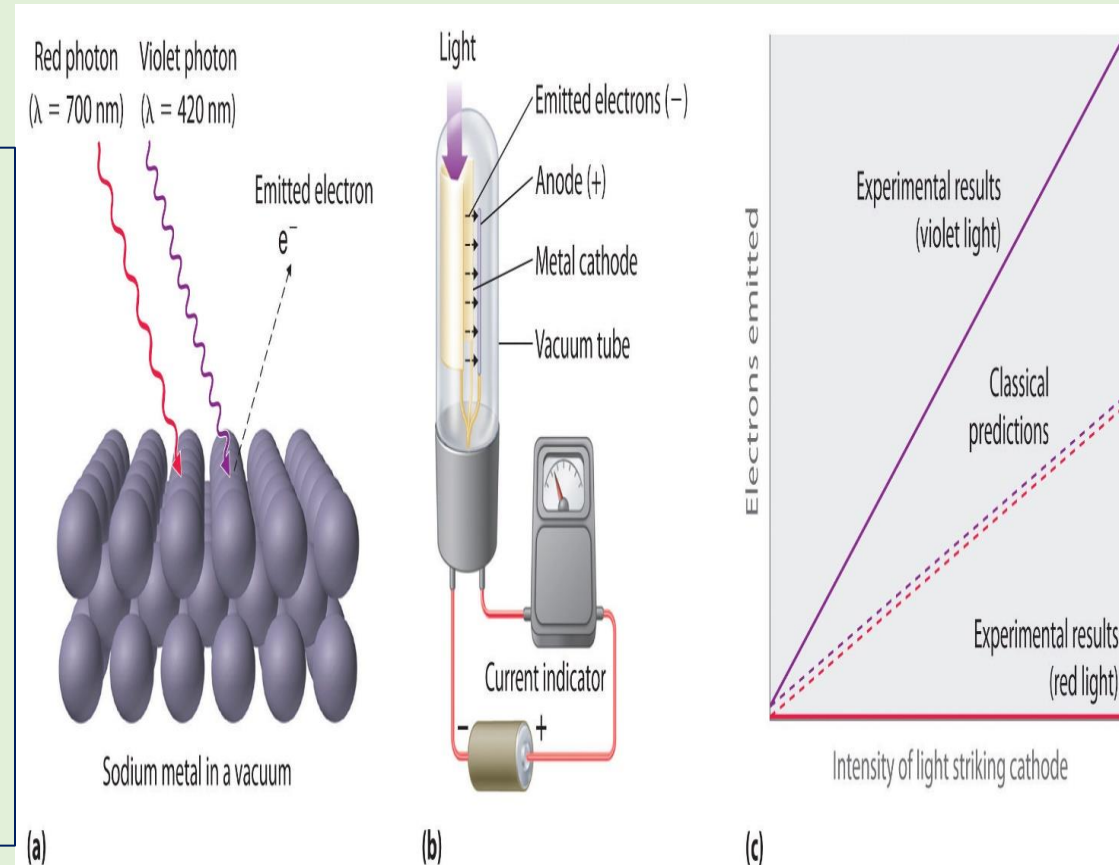# Electromagnetic Radiations-Photoelectric Effect and Photons

Photoelectric effect

Light shining on a clean metal surface causes the surface to emit electrons. Each metal has a different energy at which it ejects electrons. At lower energy, electrons are not emitted. A minimum frequency of light is required for the emission of electrons. Above the threshold frequency, the number of electrons emitted was found to be proportional to the intensity of the light, and their kinetic energy was proportional to the frequency. This phenomenon was called the photoelectric effect.

Light with a frequency of 4.60×10^{14} s^{-1} or greater causes cesium metal to emit electrons, but light of lower frequency has no effect.

Einstein (1879–1955) used Planck's theory to explain the photoelectric effect.

Radiant energy that arrives at the metal surface(photons), each possessing a particular energy E . Einstein postulated that each metal has a particular electrostatic attraction for its electrons that must be overcome before an electron can be emitted from its surface ($E_o = h\nu_o$). If photons of light with energy less than E_o strike a metal surface, no single photon has enough energy to eject an electron, so no electrons are emitted regardless of the intensity of the light. If a photon with energy greater than E_o strikes the metal, then part of its energy is used to overcome the forces that hold the electron to the metal surface, and the excess energy appears as the kinetic energy of the ejected electron. Kinetic energy of ejected electron = $E - E_o = h\nu - h\nu_o = h(\nu - \nu_o)$. When a metal is struck by light with energy above the threshold energy E_o, the number of emitted electrons is proportional to the intensity of the light beam, which corresponds to the number of photons per square centimeter, but the kinetic energy of the emitted electrons is proportional to the frequency of the light.

(a) Sodium metal in a vacuum

Red photon (λ = 700 nm) Violet photon (λ = 420 nm)
Emitted electron e⁻

(b) Light — Emitted electrons (−), Anode (+), Metal cathode, Vacuum tube, Current indicator

(c) Electrons emitted vs Intensity of light striking cathode — Experimental results (violet light), Classical predictions, Experimental results (red light)

Electromagnetic Spectrum

Depending on their characteristics (wavelength , frequency and wave number) electromagnetic radiations are of many types and constitute what is called as an electromagnetic spectrum.
The part of the spectrum that we can see is called visible spectrum and is a very small part of the overall spectrum.
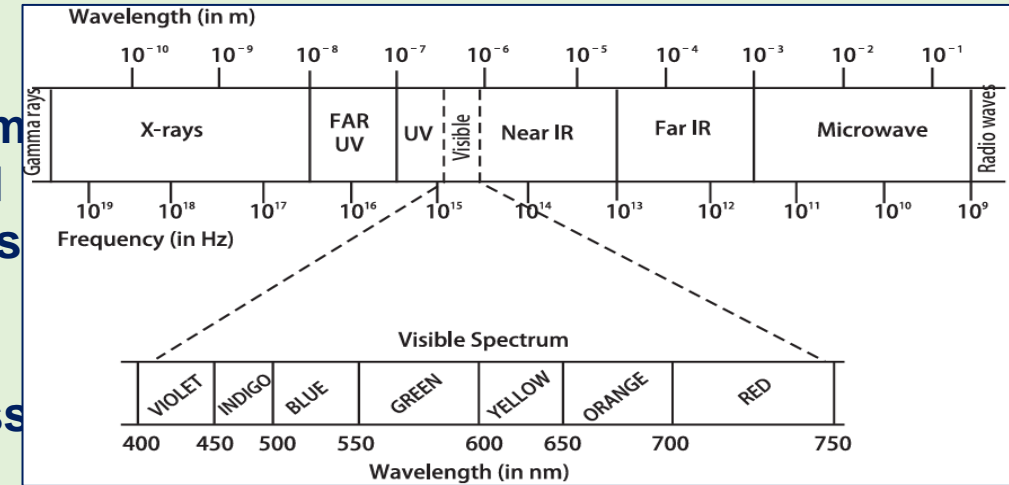
Line Spectrum

If sunlight is passed through a prism, we get a range of colors from violet to red in the form of a spectrum (like rainbow). This is called a **continuous spectrum** because the wavelengths of the light varies continuously that is without any break. Compounds of sodium impart a bright yellow color to the flame, copper gives a green flame while strontium gives a crimson red colored flame. If we pass such a light through a prism it gets separated into a set of lines. This is called as a line spectrum. **A spectrum containing radiation of only specific wavelengths.**
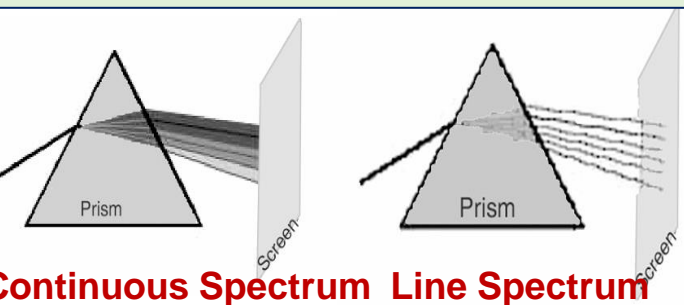
Continuous Spectrum Line Spectrum

When an electric discharge is passed through a discharge tube containing hydrogen gas at low pressure, it emits some light. When this light is passed through a prism it splits up into a set of five lines. This spectrum is called the line spectrum of hydrogen. On careful analysis of the hydrogen spectrum, it was found to consist of a few sets of lines in the ultraviolet, visible and infrared regions. These sets of lines were observed by different scientists. These spectral emission lines could be expressed in the form of a general formula as:

$$\bar{v} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ cm}^{-1} \; ; \; R_H = 109677 \text{ cm}^{-1}$$

n_1 and n_2 are positive integers (n1 < n2) and R_H is called Rydberg's constant

Line Spectrum of Hydrogen Atom

The different sets of lines observed in the hydrogen atom spectrum named after their discoverers and the values of n_1 and n_2 are given as follows-

Series	n_1	n_2	Region of spectrum
Lyman	1	2,3,4…..	Ultraviolet
Balmer	2	3,4,5…..	Visible
Paschen	3	4,5,6…..	Infrared
Bracket	4	5,6,7…..	Infrared
Pfund	5	6,7,8…..	Infrared

The line spectrum of hydrogen atom was explained by Bohr's model.

Bohr's Model

In 1913, Niels Bohr (1885-1962) proposed another model of the atom, where electrons move around the nucleus in circular paths. Bohr's atomic model is built upon a set of postulates,

- The electrons move in a definite circular paths (orbits) around the nucleus and postulated that as long as the electron is in a given orbit its energy remains fixed. These orbits were therefore referred to as stationary orbits or stationary states or non radiating orbits.

Bohr's Model

- The electron can change its orbit by absorbing or releasing energy. An electron at a lower (initial) state of energy, E_i can go to a higher state of energy, E_f by absorbing a single photon of energy as given by $E = h\nu = E_f - E_i$. When electron changes its orbit from a higher (initial) state of energy , E_i to a lower state of energy , E_f , a single photon Of energy $h\nu$ is released.
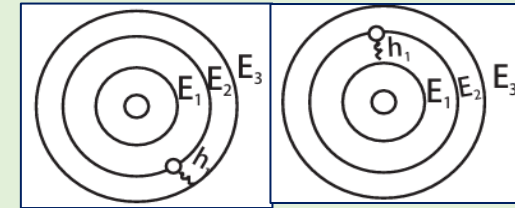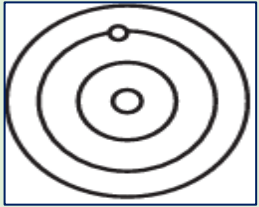
Absorption and emission of photon causes the electron to change its energy level.

- The angular momentum of an electron of mass m_e moving in a circular orbit of radius r and velocity v is an integral multiple of $h/2\pi$.

$$m_e vr = \frac{nh}{2\pi}$$

n is a positive integer, principal quantum number.

Bohr obtained the following expressions for the energy of an electron in stationary states of hydrogen atom by using his postulates :

$$E_n = -R_H\left(\frac{1}{n^2}\right)$$

$$R_H = \frac{mz^2e^4}{8h^2\varepsilon_0^2}$$

m = mass of the electron, z = nuclear charge, e = electronic charge, h = Planck's constant, ε0 = permittivity of the medium

Bohr could correlate RH to other properties as

The negative sign in the energy expression means that there is an attractive interaction between the nucleus and the electron. Certain amount of energy (ionization energy) would be required to remove the electron from the influence of the nucleus in the atom. Energies of the Bohr orbits are inversely proportional to the square of the quantum number n. As n increases the value of the energy increases (becomes lesser negative or more positive). Thus, farther from the nucleus the energy of the orbit goes on increasing.

# Explanation of Line Spectrum of Hydrogen Atom

As per the second postulate mentioned above, the energy emitted in the transition of a single electron from an initial stationary state of energy Ei to a final stationary state of energy Ef is given as hv = Ei − Ef . Substituting the expressions for energy from eq.

$$E_n = -R_H\left(\frac{1}{n^2}\right),$$

we can get the formula given in eq.

$$\bar{v} = \frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ cm}^{-1} \; ; \; R_H = 109677 \text{ cm}^{-1}.$$

Thus, Bohr's model provides an explanation for the observed line spectrum of hydrogen as summarized as-

Series	n₁	n₂	Region of spectrum
Lyman	1	2,3,4.....	Ultraviolet
Balmer	2	3,4,5.....	Visible
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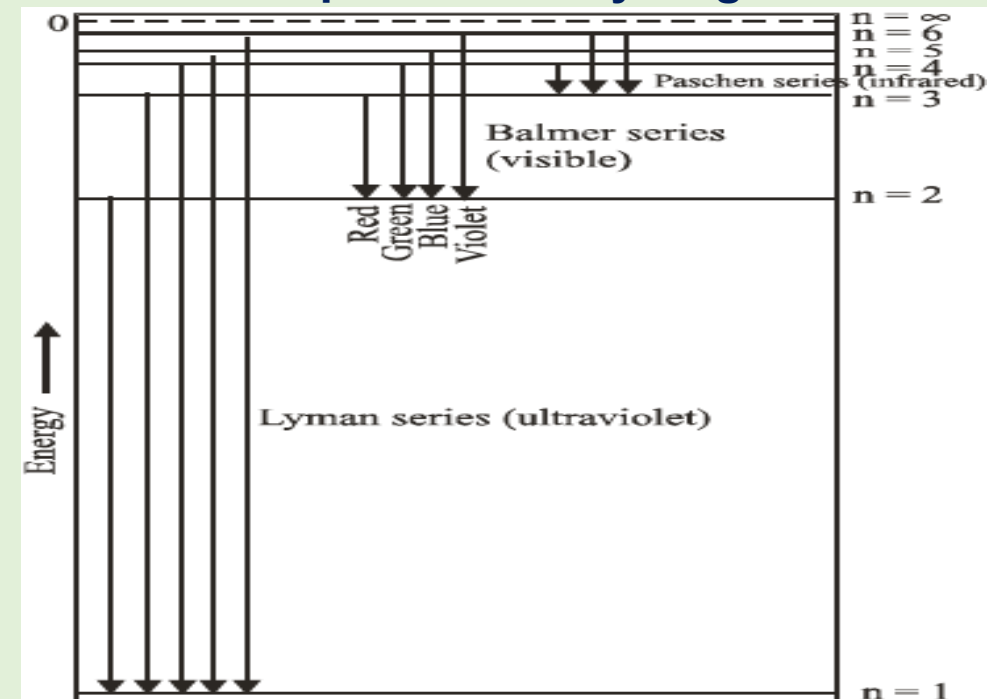
Wave – Particle Duality

- Properties of light such as diffraction and interference can be explained on of its wave nature.
- Properties like photoelectric effect and scattering of light can be explained only on of particle nature of light.

Light has a dual nature possessing the properties of both a wave and a particle, i.e., light could under some conditions behave like a particle and under other conditions behave as a wave.

In 1923, a young French physicist, Louis de Broglie proposed that matter particles should indeed have a wave nature and said that a particle of mass m moving with a velocity v has an associated wavelength, λ (sometimes called de Broglie wavelength) given by the formula

p (= mv) is the momentum of the particle

$$\lambda = \frac{h}{mv} \quad \text{or} \quad \lambda = \frac{h}{p}$$

The de Broglie wavelength of a body is inversely proportional to its momentum. Since the magnitude of h is very small, the wavelength of the objects of our everyday world would be too small to be observed.

If the electrons show wave nature, then a beam of these electrons is expected to show diffraction which is a property of waves. In 1927 G.P. Thomson and C.J. Davisson demonstrated the diffraction of electron waves by the crystal lattice of nickel.

Thus, electrons also show a dual nature.
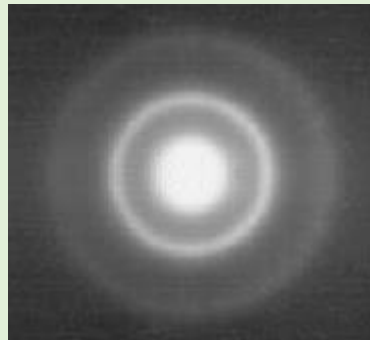
Electron diffraction pattern from nickel crystal

Heisenberg's Uncertainty Principle

An important consequence of the wave-particle duality of matter and radiation was discovered by Werner Heisenberg in 1927 and is called the uncertainty principle.

According to this principle it is not possible to simultaneously measure both the position and momentum (or velocity) of an electron accurately. If a particle's position is measured more accurately, the less accurately its momentum can be measured, and vice versa.

Mathematically, the Heisenberg principle can be expressed in terms of an inequality,

Where Äx and Äp are the uncertainities in the measurements of position and momentum respectively.

$$\ddot{A}x \, \ddot{A}p \;\geq\; \frac{h}{4\pi}$$

If the position of an object is known exactly (i.e., Äx = 0), then the uncertainty in the momentum must be infinite, meaning that we cannot say anything about the velocity. Similarly, if the velocity is known exactly, then the position would be entirely uncertain, and the particle could be anywhere. It means that we cannot say anything about the position of the particle.

In actual practice none of the two properties can be measured with certainty. Due to the small value of the Planck's constant , h (6.626 x 10^{-34} J s) this principle is not relevant while making measurements of large objects. It is relevant, only when making measurements on very small objects such as electrons. Heisenberg's principle questioned the validity of Bohr's model. It is so because according to Bohr's model we can precisely calculate the radius of the orbit (i.e., the position of the electron) and the velocity of electron in it. But it is not possible according to Heisenberg's principle. It motivated many scientists to develop newer models of the atom using the dual nature of the electron. This resulted into the development of a Quantum mechanical model or Wave Mechanical Model.

Wave Mechanical Model of Atom

Wave Mechanical Model of atom was proposed by Erwin Schrödinger- an Austrian physicist in 1926. According to this model, the motion of electron inside an atom could be described in terms of a mathematical function called, wave function, ø. The wave functions are assumed to contain all the information about the electron and are obtained by solving a differential equation called Schrödinger wave equation.

The square of the wave function $ø^2$ is a measure of the probability of finding an electron in a three-dimensional space around the nucleus.
On solving the SWE for hydrogen atom, we get a number of wave functions, which are characterized by three quantum numbers-
- Principal quantum number
- Azimuthal quantum number
- Magnetic quantum number

These quantum numbers arise in the process of logically solving the wave equation. Every electron in an atom has a unique set of quantum numbers which help to describe the three-dimensional region where there is maximum probability of finding the electron. This region is called as atomic orbital or simply orbital.

The three quantum numbers describe the size, shape, and orientation of the atomic orbitals in space. There is an additional quantum number which does not arise from the Schrödinger wave equation but is introduced to account for electron spin. The fourth quantum number thus help in designating the electrons present in the atom.

Wave Mechanical Model of Atom- Quantum Numbers

Principal quantum number, n, it describes the energy level of the electron within the atom. n can have only positive nonzero integral values (i.e., n = 1,2,3,4……). This means that in an atom, the electron can have only certain energies. n quantizes energy of the electron. It also determines the mean distance of the electron from the nucleus, i.e., its size. Greater the value of n, farther is the electron from the nucleus. Each principal shell can accommodate a maximum of $2n^2$ electrons, i.e., n =1 number of electrons : 2, n =2, n =3 number of electrons : 8 18 and so on.

Azimuthal quantum number, l, it is related to the geometrical shape of the orbital. The value of l may be zero or a positive integer less than or equal to (n–1), l = 0,1,2,3…… (n–1). Different values of l correspond to different types of subshells and each subshell contains orbitals of a given shape.

*   l = 0 , corresponds to s-subshell and contains the orbital with spherical shape called as s orbital.
*   l = 1, corresponds to p-subshell and contains the orbitals with a dumb-bell shape called as p-orbitals. There are three p-orbitals in each p-subshell.
*   l = 2 , corresponds to d-subshell and contains the orbitals with a cloverleaf shape called as d-orbitals.
*   l = 3 , corresponds to f-subshell and contain f-orbitals. There are seven f-orbitals in each f-subshell.

Magnetic quantum number, m_l, it describes the direction or orientation of the orbital in space. m_l has any integral value from – l to + l. For example, for l = 1 ; can have the values as –1,0 and 1.

Magnetic spin quantum number, m_s, it describes the spin of the electron i.e., whether it is clockwise or anticlockwise, has arbitrarily been assigned the values as +1/2 and –1/2 respectively.

Suppose an electron belonging to the third shell (n = 3). This electron can be in an s-subshell (l = 0) or a p-subshell (l = 1) or a d-subshell (l = 2). If it happens to be in a p-subshell it may be in any of the three possible p orbitals (corresponding to m_l = –1, 0 + 1 directed along x , y or z– axis. And within the orbital it may have clockwise (m_s = + ½)or anti-clockwise (m_s = -½) direction of electron spin.

Quantum Numbers for An Electron in Third Shell

| Principal quantum number, n	Azimuthal quantum number, l	Magnetic quantum number, m_l	Magnetic spin quantum number, m_s
3	0	0	+1/2
			−1/2
	1	−1	+1/2
			−1/2
		0	+1/2
			−1/2
		+1	+1/2
			−1/2
	2	−2	+1/2
			−1/2
		−1	+1/2
			−1/2
		0	+1/2
			−1/2
		+1	+1/2
			−1/2
		+2	+1/2
			−1/2

Shapes of Orbitals

An orbital is the three-dimensional region of space around the nucleus where there is maximum probability of finding the electron.

For 1s orbital (n =1 ; l =0)
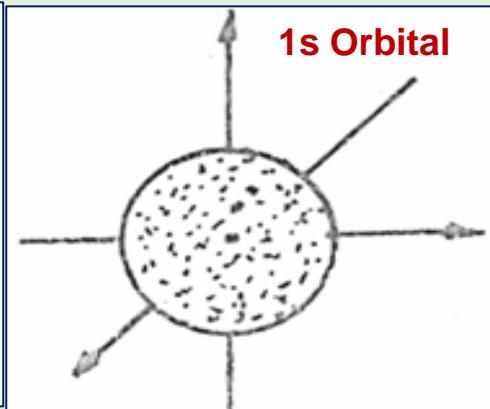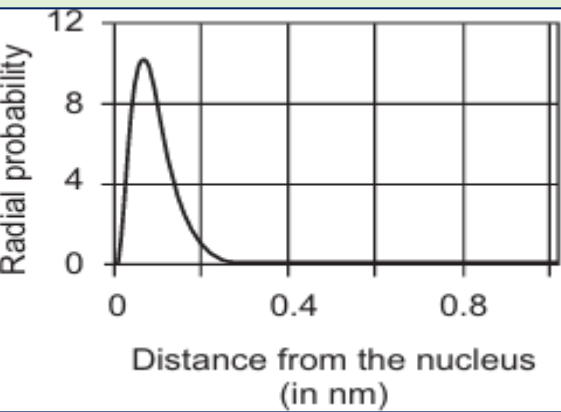
Radial Probability Curve

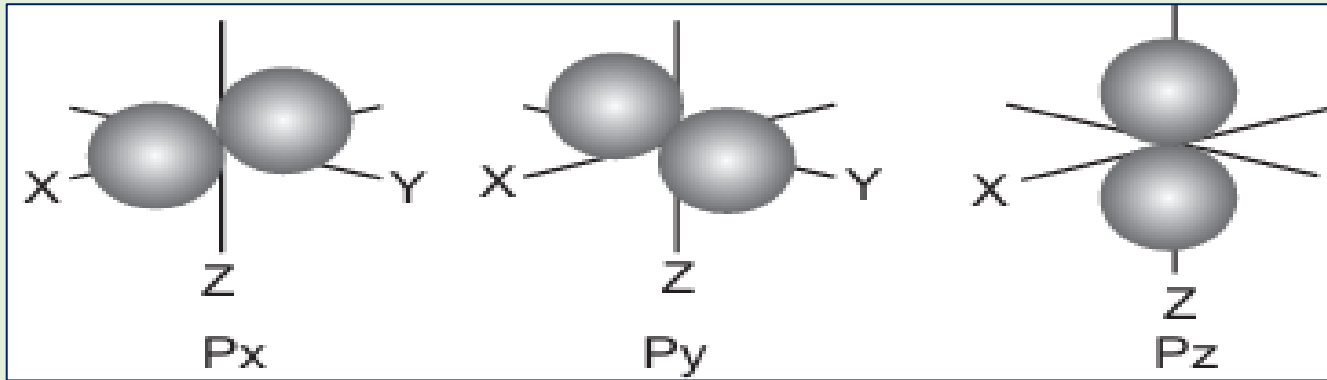1s Orbital

Boundary Surface diagram
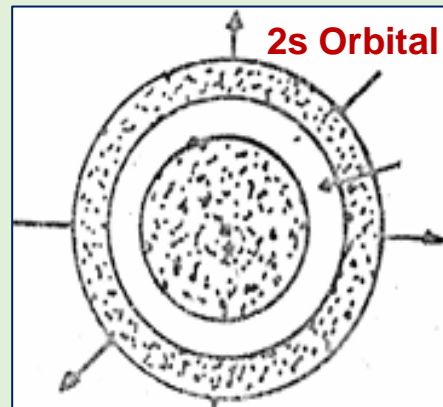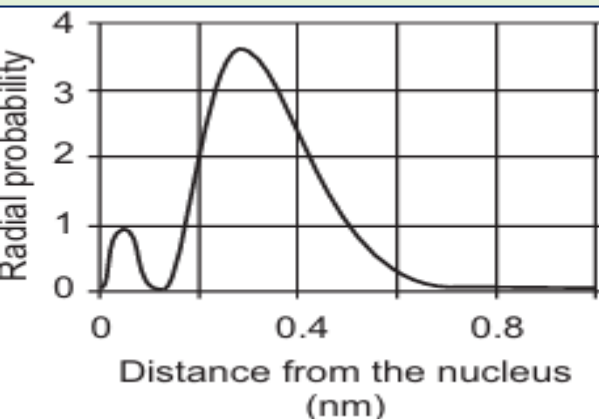
A radial probability curve gives the variation of the probability of finding the electron as a function of distance from the nucleus. For 1s orbital, the probability of finding the electron in 1s orbital increases as we move away from the nucleus and reaches a maximum at a certain distance (= 0.0529 nm or 52.9 pm for hydrogen atom) and then decreases as we go further away from it and at a certain distance it becomes close to zero. The curve shows the radial probability for a given direction. The probability would be same for all possible directions. If we put all such curves together it would give a spherical distribution of the electron probability. Since the radial probability does not become zero at any distance, we cannot specify the size of the sphere. The orbital is represented as a boundary surface diagram, which may be thought as a region of space, which contains 95 % of the probability of finding the electron, 1s orbital is represented as a sphere
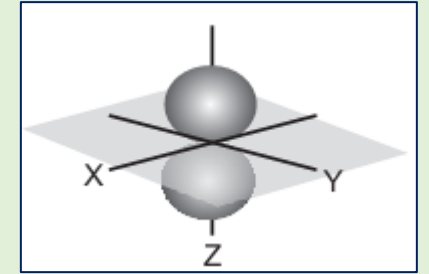

2s Orbital

For 2s orbital, the boundary surface diagram is bigger as compared to a 1s orbital. Radial probability curve shows two maxima. The probability initially increases, reaches a maximum then it decreases and comes close to zero. It increases again and decreases as we move further away from the nucleus. The region where the probability comes close to zero (before increasing again) is called a spherical node. There are (n–l)–1 spherical nodes in an orbital. A node is a region in space where the probability of finding the electron is close to zero.
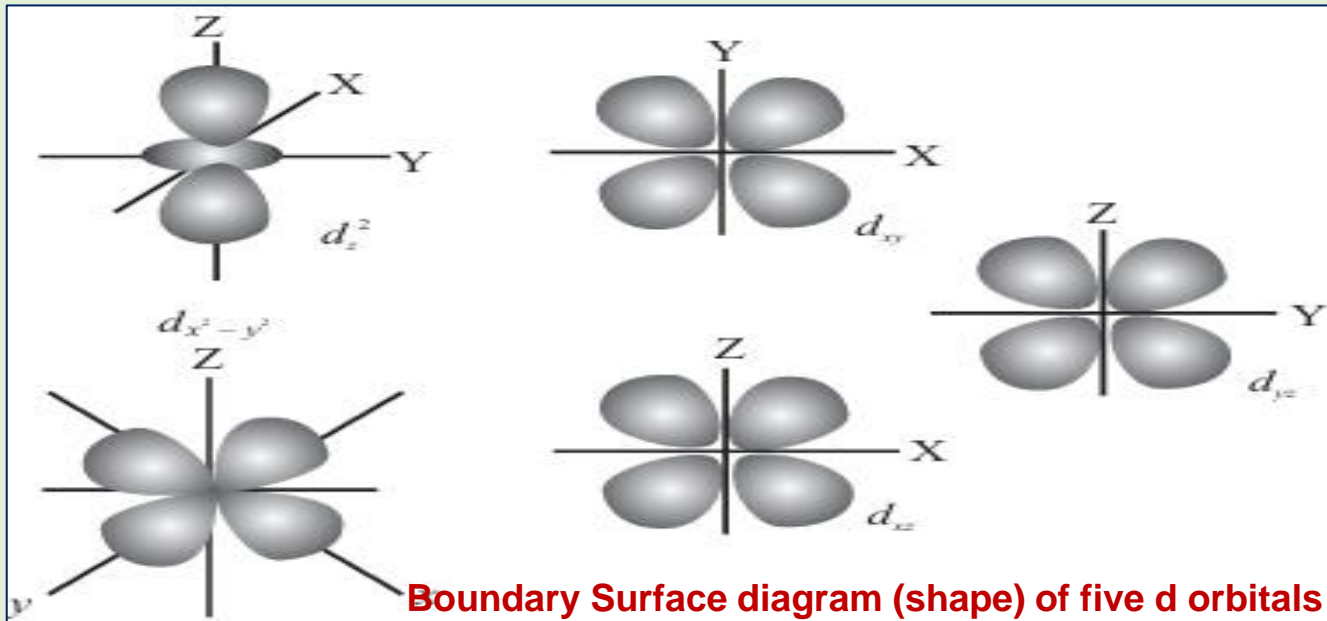
Shapes of Orbitals

p- orbital (n =1 ; l =1), The following picture shows the shape of one of the three possible p-orbitals which is directed towards the z-axis; p_z . Probability picture for a p_z orbital consists of two lobes ; one along the positive z axis and the other along the negative z-axis. Another important feature of a p orbital is the absence of the electron probability in the XY- plane. Such a plane is called a nodal plane.

Px   Py   Pz

Boundary Surface diagram of p orbitals

The boundary showing a nodal plane of the p-orbitals

d_{z^2} d_{xy} d_{yz}

$d_{x^2-y^2}$ d_{xz}

Boundary Surface diagram (shape) of five d orbitals

d-orbitals also contain nodal planes. The five d- orbitals have different shapes but they all have same energies i.e., these are degenerate.

Electronic Configuration of Elements

Atom consists of a positively charged nucleus surrounded by electrons present in orbitals of different shapes and sizes. These orbitals are part of different shells and sub-shells and are characterized by the three quantum numbers- n, l and m_l.

The distribution of electrons in these shells and sub-shells is called Electronic Configuration and is governed by three basic rules or principles.

Aufbau (or building up) Principle is concerned with the energy of the atom and states that the electrons should occupy. the orbitals in such a way that the energy of atom is minimum. In other words, the electrons in an atom are filled in the increasing order of their energies.

Higher the value of n higher the energy. This is true only for hydrogen atom. For other atoms, we need to consider both n and l. This means that different sub-shells in a given shell have different energies.

The order of orbital energies can be determined by the following (n + l) rules.

Rule 1: An orbital with a lower value for (n + l) has lower energy. For example, the 4s orbital (n + l = 4+0=4) will be filled before a 3d orbital (n + l = 3 + 2 =5).

Rule 2: If the value of (n + l) is same for two orbitals then the orbital with lower value of n will be filled first. For example, the 3d orbital (n + l = 3+2=5) will be filled before a 4p orbital (n + l = 4 + 1 =5). Following these rules the increasing order of the orbital energies comes out- 1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s

Pauli's Exclusion Principle This principle concerns the spin of electrons present in an orbital. No two electrons can have all the four quantum numbers to be same. For example, if a given electron in an atom has the set of four quantum numbers as n =2, l=1, m_l =1 and m_s = + ½ then no other electron in the atom can have the same set of quantum numbers. Electrons occupying a given orbital would have same values of the three quantum numbers (n, l, and m_l), but are distinguished in terms of their spin quantum number, m_s.

Since the spin quantum number can have only two values so only two electrons can occupy a given orbital. Fourth quantum number was introduced through Pauli's principle only.

Electronic Configuration Of Elements

Hund's Rule concerns the distribution of electrons in a set of orbitals of the same energy, i.e. constituents of a subshell.

If a number of orbitals of the same sub-shell are available then the electrons distribute in such a way that each orbital is first singly occupied with same spin. **For example, the six electrons in carbon distribute as** $1s^2\ 2s^2\ 2p^1_x\ 2p^1_y\ 2p^0_z$.

Since electrons repel each other, they remain as far as possible from one another by occupying different orbitals.

There are two common ways of representing the electronic configurations.

Orbital notation method

In this method the filled orbitals are written in the order of increasing energies. The respective electrons in them are indicated as superscripts

Electronic configuration of nitrogen atom (atomic number 7) is, $1s^2 2s^2 2p^1_x 2p^1_y\ 2p^1_x$

Orbital diagram method

In this method the filled orbitals are represented by circles or boxes and are written in the order of increasing energies. The respective electrons are indicated as arrows whose direction represents their spin.

Electronic configuration of nitrogen in the orbital diagram notation can be written
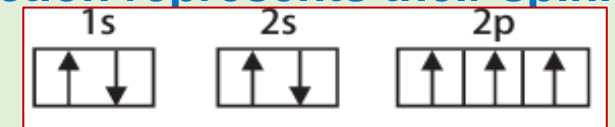
Electronic configurations can also be written in a short-hand form . In this method the last completed orbital shell is represented in terms of a noble gas. For example, the electronic configuration of lithium and sodium can be written as **Li [He]2s^1 , Na [Ne]3s^1**

The electrons in the noble gas configuration are termed as core electrons while the ones in the outer shell are called valence electrons.

Stability of Completely Filled and Half- Filled Subshells

Aufbau principle helps to determine the electronic configuration of an atom in a periodic table but in certain cases it fails to predict the correct electronic configuration where the energies of neighboring subshells are quite close e.g., 4s, 3d; 5s, 4d; 4f, 5d etc. There is shifting of energy due to electron-electron interactions.

Symmetry of Orbitals

Symmetry leads to stability. Symmetrical distribution of the electrons in the orbital lead to the electronic configuration^2 become more stable. In chromium, the Aufbau predicted configuration is $3d^4 4s^2$, but the actual configuration is $3d^5 4s^1$. Similarly in copper, the Aufbau predicted configuration is $3d^9 4s^2$, but the actual configuration is $3d^{10} 4s^1$.

This is due to extra stability of half filled or completed filled orbitals are more symmetrical, thus more stable.

Exchange Energy

The stability of half filled and completely filled orbitals is explained by exchange energy (shifting of or exchange of electrons from one orbital to another of the same subshell). Larger the number of electrons with the same spin larger is the exchange energy. Larger the exchange energy stabler is the electronic configuration. Consider the outer electron configuration of Cr which is according to Aufbau is $3d^4 4s^2$ (there are 4 electrons with same spin) but in reality, it is $3d^5 4s^1$ (there are 6 electrons with same spin). Exchange energy is larger in the latter case the preferred configuration of Cr is $3d^5 4s^1$.

3 possibility of exchange   2 possibility of exchange   possibility of exchange
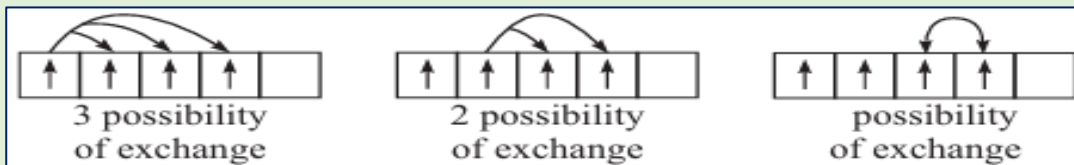
There are six possible ways by which electrons can exchange their position (parallel spins) in 3d subshell for chromium Cr – $3d^4 4s^2$.
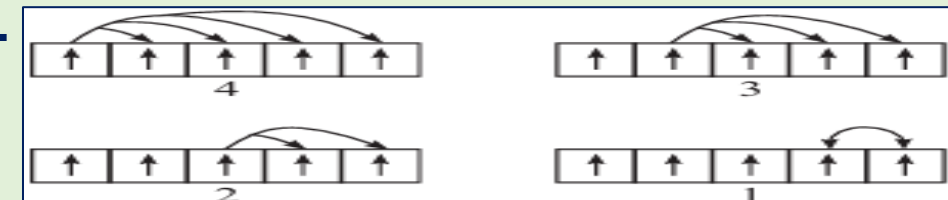
In $3d^5$ electronic configuration the electron can exchange 10 ways.

Thus, there is increase in exchange energy from $3d^4 4s^2$ to $3d^5 4s^1$ configuration. Greater the exchange energy, greater is the stability of this configuration.

Periodic Table-Introduction

Prout's Hypothesis

The atomic weights of all elements are simple multiples of atomic weight of hydrogen. Prout gave this hypothesis on the basis of Dalton's atomic theory and the atomic weights of some elements known at that time. But this hypothesis could not last longer, because there are some atomic weights which are fractional not in whole number.

Dobereiner's Triads

It was first attempt towards classification of elements. He arranged similar elements in groups of three elements called triad and the atomic mass of the middle elements of the triad is approximately the arithmetic mean of the other two

Merits: After Dobereiner, Chemists focused on chemicals in groups having similar physical and chemical properties.

Demerits: All the known elements did not follow this rule .Law of triads was rejected as some triads nearly had same atomic masses, e.g., (Fe, Co, Ni),(Ru, Rh, Pd), (Os, Ir, Pt).

Triad	Atomic Masses
Lithium	6.94
Sodium	22.99
Potassium	39.1

Newland's Law of Octaves :

When elements arranged in order of their increasing atomic weights, the properties of every eighth element were similar to those of the first one.

This type of classification was limited up to only 20 elements.

Symbol of element	Li	Be	B	C	N	O	F
	7	9	11	12	14	16	19
Symbol of element	Na	Mg	Al	Si	P	S	Cl
	23	24	27	28	31	32	35.5

Demerits

Law of octave worked quite well for lighter elements but failed with heavier elements.

Properties of elements were not taken into account and the elements were arranged in the order of their increasing atomic masses

No places were left for unknown elements and so, many elements occupied wrong positions. Thus, resulted

Periodic Table-Introduction

Lother Meyer Curve

According to Lother Meyer if a graph is between the atomic volume and atomic weights of the elements and observed that the elements with similar properties occupied similar position on the curve.

- The most strongly electropositive alkali metal occupy the peaks on the curve.
- The less strongly electropositive alkaline earth metals occupy the descending position on the curve.
- The most electronegative elements i.e. halogens occupy the ascending position on the curve.

Lother Meyer proposed that the physical properties of the elements are a periodic function of the atomic weights.

It lacked practical utility as it is not easy to remember the position of different elements on the curve.
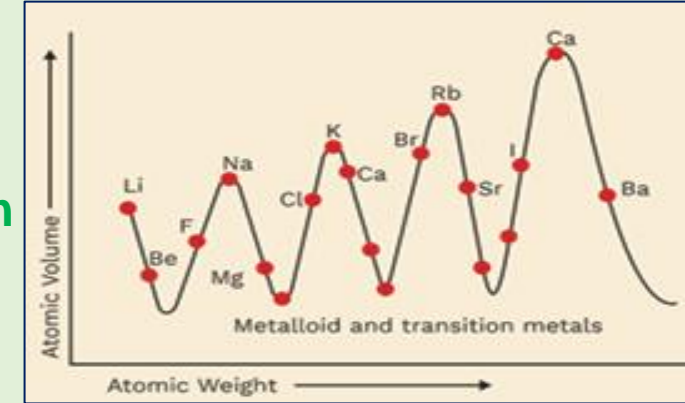
Mendeleev's Periodic Table

The physical and chemical properties of elements are the periodic function of their atomic weights, i.e., when the elements are arranged in order of their increasing atomic weights, elements with similar properties are repeated after certain regular intervals. It consists of seven horizontal rows called periods. Mendeleev's original table consists of 8 vertical columns called groups. These are numbered as I, II, III....VIII. However, 9th vertical column called zero group was added with the discovery of inert gases. Except for 8 and 0, each group is further divided into two sub-group designated as A and B. Group 8 consists of 9 elements arranged in three sets each containing three elements.

Defects- Position of hydrogen, position of isotopes, position of lanthanides and actinides, anomalous pairs of elements. Few similar elements are placed in different groups while some dissimilar elements are grouped together. Iodine having lower atomic mass than tellurium was placed ahead of tellurium.

Periodic Table

Modern Periodic Law

According to this law physical and chemical properties of the elements are a periodic function of their atomic numbers, i.e. elements are arranged in order of their increasing atomic numbers, the elements with similar properties are repeated after certain regular intervals.

Cause of Periodicity :

It is due to repetition of similar outer electronic configurations after certain regular intervals.

Period	Atomic number		Number of elements
	From	to	
First	H (1)	He (2)	2
Second	Li (3)	Ne (10)	8
Third	Na (11)	Ar (18)	8
Fourth	K (19)	Kr (36)	18
Fifth	Rb (37)	Xe (54)	18
Sixth	Cs (55)	Rn (86)	32 (including lanthanides)
Seventh	Fr (87)	Og (118)	32 (including actinides)

Seven periods

Periodic Table

Group		Number of Elements	
(a)	I A group	7 (H, Li, Na, K Rb, Cs, Fr) Alkali metals	
(b)	II A group	6 (Be, Mg, Ca, Sr, Ba, Ra) Alkaline earth metals	
(c)	III A group	**6** (B, Al, Ga, In, Tl) Boron family	**Nh**
(d)	IV A group	**6** (C, Si, Ge, Sn, Pb) Carbon family	**Fl**
(e)	V A group	**6** (N, P, As, Sb, Bi) Nitrogen family	**Mc**
(f)	VI A group	**6** (O, S, Se, Te, Po) Oxygen family (Chalcogen)	**Lv**
(g)	VII A group	**6** (F, Cl, Br, I, At) Halogen family	**Ts**
(h)	Zero group	**7** (He, Ne, Ar, Kr, Xe, Rn) Inert elements	**Og**
		32 (Sc, Y, La, Ac & 14 lanthanide elements & 14 actinide elements.)	
(i)	III B group	These are elements of IIIB group, which could not be accommodated in one column and therefore written separately outside the periodic table.	

(j)	IV B group	4 (Ti, Zr, Hf, Rf)	
(k)	V B group	4 (V, Nb, Ta, Db)	
(l)	VI B group	**4** (Cr, Mo, W)	**Sg**
(m)	VII B group	**4** (Mn, Tc, Re)	**Bh**
(n)	VIII (3) group	**12** (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt)	**Hs, Mt, Ds**
(o)	I B group	**4** (Cu, Ag, Au)	**Rg**
(p)	II B group	**4** (Zn, Cd, Hg)	**Cn**

The modern periodic table has 18 vertical columns and according to CAS system there are 16 groups having the above number of elements.

Defects
The position of hydrogen is still disputable as it was there in Mendeleev periodic table in group IA as well as IVA & VIIA.
Helium is an inert gas, but its configuration is different from that of the other inert gas elements
Lanthanide and actinide series could not be adjusted in the main periodic table and therefore they had to be provided with a place separately below the table.

Periodic Table

Electronic Configuration of Elements and the Periodic Table

Periodic table is divided into the four blocks-
- **s-Block**
- **p-Block**
- **d-Block**
- **f-Block**
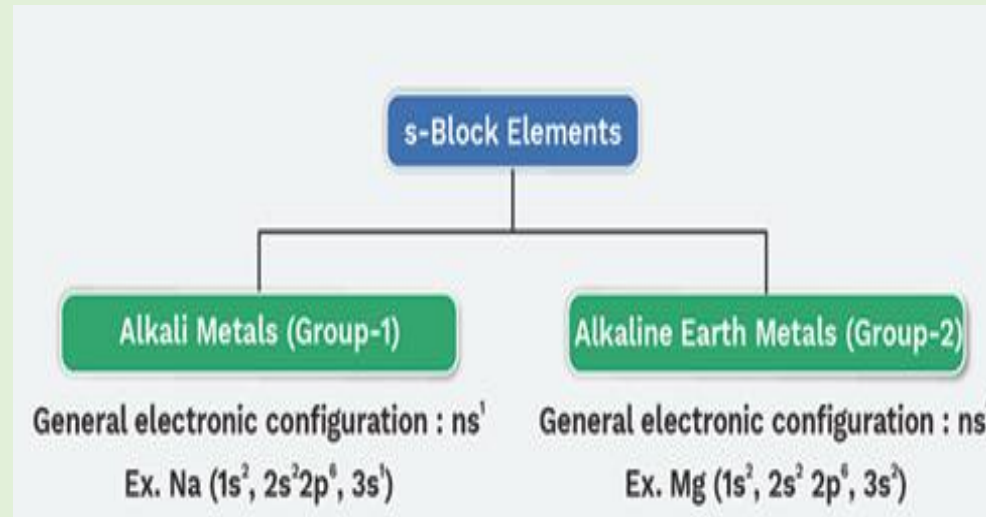
s-block Elements

Elements of groups 1 and 2 including He in which the last electron enters the s-orbitals of the valence shell are called s-block elements. There are only 14 s-block elements in the periodic table.

The electronic configuration of outermost shell of s-block elements is ns^1 (alkali metals; group1) or ns^2 (alkaline earth metals; group 2)

- **The valence of group I elements is +1 and those of group II elements is +2.**
- **These are soft metals having low melting points and boiling points.**
- **Most of these form ionic compounds on account of their lower ionization energy.**
- **Most of these metals (except Be & Mg) and their salts imparts characteristic color to the flame e.g., sodium imparts a golden yellow color; potassium imparts violet color to the flame.**
- **These are highly reactive elements and are strong reducing agents.**
- **All are good conductors of heat and electricity**

Electronic Configuration of Elements and the Periodic Table

p-Block Elements

p-block elements are present in right part of the periodic table. The electronic configuration of valence shell in p-block is ns^2np^{1-6} (n = 2 to 7). These constituted the groups IIIA to VIIA and zero groups i.e., groups 13 to 18 of the periodic table. The last electron fills in p-orbital of valence shell.

13th group- Boron family (ns^2np^1), Al $(1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1)$

14th group- Carbon family (ns^2np^2), Si $(1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2)$

15th group- Nitrogen family "Pnicogen" (ns^2np^3). Pnico means Fertilizer and Gen means to produce.
 P $(1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3)$

16th group- Oxygen family "Chalcogen" $(ns^2\ np^4)$. Chalco means Ore and Gen means to produce.
S $(1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4)$

17th group- Halogen family $(ns^2\ np^5)$. Halo means Salt and Gen means to produce.
Cl $(1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5)$

18th group (Zero group)- Inert/Noble/Rare gas (ns^2np^6)
Ar $(1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6)$ Exception : Helium shows the $1s^2$ electronic configuration.

- These elements include metals and non-metals with a few metalloids.
- The metallic character, however, decreases along the period but increases down the group.
- These possess relatively higher ionization energy which tends to increase along the period but decreases down the group.
- Most of them form covalent compounds.
- Most of these elements show negative (except some metals) as well as positive oxidation states (except F). The oxidizing power of these elements increases along the period but decreases down the group.

Electronic Configuration of Elements and the Periodic Table

d-Block Elements (Transition Elements)-There are three complete series and one incomplete series of d-block elements. These are present in the middle part of the periodic table (between s and p block elements). These constitute IIIB to VIIB, VIII, IB and IIB i.e., 3 to 12 groups of the periodic table. Filling of electrons takes places in penultimate shell. i.e., $(n - 1)$ shell.

3d Series- known as first transition series having 10 elements starting from "Scandium" (Z = 21) to "Zinc" (Z = 30). Fe- [Ar] $3d^6 4s^2$

4d Series- known as second transition series having 10 elements starting from "Yttrium" (Z = 39) to "Cadmium" (Z = 48). Pd- [Kr] $4d^{10} 5s^0$

5d Series- known as third transition series having 10 elements starting from "Lanthanum" (Z = 57) to "Mercury" (Z = 80). Au- [Xe] $5d^{10} 6s^1$

6d Series- known as fourth transition series having 10 (with elements of unknown properties) elements starting from Periodic Table "Actinium" (Z = 89) to "Copernicium" (Z = 112). Rf- [Rn] $6d^2 7s^2$.

- The electronic configuration of outermost shell of d-block elements is ns^{0-2} followed with $(n-1) s^2 p^6 d^{1-10}$.
- All (except Hg) are hard, ductile metals with high melting and boiling points.
- All of these are good conductors of heat and electricity.
- Their ionization energies are higher than s-block elements but lesser than p-block elements.
- Most of the transition metals form colored ions (Zn^{2+}, Hg^{2+}, Cd^{2+} are colorless.)
- These elements show variable oxidation states. Most of these elements possess catalytic activity.
- Metals and their ions are generally paramagnetic due to the presence of unpaired electrons.
- Most of the transition metal ions possess the tendency to form complex ions.
- Most transition metals form alloys.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Th	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn

Electronic Configuration of Elements and the Periodic Table

f-Block Elements (Inner Transition Elements)- In these elements, the f-subshell of the inner-penultimate is progressively filled up. There are two series of f-block elements each containing 14 elements. The fourteen elements from ^{58}Ce - ^{71}Lu in which, 4f-subshell is progressively filled up are called lanthanides or rare elements. Similarly, the fourteen elements from ^{90}Th – ^{103}Lr in which, 5f-subshell is progressively filled up are called actinides.

The electronic configuration of outermost shell of f-block elements is ns^2 , followed with (n–2)f$^{1-14}$, (n–1) d$^{0-2}$.

All are metals. f-Block show variable valency. The +3 is the most important oxidation state. Few elements show +2 and +4 oxidation states. They are paramagnetic in nature. Lanthanoids are also known as rare earth elements whereas most of the members of actinoid series are known as transuranic elements (made artificially).

- They form colored compounds, and they have tendency to form complexes.
- Filling of electrons takes place in antipenultimate shell. i.e. (n – 2) shell.
- Chemically, lanthanides are very similar. It is difficult to separate them form a mixture by application of a chemical property. Similarly, actinides have similar chemical properties. The members of actinides show the phenomenon of radioactivity.

Lanthanoids : (Atomic number 58–71) Lanthanoids belongs to 3rd group (III B group) and VI period having
Actinoids : (Atomic number 90–103) Actinoids belongs to 3rd group (III B group) and VII period

- Hydrogen, Helium, Thorium are exception to block classification.
- Every period starts with the filling of s-orbital & ends with p-orbital. Mainly d and f-block elements have exceptions in electronic configuration which is due to orbital contraction.
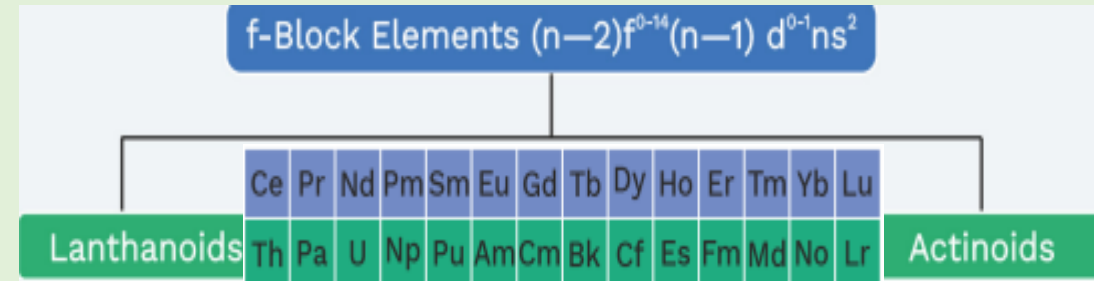
Electronic Configuration of Elements and the Periodic Table

Atomic numbers of various inert gases:

First period $\xrightarrow{2}$ He (2)

Second period $\xrightarrow{8}$ Ne (10)

Third period $\xrightarrow{8}$ Ar (18)

Fourth period $\xrightarrow{18}$ Kr (36)

Fifth period $\xrightarrow{18}$ Xe (54)

Sixth period $\xrightarrow{32}$ Rn (86)

Seventh period $\xrightarrow{32}$ Og (118)

Identification of group, block, period in periodic table

When atomic number is given

Lanthanoid (Atomic number 58 to 71)

- **3rd group**
- **6th period**
- **f-block**

Actinoid (Atomic number 90 to 103)

- **3rd group**
- **7th period**
- **f-block**

Atomic number 104 to 118– Last two digit gives group number in periodic table. Ex Atomic number 115 – group 15. (Last two digit gives group number)

- **Metalloids: Si, Ge, As, Sb, Te, At (universal metalloid).**
- **B or Se is non metal/metalloid, Po is metal/metalloid.**

Group Identification:

$$\text{Group No.} = 18 - \left(Z_{\text{inert gas}} - Z_{\text{given}} \right)$$

Total number of elements in a period:

(i) Total number of elements in a period $= \dfrac{(n+1)^2}{2}$

When n = 1, 3, 5, ...

(ii) Total number of elements in a period $= \dfrac{(n+2)^2}{2}$

When n = 2, 4, 6, ...

For 7th period n = 7 ∴ n = 7 is odd number

$\dfrac{(7+1)^2}{2} = \dfrac{64}{2} = 32$ elements

Total subshell in period $= \sqrt{\left(\dfrac{\text{Total elements}}{2} \right)}$

$\sqrt{\dfrac{32}{2}} = 4 \, (s, p, d, f)$

Electronic Configuration of Elements and the Periodic Table

Identification of group, block, period in periodic table

When configuration is given, ns → (n–2)f → (n–1)d → np

The subshell that receives last electron is block.

Period number is highest number of orbit.

Group number can be calculated as follows.

- **s-block : Group number = Number of outermost electron.**
- **p-block : Group number = 12 + Number of outermost p electron.**
- **d-block : Group number = Number of outermost electron + Number of Penultimate d electron.**
- **f-block : Group number for f-block is 3rd group.**

Typical elements : Those elements which explain the properties of there respective group. Third period elements except inert gases are called typical elements.

Elements of 2nd period are not typical elements since they have : (i) Small size (ii) High Z_{eff} (iii) Absence of vacant d-orbitals

Bridge elements : According to modern periodic table, the elements of 2nd period (Li, Be, B) are called as bridge elements.

According to Mendeleev periodic table, the elements of 3rd period (Na, Mg, Al) called as bridge elements.

Diagonal Relationship : Elements of second period are showing properties similar to elements of third period which are diagonally related to them, this is called as diagonal relationship.

The cause of diagonal relationship is similar value of ionic potential (φ).

Transuranic Elements: Those elements which are coming after Uranium in periodic table. All trans Uranic elements are radioactive and artificial (Man made). Total transuranic elements in periodic table are 26. First man made element is Technetium(Tc). First man made Lanthanoid is Promethium (Pm).

Total natural elements are 90 (1 to 90).

Periodicity

Regular repetition of properties at fixed intervals is called as periodicity. The causes of periodicity is repetition of general electronic configuration.

Z_{eff} , ionization energy, electronegativity, electron affinity, metallic character etc. are periodic properties.

Z_{eff} (Effective nuclear charge) The net positive charge attracting an electron in an atom is known as effective nuclear charge.

$$Z_{eff} = Z - \sigma$$

Z is number of protons, σ is shielding/screening constant

$$Z_{eff} \propto \frac{+ve\ charge}{-ve\ charge} \quad or \quad Z_{eff} \propto \frac{p}{e^-}$$

Shielding effect

It is the phenomenon is which nuclear charge present on outermost electron is decreased by presence of inner or outer electron.

The shielding of electron present in s-orbital is most effective, p-orbital is effective, d-orbital is poor, and f-orbital is negligible. s > p > d > f (shielding effect).

A scientist named Slater, determined the value of shielding constant and put forward some rules which are listed below-

• The shielding effect or screening effect of each electron of 1s orbital is 0.30.
• The shielding effect of each electrons of ns and np i.e. electron of the outermost orbit, is 0.35.
• The shielding effect of each electron of s, p or d orbitals of the penultimate orbit (n – 1) is 0.85.
• The shielding effect of each electron of s, p, d or f orbital of the inner penultimate orbit (n – 2) and below this is 1.0
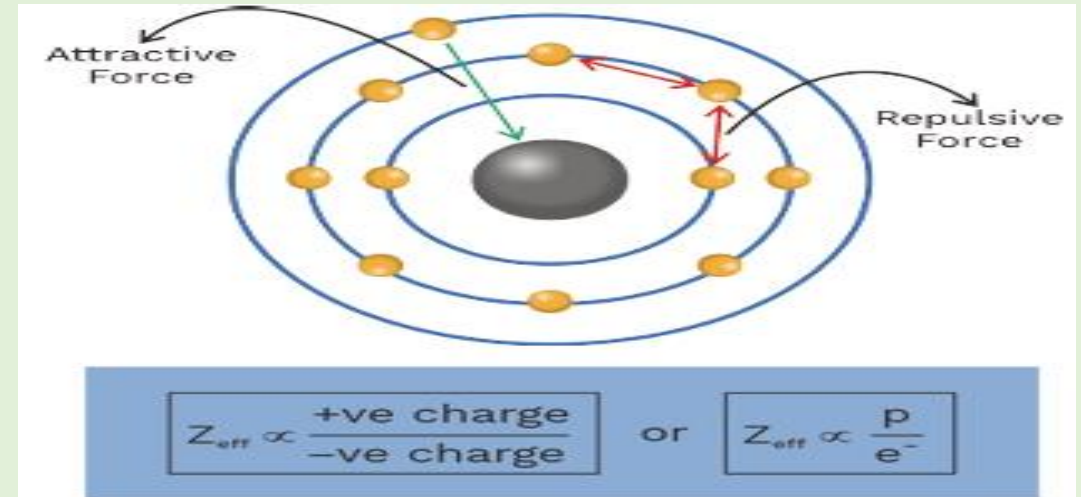
Periodicity-Atomic Radius

Atomic Radius: It refers to the distance between the center of the nucleus of the atom to the outermost shell containing electrons. Since absolute value of the atomic size cannot be determined, it is usually expressed in terms of the following operational definitions.

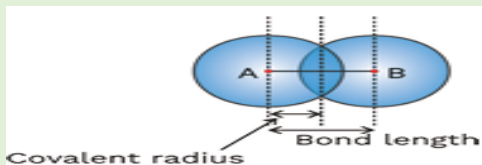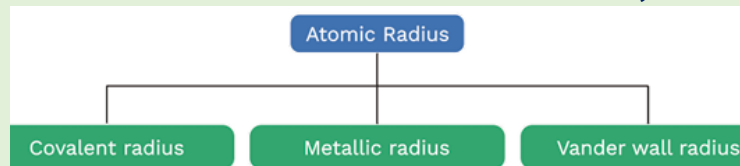**Covalent radius :** It is defined as one-half the distance between the nuclei of two covalently bonded atoms of the same element in a molecule. This is generally used for non-metals.

Atomic Radius
- Covalent radius
- Metallic radius
- Vander wall radius

$$r_{covalent\ radius} = \frac{1}{2}(Bond\ length)$$

Covalent radius / Bond length

Homoatomic molecule : $d_{A-B} = r_A + r_B$

Heteroatomic

$d_{A-B} = r_A + r_B - 0.09\ |\Delta EN|$ (Stevenson and Schoemaker formula)

Metallic radius (Crystal radius): It is half of internuclear distance present between the two adjacent metal ions in the metallic lattice. Covalent radius is always lower than metallic radius since in case of metallic radius no overlapping takes place. Generally metallic radius is present between two metal atoms.

$$r_{metallic} = \frac{d}{2}$$

Metallic radius
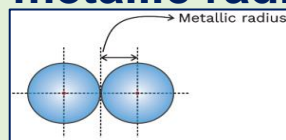
Van der Walls radius : It is half of internuclear distance between nuclei of two non-bonded isolated atoms or adjacent atoms belonging to neighboring molecules. It is also defined with respect to inert gases, it is half of the internuclear distance present between atoms of inert gas in solid state. In case of inert gases, we consider Vander Waal radius and Vander Waal radius is greater than that of metallic and covalent radius.

$$r_{vwf} = \frac{d}{2}$$

Vanderwall radius
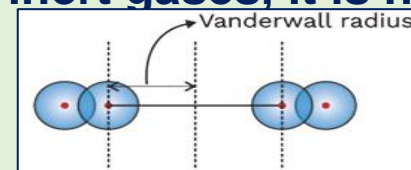
Ionic Radius-This term is used in case of ions. It is the distance of outermost shell of an anion or cation from its nucleus. In other words, it is defined as the effective distance from the nucleus of the ion which is under influence in an ionic bond.

Radius of cation / Radius of antion / Cation / Anion / Internuclear distance
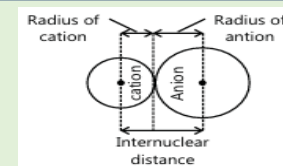
Periodicity-Atomic Radius

Trends of Atomic Radius

Along the period: On moving across a period, atomic radii decreases because effective nuclear charge increases.

Down the group: On moving down a group, atomic radii increases, because number of orbits increases.

Factors Affecting Atomic Radii

Effective nuclear charge: As the effective nuclear charge increases, the attractive force between nucleus and valence electron increases. Thus, across a period, atomic size/atomic radii decreases.

$$\text{Atomic radii} \propto \frac{1}{Z_{eff}}$$

Size of valence shell: Atomic radii is the measure of radius of valence shell. As the value of n (principal quantum no.) increases, for an orbit, its size increases, thus down a group, atomic radii increases.

Multiplicity of bond: Covalent radii decreases, as the multiplicity of bond increases.
For example, in case of carbon,

	C – C	C = C	Δ_{A-B}
D_{c-c} (Å)	1.54	1.34	1.20
r_c (Å)	0.77	0.67	0.60

Percentage ionic character in bond: Covalent radii of an atom in a bond depends upon % of ionic character. Increase in ionic character % leads in shortening of bond, decreasing the atomic radii.

Cationic Radii: Size of cation is always lesser than its parent atom and greater the charge on cation, smaller is its ionic radii. e.g. $Fe > Fe^+ > Fe^{2+} > Fe^{3+}$ (decreasing ionic radii) Formation of cation involves loss of electron. Thus, effective nuclear charge increases, pulling the remaining electrons more tightly towards the nucleus.

Anionic Radii: Size of an anion is always larger than its parent atom. Formation of an anion involves gain of electrons by an atom and so, effective nuclear charge decreases. Thus, the valence shell electrons are less tightly held by the nucleus.

Periodicity-Ionization Potential

It is the amount of energy required to remove the most loosely bound electron from an isolated gaseous atom i.e

$$M(g) + IE \rightarrow M^+(g) + e^-$$

The amount of energy required to remove the first, second, third etc. electrons from an Isolated gaseous atom are called successive ionization energies and are designated as IE_1 , IE_2 , IE_3 etc. It may be noted that IE_2 is always greater than IE_1 .Thus, the order is- $IE_3 > IE_2 > IE_1$. The removal of a second electron is relatively more difficult because after the removal of the first electron, remaining electrons in the cation are more effectively pulled by the nucleus due to increased effective nuclear charge.

Factors affecting Ionization Potential

Number of shells: With the increase in the number of shells, the atomic radius increases i.e. the distance of outermost shell electron from the nucleus increases and hence the ionization potential decreases.

Effective Nuclear Charge: Atomic size decreases with the increase in effective nuclear charge because, higher the effective nuclear charge, stronger will be the attraction of the nucleus towards the electron of the outermost orbit and higher will be the ionization potential.

Shielding Effect: The electrons of the inner orbits repel the electrons of the outermost orbit due to which the attraction of the nucleus towards the electrons of the outermost orbit decreases and thus the atomic size increases and the value of ionization potential decreases.

Stability of half-filled and fully filled orbitals: The atoms whose orbitals are half-filled (p^3 ,d^5 ,f^7 or fully filled (s^2 , p^6, d^{10}, f^{14}) have greater stability than the other. Therefore, they require greater energy to remove an electron. However, stability of fully filled orbitals is greater than that of the half-filled orbitals.

Penetration power: In any atom, the s-orbital is nearer to the nucleus in comparison to p, d, and f orbitals. Therefore, greater energy is required to remove an electron from s-orbital than from p, d and f orbitals. The order is as follows- s > p > d > f

Periodic Trends in Ionization Potential

In a Period, the value of ionization potential normally increase across a period, because effective nuclear charge increases and the atomic size decreases.

Exceptions:

- In the second period, ionization potential of Be is greater than that of B, and in the third period, ionization potential of Mg is greater than that of Al due to the high stability of fully filled orbitals.
- In the second period, ionization potential of N is greater than O and in the third period, ionization potential of P is greater than that of S, due to the stability of half-filled orbitals.

In a Group, the value of ionization potential normally decreases down the group because both, atomic size and shielding effect increase.

Exception:

- The value of ionization potential remains almost constant from Al to Ga in the III A group. (B > Al, Ga > In).
- In IV B group i.e. Ti, Zr and Hf, the I.P. of Hf is higher than that of Zr due to Lanthanide contraction. Thus the I.P. of IV B group varies as Ti > Zr < Hf.

Ionization Potential of Transition Elements: In transition elements, the value of ionization potential has changes very little across a period. This is because, the outermost orbit remains the same, but electrons get filled up in the $(n-1)d$ orbitals resulting in very little increase in the values of ionization potential. In transition element series, the first ionization potential normally increases with increase in atomic number on going from left to right, but this periodicity is not uniform. The value of ionization potential of transition elements depends on two important factors-

- The value of ionization potential increases with increase in effective nuclear charge.
- The value of ionization potential decreases with increase in shielding effect when number of electrons increase in $(n-1)$ orbitals.

Periodic Trends in Ionization Potential

- In the first transition element series, the first ionization potential normally increases on going from left to right from Sc to Cr because shielding effect is much weaker in comparison to effective nuclear charge.
- The value of first ionization potential of Fe, Co and Ni remains constant, because shielding effect and effective nuclear charge balance each other.
- The value of ionization potential shows a slight increase from Cu to Zn because they have fully filled s and d orbitals.
- The value of first ionization potential of Mn is maximum because it has maximum stability due to fully filled s and half-filled orbitals.

Inner Transition Elements:
- The size of inner transition elements is greater than that of d block elements. Therefore, the value of ionization potential of f- block elements is smaller than that of d- block elements.
- Due to the almost constant atomic size of f- block elements in a period, the value of their ionization potential remains more constant than that of d- block elements.

Ionization energy and the stable oxidation states of elements
- When difference in two successive IE values (Δ^2) for an atom is approximately 10-15 eV or less, then, the higher ox. state will be more stable. E.g. For Al, $I.E_1$ = 6.0 eV. $I.E_2$ = 18.8 eV, $I.E_3$ = 28.4 eV and $I.E_4$ = 120 eV.

Al(II); Δ I.E. $_{(1,2)}$ = 12.8 eV
Al (III); Δ I.E. $_{(2,3)}$ = 9.6 eV
Al (IV); Δ I.E. $_{(3,4)}$ = 91.6 eV
So, Al (III) is more stable than Al (I) or Al (II).

- If the value of $\propto$ is greater than 16.0 eV, then, the lower ox. state will be more stable. E.g., For Na, $I.E._1$ = 5.1 eV; $I.E_2$ = 47.3 eV

Δ I.E. $_{(1,2)}$ = 42.4 eV So, Na(I) is formed and not Na(II)
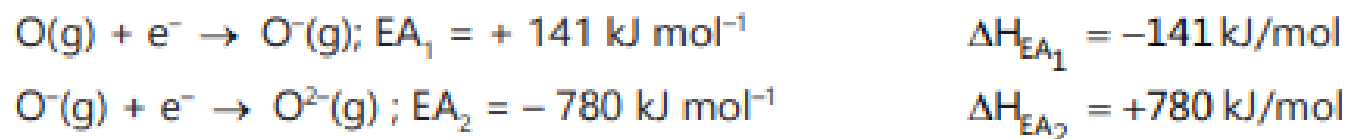
Periodicity-Electron Affinity

It is the amount of energy released when a neutral isolated gaseous atom accepts an electron to form a gaseous anion.

$$X (g) + E \rightarrow X^- (g) + EA$$

Second and third electron can be added to form gaseous dinegative and trinegative ions. The energy changes accompanying the addition of first, second, third etc. electrons to neutral isolated gaseous atoms are called successive electron affinities and are designated as EA_1 , EA_2 , EA_3 , etc.

Since an atom has a natural tendency to accept an electron, therefore, the first electron affinity (EA_1) is always taken as positive. However, the addition of second electron to the negatively charged ion is opposed by columbic repulsion.

Hence, energy has to be supplied for the addition of second electron. Thus, second electron affinity (EA_2) of an element is taken as negative. For example,

Factors Affecting Electron Affinity

$$O(g) + e^- \rightarrow O^-(g); EA_1 = + 141 \text{ kJ mol}^{-1} \qquad \Delta H_{EA_1} = -141 \text{ kJ/mol}$$
$$O^-(g) + e^- \rightarrow O^{2-}(g) ; EA_2 = - 780 \text{ kJ mol}^{-1} \qquad \Delta H_{EA_2} = +780 \text{ kJ/mol}$$

Atomic size or atomic radius:

When the atomic size/radius increases, the electrons entering the outermost orbit is more weakly attracted by the nucleus and the value of electron affinity is lower.

Effective Nuclear charge:

When effective nuclear charge is more, then, the atomic size is less. Then, the atom can easily gain an electron and possess a higher value of electron affinity.

Stability of Fully-Filled and Half-Filled orbitals:

The stability of the configuration having fully-filled orbitals (p^6 , d^{10} & f^{14}) and half—filled orbitals (p^3 , d^5 & f^7) is relatively higher than that of other configurations. Such type of atoms have a lesser tendency to gain an electron, therefore, their electron affinity values will be very low or zero.

Periodicity-Electron Affinity

Trends in Electron Affinity:

In a period, atomic size decreases with the increase in effective nuclear charge and hence, increases the electron affinity.

Exception:

- From ^{6}C to ^{7}N in the second period, the values of electron affinity decrease instead of increasing. This is because there are half-filled ($2p^3$) orbitals in the outermost orbit of N, which are more stable. On the other hand, the outermost orbit in C has a $2p^2$ configuration.
- In the third period, the value of electron affinity of Si is greater than that of P. This is because the electronic configuration of the outermost orbit in P atom is $3p^3$, which being half-filled, is relatively more stable.
- The values of electron affinity of inert gases are zero, because their outermost orbit has fully-filled p orbitals.
- In a period, the value of electron affinity goes on decreasing on going from group IA to group IIA. The value of electron affinity of the elements of group IIA is zero because ns orbitals are fully filled, and such orbitals have no tendency to accept electrons.

In a Group: The values of electron affinity normally decrease down a group because the atomic size increases, decreasing the actual attractive force of the nucleus.

Exceptions:

- The value of the electron affinity of F is lower than that of Cl, because the size of F is very small and compact, and the charge density is high on the surface. Therefore, the incoming electron/s experience more repulsion in comparison to Cl accounting for the highest value of Cl in the periodic table.
- The values of electron affinity of alkali metals and alkaline earth metals can be regarded as zero, because they do not have the tendency to form anions by accepting electron/s.

Periodicity-Electron Affinity

- **Cl has the highest electron affinity**
- **Higher the EA of an element, easier is the addition of an electron.**

Following are some important observations derived from the general trend of electron affinity:

- **More the tendency to gain an electron, more is the non-metallic nature. Therefore, non-metallic nature increases along the period but decreases down the group.**
- **More the tendency to form an anion, more is the tendency to show ionic bonding. Therefore, tendency of non- metals to show ionic bonding increases along the period but decreases down the group.**
- **More the tendency to get reduced, more is the oxidizing nature. Therefore, oxidizing power increases along the period but decreases down the group order of Oxidizing power- F > Cl > Br > I.**

The electron gain enthalpy of O is highly negative while that of N is slightly positive.

Reason: The electronic configuration of N is quite stable ($1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$), since it has exactly half-filled 2p-orbitals and hence has no tendency to accept an extra electron. In other words, energy has to be supplied to add an extra electron. Thus, electron-gain enthalpy of N is slightly positive. In contrast, the electronic configuration of O ($1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$) is not so stable but it has a higher nuclear charge and smaller atomic size than N and hence, it has a higher tendency to accept an extra electron. In other words, electron gain enthalpy of O is highly negative.

S has more negative electron gain enthalpy than O

Reason: The size of O is much smaller than that of S. As a result, the electron-electron repulsions in the smaller 2p-subshell of O are comparatively more than those present in the bigger 3p-subshell of S. Therefore, S has a higher tendency to accept an additional electron than O.

C has a more negative electron gain enthalpy than Si.

Reason: This is because C-atom has a smaller size than Si-atom. (Note that the electron-electron repulsions in these atoms are not very large because they contain only 4 electrons in the outermost shell.

Periodicity-Electronegativity

The tendency of an atom to attract the shared pair of electrons of the covalent bond towards itself is called electronegativity of that atom.

Factors Affecting Electronegativity

Atomic size: Electronegativity of a bonded atom decreases with increase in size since the attractive force on the valence electrons decreases and hence electronegativity decreases.

Hybridization state of atom: Electronegativity increases with increase in the s-character of the hybrid orbital. This is because, the s-orbital is nearer to the nucleus and thus, suffers greater attraction leading to increased electronegativity. The number of covalent bonds present between two bonded atoms is known as its bond order. With increase in the bond order, the bond distance decreases, effective nuclear charge increases and thus electronegativity increases. Increasing order of electronegativity is as follows: C – C < C = C < C ≡C. When effective nuclear charge is high, the nucleus will attract the shared electrons with greater strength to give high electronegativity.

Oxidation number: The electronegativity value increases with the increase in oxidation number since the radius decreases with the increase in oxidation number. The increasing order of electronegativity is as follows: $Fe < Fe^{+2} < Fe^{+3}$

Trends in Electronegativity: Atomic size decreases across a period. Thus, electronegativity increases. Atomic size increases down a group decreasing the electronegativity. F has maximum electronegativity value in the periodic table, while Cs has minimum. According to the Pauling scale, the electronegativity value of F is 4.0, O is 3.5 N is 3.0 and Cl is 3.1

Exceptions

- The elements of group IIB i.e. Zn, Cd and Hg show increase in electronegativity value down the group.
- The elements of group IIIA, i.e. Al to Ga show increase in electronegativity value down the group.
- The elements of group IVA, Si onwards, show no change in electronegativity value down the group.

Trends in Chemical Properties

Valency/valence, also known as valence number, is the number of valence bonds a given atom has formed, or can form, with one or more atoms.

Variation of valence in a group

Group		1	2	13	14	15	16	17	18
Number of valence electron/s		1	2	3	4	5	6	7	8
Valence		1	2	3	4	3,5	2,6	1,7	0,8

- **Variation of valence in a period:**
- **On moving along the period, the number of valence electrons increases from 1 to 8.**
- **The valence of the elements with respect to hydrogen increases from 1 to 4 up to group IV and then decreases to 1 as shown in the table.**
- **Valence with respect to oxygen increases from one to seven along the period.**

Variation of valence in group:

On moving down the group, the number of valence electrons remains the same. All the elements in a group have the same valence. For example, elements of group I have valency 1 and elements of group II have valency 2.

Variation of valence in transition elements:

Transition metals show variable valence of 1, 2 or 3 as they can use electrons from their outermost as well as penultimate shell, during chemical reactions as energy difference between them is small.

Trends in Chemical Properties

Some anomalous properties of second period elements

II period: Li Be B C N O F Ne The elements of group. 1, 2 (Li & Be) and of group. 13–17 (B to F) differ in many respects from other members of their group.

Covalence:

The maximum covalency of 2nd period elements is four while, other members may also show higher covalency. e.g., BF_4^- exists but $[BF_6]_3^-$ is known. Similarly, OF_2 is known but OF_4, OF_6 are not while, SF_4 are SF_6 are known, N is never pentavalent etc.

Explanation:

These elements have only two shells in their atom and the valence shell contain 4 orbitals only (one 2s and three 2p) so, a maximum of four bonds can be formed. In the 3rd period and onwards, the valence shell contain empty d–orbitals also. So, covalency may be more than four.

π – π Multiple bonding:

Bonds like C=C, C≡C, N≡N, C=O etc. exist due to π− π multiple bonding. These elements are smaller in size and mostly electronegative in their respective groups thus forming multiple bonds.

Diagonal relationship:

Li	Be	B	C
Na	Mg	Al	Si

Diagonal relationship between elements of II & III periods. Li Be B C Na Mg Al Si Diagonal relationship between these elements can be explained on the basis of approximately similar charge/ size ratio of diagonally related elements.

Periodicity along the Period

Ionization enthalpy: Increases along the period (with exception).

Electron gain enthalpy: Increases along the period (with exception).

Electronegativity: Increases along the period.

Atomic radius: Decreases along the period.

Ionic radius: The radii of isoelectronic ions decrease with increase in atomic number.

Atomic volume: Volume occupied by 1 g-atom of an element in solid state is Atomic Volume. Atomic volume decreases up to metals and then increases.

	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic volume (cm³)	24	14	10	12	17	16	19	23.7

Melting point, Boiling point: Increases along the period for metals.

	Na	Mg	Al
M.P (°C)	98	649	660
B.P (°C)	883	1100	1800

Density: Increases along the period.

Reducing behavior: Decreases along the period.

Na Mg Al Si P S Cl
Strong reductants   Strong oxidants

Metallic character: Decreases along the period.

Na Mg Al   Si   P S Cl
Metals   Metalloid   Non–metals

Increasing non-metallic nature →
Decreasing metallic nature

Electropositive character: Decreases along the period. **Nature of oxides:** The basic character of oxides decreases and acidic character increases along the period.

Elements: Na   Mg   Al   Si   P S Cl

Oxides: Na_2O MgO Al_2O_3 SiO_2 P_2O_5 SO_3 Cl_2O_7
                                        Amphoteric
        Basic

**Nature of hydrides:** The basic character of hydrides decreases along the period.

Valency: Valency with respect to oxygen increases from one to seven along the

| Group	I	II	III	IV	V	VI	VIII
Valency with respect to oxygen	1	2	3	4	5	6	7
Formula of the oxide	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7

Periodicity along the Group

- **Ionisation enthalpy : Decreases**
- **Electron gain enthalpy : Decreases**
- **Electronegativity : Decreases**
- **Atomic radii : Increases**
- **Ionic radii : Increases**
- **Atomic volume : Increases**
- **M.P./B.P : Decreases**
- **Density : Increases**
- **Oxidant-Reductant nature : * Reducing nature of metals : Increases * Oxidizing nature of non-metals : Decreases**
- **Metallic character : Increases**
- **Electro positive character : Increases**
- **Basic character of oxide : Increases**
- **Basic character of hydride : Decreases**
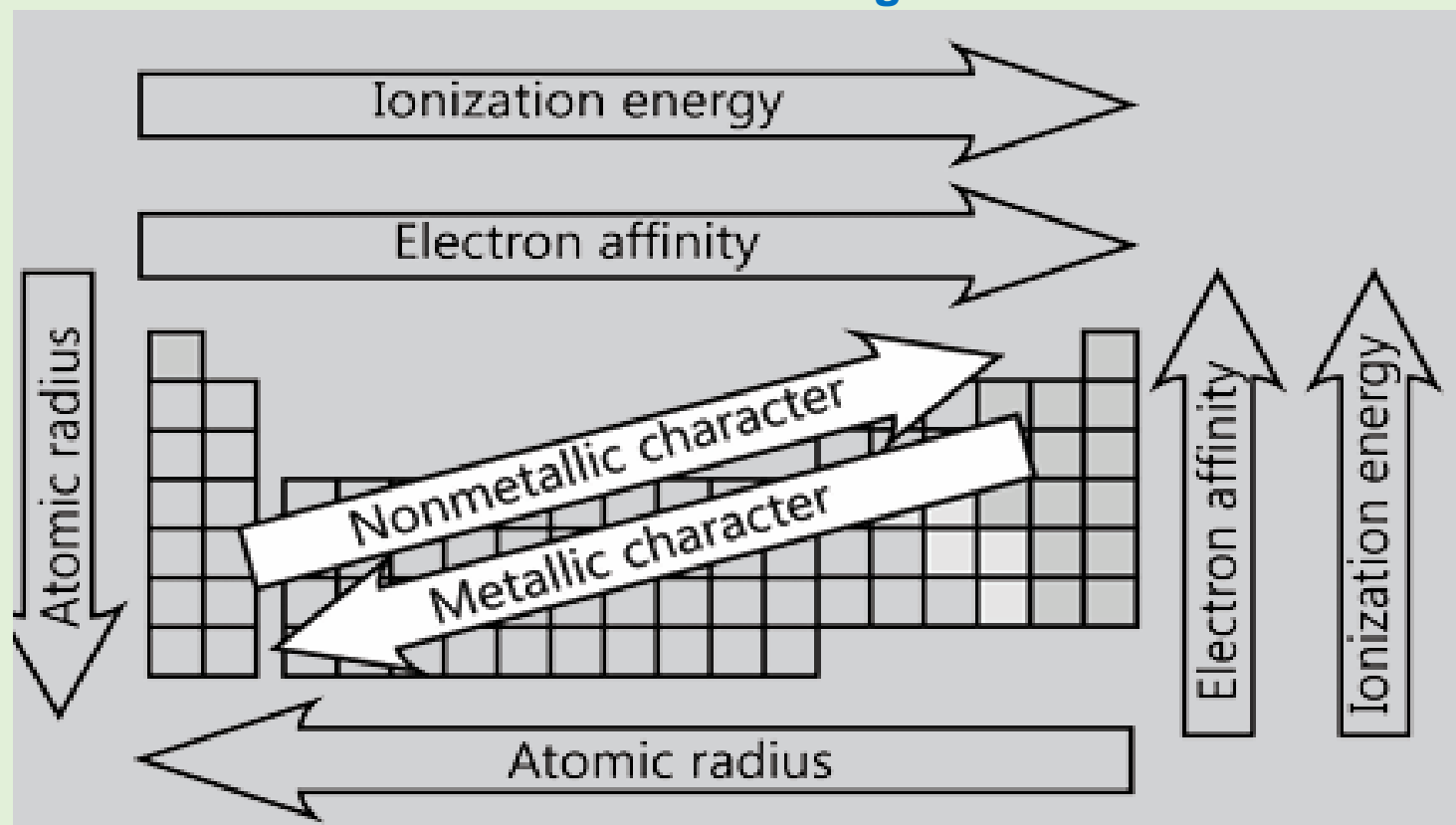
Check List

1. Give the number of protons, neutrons, and electrons in each of the following species: (a) $^{17}_{8}O$ (b) $^{199}_{80}Hg$ (c) $^{200}_{80}Hg$
2. What was the aim of Rutherford's α-rays scattering experiment?
3. On what basis was the Rutherford's model rejected?
4. microwave radiation has a frequency of 12 gigahertz. Calculate the energy of the photon corresponding to this radiation. (h = 6. A 626 × 10–34 J s and 1 gigahertz = 109 Hz.).
5. What is the difference between a 'quantum' and a ' photon'?
6. Calculate the wavelength of the Balmer line corresponding to $n_2 = 3$.
7. How does the energy of a Bohr orbit vary with the principal quantum number 'n'.
8. Calculate the de Broglie wavelength associated with a cricket ball weighing 380 g thrown at a speed of 140 km per hour.
9. Give the significance of the principal, azimuthal and magnetic quantum numbers?
10. What do you understand by a spherical node and a nodal plane?
11. Which of the following orbitals will be filled first? i) 2p or 3s ii) 3d or 4s.
12. The electronic configuration of Cr is (Ar) $3d^5 4s^1$ not $3d^4 4s^2$
13. How many elements from the following atomic number are p-block elements? 83, 79, 42, 64, 37, 54 34
14. Write the electronic configuration of the elements given below: A (At. No. = 9), B (At. No. = 12), C (At. No. = 29), D (At. No. = 54) and E (At. No. = 58). Also predict the period, group number and block to which they belong.
15. Which one of the following pairs would have a large size? Explain. (i) K or K^+ (ii) Br or Br^- (iii) O^{2-} or F^- (iv) Li^+ or Na^+ (v) P or As (vi) Na^+ or Mg^{2+}
16. Arrange the following in order of increasing radii? (i) I, I^+, I^- (ii) C, N, Si, P (iii) O^{2-}, N^{3-}, S^{2-} F^-
17. From each set, choose the atom which has the largest ionization enthalpy and explain your answer. (i) F, O, N (ii) Mg, P Ar (iii) B, Al, Ga
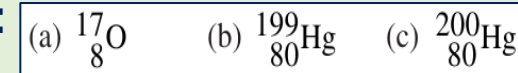
Check List

18. Compare qualitatively the first and second ionization potentials of copper and zinc. Explain the observation.

IE_1 kJ mol^{-1} IE_2 kJ mol^{-2}

Cu   744   1961

Zn   906   1736

19. The electron gain enthalpy of chlorine is -349 kJ mol^{-1}. How much energy in kJ is released when 3.55 g of chlorine is converted completely into Cl$^-$ ion in the gaseous state?

20. Which of the following pairs of elements would have more negative electron gain enthalpy? Explain

(i)   N or O (ii) S or O (iii) C or Si

21. Arrange the following elements in order of decreasing electron gain enthalpy: B, C, N, O.

22. Among the following, how many elements have lower electronegativity than oxygen atom-F, Cl, Br, I, H, S, P, K, Ca