Chemistry

Atomic Structure

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John Dalton 1808, believed that matter is made up of extremely minute indivisible particles, called atom which can takes part in chemical reactions. These can neither be created nor be destroyed. However, modern researches have conclusively proved that atom is no longer an indivisible particle. Modern structure of atom is based on Rutherford's scattering experiment on atoms and on the concepts of quantization of energy.

1. Composition of atom.

The works of J.J. Thomson and Ernst Rutherford actually laid the foundation of the modern picture of the atom. It is now believed that the atom consists of several sub-atomic particles like electron, proton, neutron, positron, neutrino, meson etc. Out of these particles, the electron, proton and the neutron are called fundamental subatomic particles and others are non-fundamental particles.

Electron (–1eo)

(1) It was discovered by J.J. Thomson (1897) and is negatively charged particle. Electron is a component particle of cathode rays.

(2) Cathode rays were discovered by William Crooke's & J.J. Thomson (1880) using a cylindrical hard glass tube fitted with two metallic electrodes. The tube has a side tube with a stop cock. This tube was known as discharge tube. They passed electricity (10,000V) through a discharge tube at very low pressure (10^{-2} to $10^{-3}\,mm\,Hg$). Blue rays were emerged from the cathode. These rays were termed as Cathode rays.

Discharge tube experiment for production of cathode
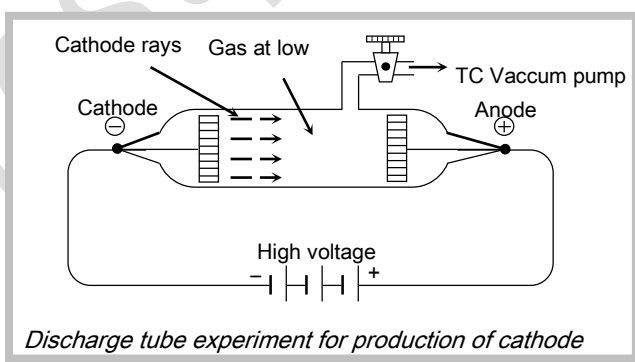
(3) Properties of Cathode rays

(I) Cathode rays travel in straight line.

(ii) Cathode rays produce mechanical effect, as they can rotate the wheel placed in their path.

(iii) Cathode rays consist of negatively charged particles known as electron.

(iv) Cathode rays travel with high speed approaching that of light (ranging between 10^{-9} to 10^{-11} cm/sec)

(v) Cathode rays can cause fluorescence.

(vi) Cathode rays heat the object on which they fall due to transfer of kinetic energy to the Object.

(vii) When cathode rays fall on solids such as $Cu, X-$ rays are produced.

(viii) Cathode rays possess ionizing power i.e., they ionize the gas through which they pass.

(ix) The cathode rays produce scintillation the photographic plates.

(x) They can penetrate through thin metallic sheets.

(xi) The nature of these rays does not depend upon the nature of gas or the cathode material used in discharge tube.

(xii) The e/m (charge to mass ratio) for cathode rays was found to be the same as that for an e^- (-1.76×10^8 coloumb per gm). Thus, the cathode rays are a stream of electrons.

Note: When the gas pressure in the discharge tube is 1 atmosphere no electric current flows through the tube. This is because the gases are poor conductor of electricity.

The television picture tube is a cathode ray tube in which a picture is produced due to fluorescence on the television screen coated with suitable material. Similarly, fluorescent light tubes are also cathode rays tubes coated inside with suitable materials which produce visible light on being hit with cathode rays.

(4) R.S. Mullikan measured the charge on an electron by oil drop experiment. The charge on each electron is $-1.602 \times 10^{-19} C$.

(5) Name of electron was suggested by J.S. Stoney. The specific charge (e/m) on electron was first determined by J.J. Thomson.

(6) Rest mass of electron is $9.1 \times 10^{-28} gm = 0.000549 amu = 1/1837$ of the mass of hydrogen atom.

(7) According to Einstein's theory of relativity, mass of electron in motion is, m'

$$= \frac{\text{Rest mass of electron(m)}}{\sqrt{[1-(u/c)^2]}}$$

Where u = velocity of electron, c= velocity of light.

When u=c than mass of moving electron $=\infty$.

(8) Molar mass of electron = Mass of electron × Avogadro number $= 5.483 \times 10^{-4}$.

(9) 1.1×10^{27} electrons =1gram.

(10) 1 mole electron = 0.5483 mili gram.

(11) Energy of free electron is ≈ 0. The minus sign on the electron in an orbit, represents attraction between the positively charged nucleus and negatively charged electron.

(12) Electron is universal component of matter and takes part in chemical combinations.

(13) The physical and chemical properties of an element depend upon the distribution of electrons in outer shells.
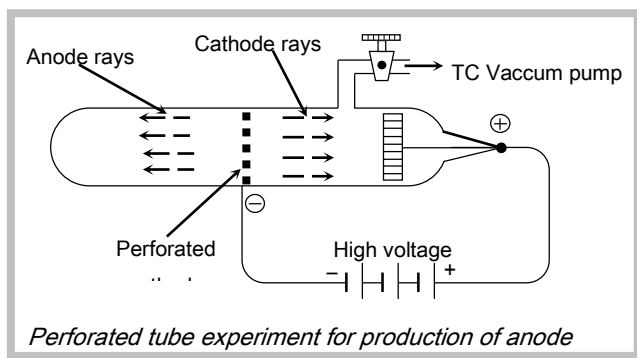
(14) The radius of electron is $4.28 \times 10^{-12} cm.$

(15) The density of the electron is $= 2.17 \times 10^{-17} g/mL$.

Proton (1H1, H+, P)

(1)   Proton was discovered by Goldstein and is positively charged particle. It is a component particle of anode rays.

(2)   Goldstein (1886) used perforated cathode in the discharge tube and repeated Thomson's experiment and observed the formation of anode rays. These rays also termed as positive or canal rays.

Perforated tube experiment for production of anode

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(3) Properties of anode rays

(I) Anode rays travel in straight line.

(ii) Anode rays are material particles.

(iii) Anode rays are positively charged.

(iv) Anode rays may get deflected by external magnetic field.

(v) Anode rays also affect the photographic plate.

(vi) The e/m ratio of these rays is smaller than that of electrons.

(vii) Unlike cathode rays, their e/m value is dependent upon the nature of the gas taken in the tube. It is maximum when gas present in the tube is hydrogen.

(viii) These rays produce flashes of light on ZnS screen.

(4) Charge on proton = 1.602×10^{-19} coulombs = $4.80 \times 10^{-10} e.s.u.$

(5) Mass of proton = Mass of hydrogen atom= $1.00728 amu = 1.673 \times 10^{-24} gram = 1837$ of the mass of electron.

(6) Molar mass of proton = mass of proton $\times$ Avogadro number $= 1.008$ (approx.).

(7) Proton is ionized hydrogen atom (H^+) i.e., hydrogen atom minus electron is proton.

(8) Proton is present in the nucleus of the atom and its number is equal to the number of electron.

(9) Mass of 1 mole of protons is ≈ 1.007 gram.

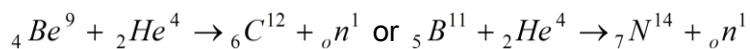(10) Charge on 1 mole of protons is $\approx$ 96500 coulombs.

(11) The volume of a proton (volume = $\frac{4}{3}\pi r^3$) is $\approx 1.5 \times 10^{-38} cm^3$.

(12) Specific charge of a proton is 9.58×10^4 Coulomb/gram.

Neutron (on1, N)

(1) Neutron was discovered by James Chadwick (1932) according to the following nuclear reaction,

$$_4Be^9 + {}_2He^4 \rightarrow {}_6C^{12} + {}_0n^1 \text{ or } {}_5B^{11} + {}_2He^4 \rightarrow {}_7N^{14} + {}_0n^1$$

(2) The reason for the late discovery of neutron was its neutral nature.

(3) Neutron is slightly heavier (0.18%) than proton.

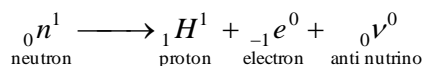(4) Mass of neutron = $1.675 \times 10^{-24} \, gram$ = $1.675 \times 10^{-27} \, kg$ = $1.00899 \, amu \approx$ mass of hydrogen atom.

(5) Specific charge of a neutron is zero.

(6) Density = $1.5 \times 10^{-14} \, gram/c.c.$

(7) 1 mole of neutrons is $\approx$ 1.008 gram.

(8) Neutron is heaviest among all the fundamental particles present in an atom.

(9) Neutron is an unstable particle. It decays as follows:

$$\underset{\text{neutron}}{_0n^1} \longrightarrow \underset{\text{proton}}{_1H^1} + \underset{\text{electron}}{_{-1}e^0} + \underset{\text{anti nutrino}}{_0\nu^0}$$

(10) Neutron is fundamental particle of all the atomic nucleus, except hydrogen or protium.

Comparison of mass, charge and specific charge of electron, proton and neutron

Name of constant	Unit	Electron(e–)	Proton(p+)	Neutron(n)
Mass (m)	amu kg Relative	0.000546 9.109×10^{-31} 1/1837	1.00728 1.673×10^{-27} 1	1.00899 1.675×10^{-24} 1
Charge(e)	Coulomb (C) esu Relative	$- 1.602 \times 10^{-19}$ $- 4.8 \times 10^{-10}$ $- 1$	$+1.602 \times 10^{-19}$ $+4.8 \times 10^{-10}$ $+1$	Zero Zero Zero
Specific charge (e/m)	C/g	1.76×10^8	9.58×10^4	Zero

• The atomic mass unit (amu) is 1/12 of the mass of an individual atom of ${}_6C^{12}$, i.e. $1.660 \times 10^{-27} \, kg$.

Other non-fundamental particles

Particle	Symbol	Nature	Charge esu ×10–10	Mass (amu)	Discovered by
Positron	$e^+, 1e^0, \beta^+$	+	+ 4.8029	0.0005486	Anderson (1932)
Neutrino	ν	0	0	< 0.00002	Pauli (1933) and Fermi (1934)
Anti-proton	p^-	–	– 4.8029	1.00787	Chamberlain Sugri (1956) and Weighland (1955)
Positive mu meson	μ^+	+	+ 4.8029	0.1152	Yukawa (1935)
Negative mu meson	μ^-	–	– 4.8029	0.1152	Anderson (1937)
Positive pi meson	π^+	+	+ 4.8029	0.1514	Powell (1947)
Negative pi meson	π^-	–	– 4.8029	0.1514	
Neutral pi meson	π^0	0	0	0.1454	

2.   Atomic number, Mass number and Atomic species.

(1) Atomic number or nuclear charge

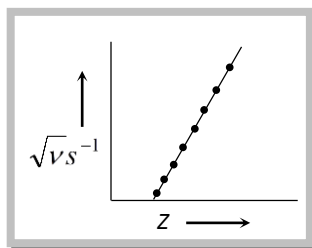   (I) The number of protons present in the nucleus of the atom is called atomic number (Z).

   (ii) It was determined by Moseley as,

   $$\sqrt{\nu} = a(Z - b) \text{ or } aZ - ab$$

   Where, $\nu = X -$ rays frequency

   Z= atomic number of the metal

   $a \& b$ are constant.

   (iii) Atomic number = Number of positive charge on nucleus = Number of protons in nucleus = Number of electrons in neutral atom.

   (iv) Two different elements can never have identical atomic number.

(2) Mass number

(I) The sum of proton and neutrons present in the nucleus is called mass number.

Mass number (A) = Number of protons + Number of neutrons or Atomic number (Z)

or Number of neutrons = A – Z.

(ii) Since mass of a proton or a neutron is not a whole number (on atomic weight scale), weight is not necessarily a whole number.

(iii) The atom of an element X having mass number (A) and atomic number (Z) may be represented by a symbol,

e.g. $_9F^{19}, _8O^{16}, _7N^{14}$ etc.
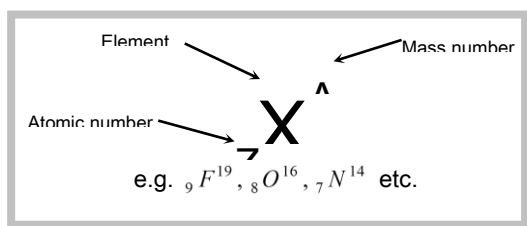
Note: A part of an atom up to penultimate shell is a kernel or atomic core.

Negative ion is formed by gaining electrons and positive ion by the loss of electrons.

Number of lost or gained electrons in positive or negative ion = Number of protons $\pm$ charge on ion.

(3) Different Types of Atomic Species

Atomic species	Similarities	Differences	Examples
Isotopes (Soddy)	(I) Atomic No. (Z) (ii) No. of protons (iii) No. of electrons (iv) Electronic configuration (v) Chemical properties (vi) Position in the periodic table	(I) Mass No. (A) (ii) No. of neutrons (iii) Physical properties	(I) $_1^1 H, _1^2 H, _1^3 H$ (ii) $_8^{16} O, _8^{17} O, _8^{18} O$ (iii) $_{17}^{35} Cl, _{17}^{37} Cl$
Isobars	(I) Mass No. (A) (ii) No. of nucleons	(I) Atomic No. (Z) (ii) No. of protons, electrons and neutrons (iii)Electronic configuration (iv) Chemical properties (v) Position in the periodic table.	(I) $_{18}^{40} Ar, _{19}^{40} K, _{20}^{40} Ca$ (ii) $_{52}^{130} Te, _{54}^{130} Xe, _{56}^{130} Ba$

Isotones	No. of neutrons	(I) Atomic No. (ii) Mass No., protons and electrons. (iii) Electronic configuration (iv) Physical and chemical properties (v) Position in the periodic table.	(I) $^{30}_{14}Si, ^{31}_{15}P, ^{32}_{16}S$ (ii) $^{39}_{19}K, ^{40}_{20}Ca$ (iii) $^{3}_{1}H, ^{4}_{2}He$ (iv) $^{13}_{6}C, ^{14}_{7}N$
Isodiaphers	Isotopic No. (N − Z) or (A − 2Z)	(I) At No., mass No., electrons, protons, neutrons. (ii) Physical and chemical properties.	(I) $_{92}U^{235}, _{90}Th^{231}$ (ii) $_{19}K^{39}, _{9}F^{19}$ (iii) $_{29}Cu^{65}, _{24}Cr^{55}$
Isoelectronic species	(I) No. of electrons (ii) Electronic configuration	At. No., mass No.	(I) $N_2O, CO_2, CNO^{-}(22e^{-})$ (ii) $CO, CN^{-}, N_2(14e^{-})$ (iii) $H^{-}, He, Li^{+}, Be^{2+}(2e^{-})$ (iv) $P^{3-}, S^{2-}, Cl^{-}, Ar, K^{+} and Ca^{2+}(18e^{-})$
Isosters	(I) No. of atoms (ii) No. of electrons (iii) Same physical and chemical properties.		(I) N_2 and CO (ii) CO_2 and N_2O (iii) HCl and F_2 (iv) CaO and MgS (v) C_6H_6 and $B_3N_3H_6$

Note: In all the elements, tin has maximum number of stable isotopes (ten).

Average atomic weight/ the average isotopic weight

3. Electromagnetic Radiations.

(1) Light and other forms of radiant energy propagate without any medium in the space in the form of waves are known as electromagnetic radiations. These waves can be produced by a charged body moving in a magnetic field or a magnet in an electric field. E.g. $\alpha -$ rays, $\gamma -$ rays, cosmic rays, ordinary light rays etc.

(2) Characteristics: (I) All electromagnetic radiations travel with the velocity of light. (ii) These consist of electric and magnetic fields components that oscillate in directions perpendicular to each other and perpendicular to the direction in which the wave is travelling.

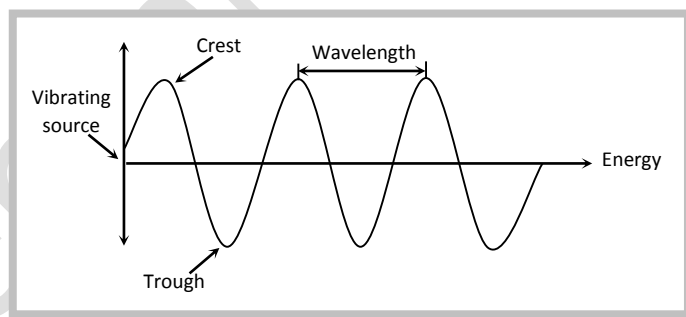(3) A wave is always characterized by the following five characteristics:

(I) Wavelength: The distance between two nearest crests or nearest troughs is called the wavelength. It is denoted by λ (lambda) and is measured is terms of centimeter (cm), angstrom (Å), micron (μ) or nanometer (nm).

$$1\overset{\circ}{A} = 10^{-8} \, cm = 10^{-10} \, m$$

$$1\mu = 10^{-4} \, cm = 10^{-6} \, m$$

$$1nm = 10^{-7} \, cm = 10^{-9} \, m$$

$$1cm = 10^{8} \, \overset{\circ}{A} = 10^{4} \, \mu = 10^{7} \, nm$$

(ii) Frequency: It is defined as the number of waves which pass through a point in one second. It is denoted by the symbol ν (nu) and is expressed in terms of cycles (or waves) per second (cps) or hertz (Hz).

$$\lambda\nu = \text{Distance travelled in one second = velocity =c}$$

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

(iii) Velocity: It is defined as the distance covered in one second by the wave. It is denoted by the letter 'c'. All electromagnetic waves travel with the same velocity, i.e., $3 \times 10^{10} \, cm / \sec$.

$$\boxed{c = \lambda\nu = 3 \times 10^{10} \, cm / \sec}$$

Thus, a wave of higher frequency has a shorter wavelength while a wave of lower frequency has a longer wavelength.

(iv) Wave number: This is the reciprocal of wavelength, i.e., the number of wavelengths per centimeter. It is denoted by the symbol $\bar{v}$ (nu bar). It is expressed in cm^{-1} or m^{-1}.

$$\boxed{\bar{v} = \frac{1}{\lambda}}$$

(v) Amplitude: It is defined as the height of the crest or depth of the trough of a wave. It is denoted by the letter 'A'. It determines the intensity of the radiation.

The arrangement of various types of electromagnetic radiations in the order of their increasing or decreasing wavelengths or frequencies is known as electromagnetic spectrum.

Name	Wavelength (Å)	Frequency (Hz)	Source
Radio wave	$3 \times 10^{14} - 3 \times 10^{7}$	$1 \times 10^{5} - 1 \times 10^{9}$	Alternating current of high frequency
Microwave	$3 \times 10^{7} - 6 \times 10^{6}$	$1 \times 10^{9} - 5 \times 10^{11}$	Klystron tube
Infrared (IR)	$6 \times 10^{6} - 7600$	$5 \times 10^{11} - 3.95 \times 10^{16}$	Incandescent objects
Visible	$7600 - 3800$	$3.95 \times 10^{16} - 7.9 \times 10^{14}$	Electric bulbs, sun rays
Ultraviolet (UV)	$3800 - 150$	$7.9 \times 10^{14} - 2 \times 10^{16}$	Sun rays, arc lamps with mercury vapors
X-Rays	$150 - 0.1$	$2 \times 10^{16} - 3 \times 10^{19}$	Cathode rays striking metal plate
$\gamma -$ Rays	$0.1 - 0.01$	$3 \times 10^{19} - 3 \times 10^{20}$	Secondary effect of radioactive decay
Cosmic Rays	0.01- zero	$3 \times 10^{20} -$ infinity	Outer space

4. Atomic spectrum - Hydrogen spectrum.

Atomic spectrum

(1) Spectrum is the impression produced on a photographic film when the radiation (s) of particular wavelength (s) is (are) analyzed through a prism or diffraction grating. It is of two types, emission and absorption.

(2) Emission spectrum: A substance gets excited on heating at a very high temperature or by giving energy and radiations are emitted. These radiations when analyzed with the help of spectroscope, spectral lines are obtained. A substance may be excited, by heating at a higher temperature, by passing electric current at a very low pressure in a discharge tube filled with gas and passing electric current into metallic filament.   Emission spectra is of two types,

   (I) Continuous spectrum: When sunlight is passed through a prism, it gets dispersed into continuous bands of different colors. If the light of an incandescent object resolved through prism or spectroscope, it also gives continuous spectrum of colors.

   (ii) Line spectrum: If the radiations obtained by the excitation of a substance are analyzed with help of a spectroscope a series of thin bright lines of specific colors are obtained. There is dark space in between two consecutive lines. This type of spectrum is called line spectrum or atomic spectrum.

(3) Absorption spectrum: When the white light of an incandescent substance is passed through any substance, this substance absorbs the radiations of certain wavelength from the white light. On analyzing the transmitted light we obtain a spectrum in which dark lines of specific wavelengths are observed. These lines constitute the absorption spectrum. The wavelength of the dark lines correspond to the wavelength of light absorbed.

Hydrogen spectrum

(1) Hydrogen spectrum is an example of line emission spectrum or atomic emission spectrum.

(2) When an electric discharge is passed through hydrogen gas at low pressure, a bluish light is emitted.

(3) This light shows discontinuous line spectrum of several isolated sharp lines through prism.

(4) All these lines of H-spectrum have Lyman, Balmer, Paschen, Barckett, Pfund and Humphrey series. These spectral series were named by the name of scientist discovered them.

(5) To evaluate wavelength of various H-lines Ritz introduced the following expression,

$$\bar{v} = \frac{1}{\lambda} = \frac{v}{c} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Where R is universal constant known as Rydberg's constant its value is 109, 678 cm^{-1} .

5. Thomson's model.

(1) Thomson regarded atom to be composed of positively charged protons and negatively charged electrons. The two types of particles are equal in number thereby making atom electrically neutral.

(2) He regarded the atom as a positively charged sphere in which negative electrons are uniformly distributed like the seeds in a water melon.

(3) This model failed to explain the line spectrum of an element and the scattering experiment of Rutherford.

Positive charge spreaded throughout the sphere
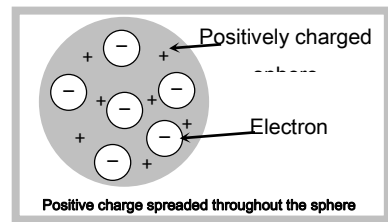
6.   Rutherford's nuclear model.

(1) Rutherford carried out experiment on the bombardment of thin (10–4 mm) Au foil with high speed positively charged $\alpha -$ particles emitted from Ra and gave the following observations, based on this experiment :

(I) Most of the $\alpha -$ particles passed without any deflection.

(ii) Some of them were deflected away from their path.

(iii) Only a few (one in about 10,000) were returned back to their original direction of propagation.

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$$\propto \frac{1}{\sin^4\left(\dfrac{\theta}{2}\right)}.$$
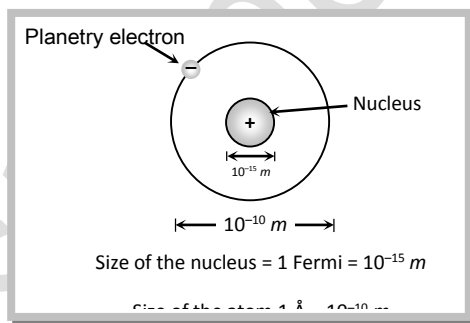
(iv) The scattering of $\alpha-$ particles

Scattering of α-particle

α-particle
(energy E eV)

b

r_0

Nucleus

θ
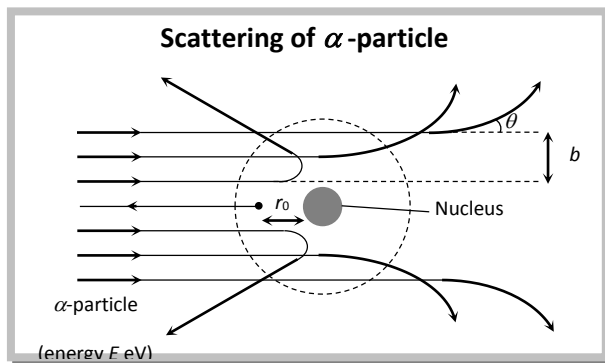
(2) From the above observations he concluded that, an atom consists of

(I) Nucleus which is small in size but carries the entire mass i.e. contains all the neutrons and protons.

(ii) Extra nuclear part which contains electrons. This model was similar to the solar system.

Planetry electron

Nucleus

$+$

$10^{-15}\,m$

$\longleftarrow 10^{-10}\,m \longrightarrow$

Size of the nucleus = 1 Fermi = $10^{-15}\,m$

Size of the atom 1 Å = $10^{-10}\,m$

(3)   Properties of the Nucleus

(I) Nucleus is a small, heavy, positively charged portion of the atom and located at the center of the atom.

(ii) All the positive charge of atom (i.e. protons) are present in nucleus.

(iii) Nucleus contains neutrons and protons, and hence these particles collectively are also referred to as nucleons.

(iv) The size of nucleus is measured in Fermi (1 Fermi = 10–13 cm).

(v) The radius of nucleus is of the order of $1.5 \times 10^{-13} \, cm.$ to $6.5 \times 10^{-13} \, cm.$ i.e. 1.5 to 6.5 Fermi. Generally the radius of the nucleus (r_n) is given by the following relation

$$r_n = r_o (= 1.4 \times 10^{-13} \, cm) \times A^{1/3}$$

This exhibited that nucleus is 10^{-5} times small in size as compared to the total size of atom.

(vi) The Volume of the nucleus is about $10^{-39} \, cm^3$ and that of atom is $10^{-24} \, cm^3$, i.e., volume of the nucleus is 10^{-15} times that of an atom.

(vii) The density of the nucleus is of the order of $10^{15} \, g \, cm^{-3}$ or 10^8 tonnes cm^{-3} or $10^{12} \, kg/cc$. If nucleus is spherical than,

$$\text{Density} = \frac{\text{mass of the nucleus}}{\text{volume of the nucleus}} = \frac{\text{mass number}}{6.023 \times 10^{23} \times \frac{4}{3} \pi r^3}$$

(4) Drawbacks of Rutherford's model

(I) It does not obey the Maxwell theory of electrodynamics, according to it "A small charged particle moving around an oppositely charged center continuously loses its energy". If an electron does so, it should also continuously lose its energy and should set up spiral motion ultimately failing into the nucleus.

(ii) It could not explain the line spectra of $H-$ atom and discontinuous spectrum nature.

Unstability of atom
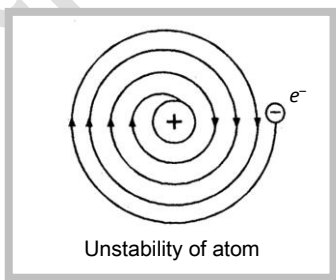
7. Planck's Quantum theory and Photoelectric effect.

Planck's Quantum theory

(1) Max Planck (1900) to explain the phenomena of 'Black body radiation' and 'Photoelectric effect' gave quantum theory. This theory extended by Einstein (1905).

(2) If the substance being heated is a black body (which is a perfect absorber and perfect radiator of energy) the radiation emitted is called black body radiation.

(3) Main points

(I) The radiant energy which is emitted or absorbed by the black body is not continuous but discontinuous in the form of small discrete packets of energy, each such packet of energy is called a 'quantum'. In case of light, the quantum of energy is called a 'photon'.

(ii) The energy of each quantum is directly proportional to the frequency (ν) of the radiation, i.e.

$$E \propto \nu \text{ or } E = h\nu = \frac{hc}{\lambda}$$

Where, $h =$ Planck's constant = 6.62×10–27 erg. sec. or $6.62 \times 10^{-34} \, Joules \, \sec$.

(iii) The total amount of energy emitted or absorbed by a body will be some whole number quanta. Hence $E = nh\nu$, where n is an integer.

(iv) The greater the frequency (i.e. shorter the wavelength) the greater is the energy of the radiation.

Thus, $\dfrac{E_1}{E_2} = \dfrac{\nu_1}{\nu_2} = \dfrac{\lambda_2}{\lambda_1}$

(v) Also $E = E_1 + E_2$, hence, $\dfrac{hc}{\lambda} = \dfrac{hc}{\lambda_1} + \dfrac{hc}{\lambda_2}$ or $\dfrac{1}{\lambda} = \dfrac{1}{\lambda_1} + \dfrac{1}{\lambda_2}$.

Photoelectric effect

(1) When radiations with certain minimum frequency (ν_0) strike the surface of a metal, the electrons are ejected from the surface of the metal. This phenomenon is called photoelectric effect and the electrons emitted are called photo-electrons. The current constituted by photoelectrons is known as photoelectric current.

(2) The electrons are ejected only if the radiation striking the surface of the metal has at least a minimum frequency (ν_0) called Threshold frequency. The minimum potential at which the plate photoelectric current becomes zero is called stopping potential.

(3)The velocity or kinetic energy of the electron ejected depend upon the frequency of the incident radiation and is independent of its intensity.

(4) The number of photoelectrons ejected is proportional to the intensity of incident radiation.

(5) Einstein's photoelectric effect equation: According to Einstein,

Maximum kinetic energy of the ejected electron = absorbed energy – threshold energy

$$\frac{1}{2}mv_{max}^2 = h\nu - h\nu_0 = hc\left[\frac{1}{\lambda} - \frac{1}{\lambda_0}\right]$$

Where, ν_0 and λ_0 are threshold frequency and threshold wavelength.

Note: Nearly all metals emit photoelectrons when exposed to u.v. light. But alkali metals like lithium, sodium, potassium, rubidium and caesium emit photoelectrons even when exposed to visible light.
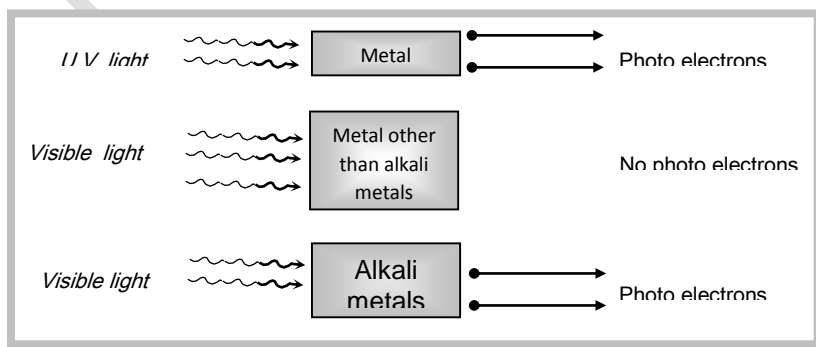
Caesium (Cs) with lowest ionization energy among alkali metals is used in photoelectric cell.

8. Bohr's atomic model.

(1) This model was based on the quantum theory of radiation and the classical law of physics. It gave new idea of atomic structure in order to explain the stability of the atom and emission of sharp spectral lines.

(2) Postulates of this theory are:

(I) The atom has a central massive core nucleus where all the protons and neutrons are present. The size of the nucleus is very small.

(ii) The electron in an atom revolve around the nucleus in certain discrete orbits. Such orbits are known as stable orbits or non – radiating or stationary orbits.

(iii) The force of attraction between the nucleus and the electron is equal to centrifugal force of the moving electron.

Force of attraction towards nucleus = centrifugal force

(iv) An electron can move only in those permissive orbits in which the angular momentum (mvr) of the electron is an integral multiple of $h/2\pi$. Thus, $\mathrm{mvr} = n\dfrac{h}{2\pi}$

Where, m = mass of the electron, r = radius of the electronic orbit, v = velocity of the electron in its orbit.

(v) The angular momentum can be $\dfrac{h}{2\pi}, \dfrac{2h}{2\pi}, \dfrac{3h}{2\pi}, \ldots\ldots \dfrac{nh}{2\pi}$. this principal is known as quantization of angular momentum. In the above equation 'n' is any integer which has been called as principal quantum number. It can have the values n=1, 2, 3, ------- (from the nucleus). Various energy levels are designed as K (n=1), L (n=2), M (n=3) ------- etc. Since the electron present in these orbits is associated with some energy, these orbits are called energy levels.

(vi)   The emission or absorption of radiation by the atom takes place when an electron jumps from one stationary orbit to another.

Emission

Absorption
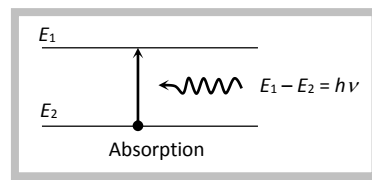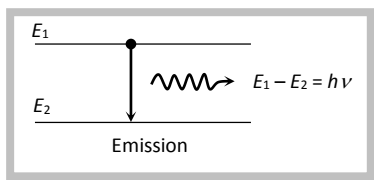
(vii) The radiation is emitted or absorbed as a single quantum (photon) whose energy $h\nu$ is equal to the difference in energy ΔE of the electron in the two orbits involved. Thus, $h\nu = \Delta E$

Where 'h' =Planck's constant, ν = frequency of the radiant energy. Hence the spectrum of the atom will have certain fixed frequency.

(viii) The lowest energy state (n=1) is called the ground state. When an electron absorbs energy, it gets excited and jumps to an outer orbit. It has to fall back to a lower orbit with the release of energy.

(3) Advantages of Bohr's theory

(I) Bohr's theory satisfactorily explains the spectra of species having one electron, viz. hydrogen atom, He^+, Li^{2+} etc.

(ii) Calculation of radius of Bohr's orbit: According to Bohr, radius of orbit in which electron moves is

$$r = \left[\frac{h^2}{4\pi^2 m e^2 k}\right] \cdot \frac{n^2}{Z}$$

Where, n =Orbit number, m =Mass number $\left[9.1 \times 10^{-31} kg\right]$, e =Charge on the electron $\left[1.6 \times 10^{-19}\right]$ Z =Atomic number of element, k = Coulombic constant $\left[9 \times 10^9 \, Nm^2 c^{-2}\right]$

After putting the values of m,e,k,h, we get.

$$r_n = \frac{n^2}{Z} \times 0.529 \text{Å} \text{ or } r_n = \frac{n^2}{Z} \times 0.529 nm$$

(a) For a particular system [e.g., H, He+ or Li+2]

$r \propto n^2$ [Z = constant]

Thus we have $\dfrac{r_1}{r_2} = \dfrac{n_1^2}{n_2^2}$ i.e., $r_1 : r_2 : r_3 \ldots \ldots :: 1 : 4 : 9 \ldots \ldots r_1 < r_2 < r_3$

(b) For particular orbit of different species

$r \propto \dfrac{1}{Z}$ [Z =constant] Considering A and B species, we have $\dfrac{r_A}{r_B} = \dfrac{Z_B}{Z_A}$

Thus, radius of the first orbit H, He^+, Li^{+2} and Be^{+3} follows the order: $H > He^+ > Li^{+2} > Be^{+3}$

(iii) Calculation of velocity of electron

$$V_n = \frac{2\pi e^2 ZK}{nh}, V_n = \left[\frac{Ze^2}{mr}\right]^{1/2}$$

For H atom, $V_n = \frac{2.188 \times 10^8}{n} cm.\sec^{-1}$

(a) For a particular system [H, He+ or Li+2]

$V \propto \dfrac{1}{n}$ [Z = constant] Thus, we have, $\dfrac{V_1}{V_2} = \dfrac{n_2}{n_1}$

The order of velocity is $V_1 > V_2 > V_3 ....$ or $V_1 : V_2 : V_3 .... :: 1 : \dfrac{1}{2} : \dfrac{1}{3} ....$

(b) For a particular orbit of different species

$V \propto Z$ [n =constant] Thus, we have $H < He^+ < Li^{+2}$

(c) For H or He+ or Li+2, we have

$V_1 : V_2 = 2 : 1; \ V_1 : V_3 = 3 : 1; \ V_1 : V_4 = 4 : 1$

(iv) Calculation of energy of electron in Bohr's orbit

Total energy of electron = K.E. + P.E. of electron $= \dfrac{kZe^2}{2r} - \dfrac{kZe^2}{r} = -\dfrac{kZe^2}{2r}$

Substituting of r, gives us $E = \dfrac{-2\pi^2 mZ^2 e^4 k^2}{n^2 h^2}$ Where, n=1, 2, 3..........∞

Putting the value of m, e, k, h, π we get

$E = 21.8 \times 10^{-12} \times \dfrac{Z^2}{n^2} erg\, per\, atom = -21.8 \times 10^{-19} \times \dfrac{Z^2}{n^2} J\, per\, atom (1J = 10^7 erg)$

$$E = -13.6 \times \frac{Z^2}{n^2} eV \, per \, atom (1eV = 1.6 \times 10^{-19} J) = -313.6 \times \frac{Z^2}{n^2} kcal./mole$$ (1 cal = 4.18J)

or $$\frac{-1312}{n^2} Z^2 kJmol^{-1}$$

(a) For a particular system [H, He+ or Li+2]

$E \propto -\dfrac{1}{n^2}$ [Z =constant] Thus, we have $\dfrac{E_1}{E_2} = \dfrac{n_2^2}{n_1^2}$

The energy increase as the value of n increases

(b) For a particular orbit of different species

$E \propto -Z^2$ [n =constant] Thus, we have $\dfrac{E_A}{E_B} = \dfrac{Z_A^2}{Z_B^2}$

For the system H, He+ , Li+2, Be+3 (n-same) the energy order is $H > He^+ > Li^{+2} > Be^{+3}$

The energy decreases as the value of atomic number Z increases.

When an electron jumps from an outer orbit (higher energy) n_2 to an inner orbit (lower energy) n_1, then the energy emitted in form of radiation is given by

$$\Delta E = E_{n_2} - E_{n_1} = \frac{2\pi^2 k^2 m e^4 Z^2}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \Rightarrow \Delta E = 13.6 Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) eV / atom$$

As we know that $E = h\bar{v}, c = v\lambda$ and $\bar{v} = \dfrac{1}{\lambda} = \dfrac{\Delta E}{hc}, = \dfrac{2\pi^2 k^2 m e^4 Z^2}{ch^3}\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$

This can be represented as $\dfrac{1}{\lambda} = \bar{v} = RZ^2\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$ where, $R = \dfrac{2\pi^2 k^2 m e^4}{ch^3} R$ is known as Rydberg constant. Its value to be used is $109678 cm^{-1}$.

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(4) Quantization of energy of electron

(I) In ground state: No energy emission. In ground state energy of atom is minimum and for 1st orbit of   H-atom, n=1.

$$\therefore E_1 = -13.6 eV.$$

(ii) In excited state: Energy levels greater than n_1 are excited state. i.e. for H- atom n_2, n_3, n_4 are excited state. For H- atom first excitation state is $= n_2$

(iii) Excitation potential: Energy required to excite electron from ground state to any excited state.

Ground state $\longrightarrow$ Excited state

Ist excitation potential = $E_2 - E_1 = -3.4 + 13.6 =$ 10.2 eV.

IInd excitation potential = $E_3 - E_1 = -1.5 + 13.6 = 12.1 \, eV.$

(iv) Ionization energy: The minimum energy required to relieve the electron from the binding of nucleus.

$$\boxed{E_{\text{ionisation}} = E_\infty - E_n = +13.6 \frac{Z_{\text{eff.}}^2}{n^2} eV.}$$

(v) Ionization potential: $V_{\text{ionisation}} = \dfrac{E_{ionisation}}{e}$

(vi) Separation energy: Energy required to excite an electron from excited state to infinity.

S.E. = $E_\infty - E_{excited}$.

(vii) Binding energy: Energy released in bringing the electron from infinite to any orbit is called its binding energy (B.E.).

Note: Principal Quantum Number 'n' = $\sqrt{\dfrac{13.6}{(B.E.)}}$.

(5) Spectral evidence for quantization (Explanation for hydrogen spectrum on the basis of Bohr atomic model)

(I) The light absorbed or emitted as a result of an electron changing orbits produces characteristic absorption or emission spectra which can be recorded on the photographic plates as a series of lines, the optical spectrum of hydrogen consists of several series of lines called

Lyman, Balmar, Paschen, Brackett, Pfund and Humphrey. These spectral series were named by the name of scientist who discovered them.

(ii) To evaluate wavelength of various H-lines Ritz introduced the following expression,

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Where, R is = $\dfrac{2\pi^2 m e^4}{ch^3}$ = Rydberg's constant

Its theoretical value = 109,737 cm–1 and its experimental value = $109,677.581 cm^{-1}$

This remarkable agreement between the theoretical and experimental value was great achievement of the Bohr model.

(iii) Although H- atom consists only one electron yet its spectra consist of many spectral lines as shown in fig.
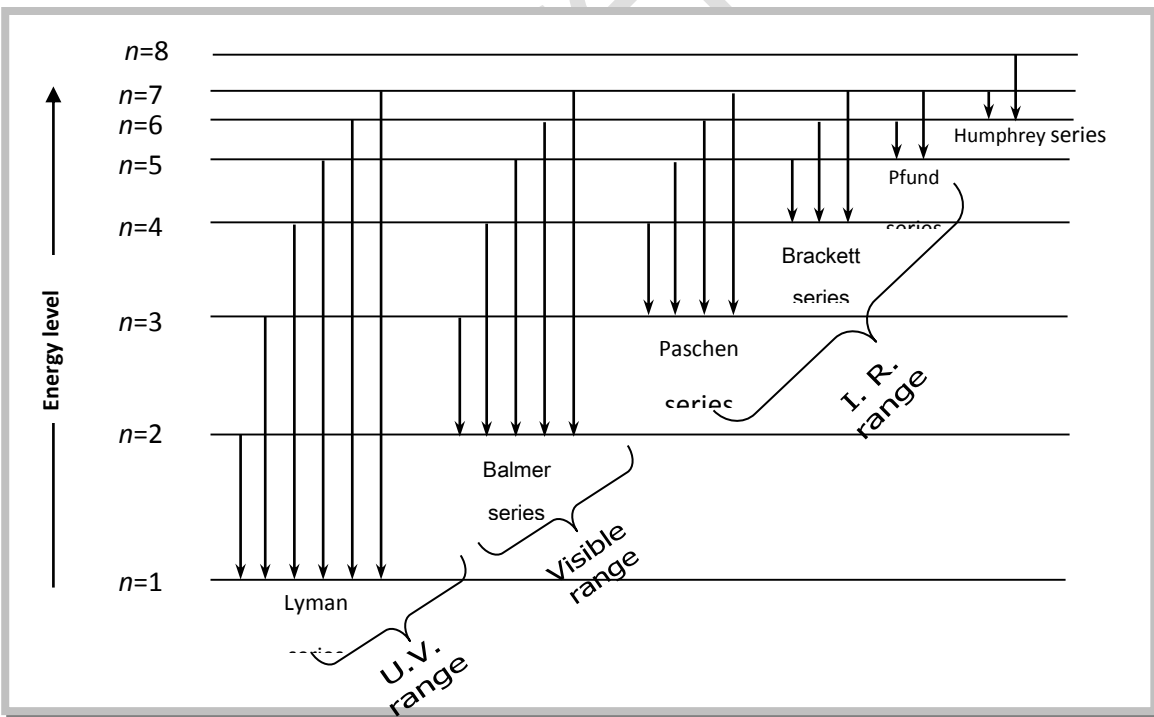
(iv) Comparative study of important spectral series of Hydrogen

S.No.	Spectral series	Lies in the region	Transition $n_2 > n_1$	$\lambda_{max} = \dfrac{n_1^2 n_2^2}{(n_2^2 - n_1^2)R}$	$\lambda_{min} = \dfrac{n_1^2}{R}$	$\dfrac{\lambda_{max}}{\lambda_{min}} = \dfrac{n_2^2}{n_2^2 - n_1^2}$
(1)	Lymen series	Ultraviolet region	$n_1 = 1$ $n_2 = 2,3,4....\infty$	$n_1 = 1$ and $n_2 = 2$ $\lambda_{max} = \dfrac{4}{3R}$	$n_1 = 1$ and $n_2 = \infty$ $\lambda_{min} = \dfrac{1}{R}$	$\dfrac{4}{3}$
(2)	Balmer series	Visible region	$n_1 = 2$ $n_2 = 3,4,5....\infty$	$n_1 = 2$ and $n_2 = 3$ $\lambda_{max} = \dfrac{36}{5R}$	$n_1 = 2$ and $n_2 = \infty$ $\lambda_{min} = \dfrac{4}{R}$	$\dfrac{9}{5}$
(3)	Paschen series	Infra red region	n1 = 3 $n_2 = 4,5,6....\infty$	$n_1 = 3$ and $n_2 = 4$ $\lambda_{max} = \dfrac{144}{7R}$	$n_1 = 3$ and $n_2 = \infty$ $\lambda_{min} = \dfrac{9}{R}$	$\dfrac{16}{7}$
(4)	Brackett series	Infra red region	$n_1 = 4$ $n_2 = 5,6,7....\infty$	$n_1 = 4$ and $n_2 = 5$ $\lambda_{max} = \dfrac{16 \times 25}{9R}$	$n_1 = 4$ and $n_2 = \infty$ $\lambda_{min} = \dfrac{16}{R}$	$\dfrac{25}{9}$
(5)	Pfund series	Infra red region	$n_1 = 5$ $n_2 = 6,7,8....\infty$	$n_1 = 5$ and $n_2 = 6$ $\lambda_{max} = \dfrac{25 \times 36}{11R}$	$n_1 = 5$ and $n_2 = \infty$ $\lambda_{min} = \dfrac{25}{R}$	$\dfrac{36}{11}$
(6)	Humphrey series	Far infrared region	$n_1 = 6$ $n_2 = 7,8....\infty$	$n_1 = 6$ and $n_2 = 7$ $\lambda_{max} = \dfrac{36 \times 49}{13R}$	$n_1 = 6$ and $n_2 = \infty$ $\lambda_{min} = \dfrac{36}{R}$	$\dfrac{49}{13}$

(v) If an electron from nth excited state comes to various energy states, the maximum spectral lines obtained will be = $\dfrac{n(n-1)}{2}$. n= principal quantum number.

As n=6 than total number of spectral lines = $\dfrac{6(6-1)}{2} = \dfrac{30}{2} = 15.$

(vi) Thus, at least for the hydrogen atom, the Bohr Theory accurately describes the origin of atomic spectral lines.

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(6) Failure of Bohr Model

(I) Bohr Theory was very successful in predicting and accounting the energies of line spectra of hydrogen i.e. one electron system. It could not explain the line spectra of atoms containing more than one electron.

(ii) This theory could not explain the presence of multiple spectral lines.

(iii) This theory could not explain the splitting of spectral lines in magnetic field (Zeeman Effect) and in electric field (Stark effect). The intensity of these spectral lines was also not explained by the Bohr atomic model.

(iv) This theory was unable to explain of dual nature of matter as explained on the basis of De broglies concept.

(v) This theory could not explain uncertainty principle.

(vi) No conclusion was given for the concept of quantization of energy.

9.   Bohr – Sommerfeld's model.

(1) In 1915, Sommerfield introduced a new atomic model to explain the fine spectrum of hydrogen atom.

(2) He gave concept that electron revolve round the nucleus in elliptical orbit. Circular orbits are formed in special conditions only when major axis and minor axis of orbit are equal.

(3) For circular orbit, the angular momentum = $\dfrac{nh}{2\pi}$ where n= principal quantum number only one component i.e. only angle changes.

(4) For elliptical orbit, angular momentum = vector sum of 2 components. In elliptical orbit two components are,
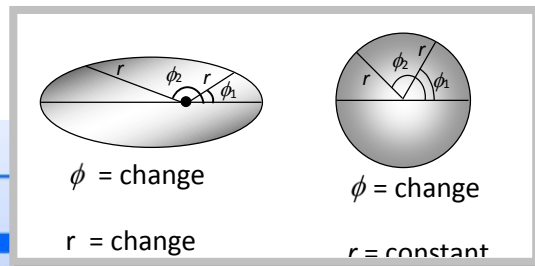
(I) Radial component (along the radius) = $n_r \dfrac{h}{2\pi}$

Where, n_r = radial quantum number

(ii) Azimuthal component = $n_\phi \dfrac{h}{2\pi}$

Where, n_ϕ = azimuthal quantum number

So angular momentum of elliptical orbit = $n_r \dfrac{h}{2\pi} + n_\phi \dfrac{h}{2\pi}$

ϕ = change

r = change

ϕ = change

r = constant

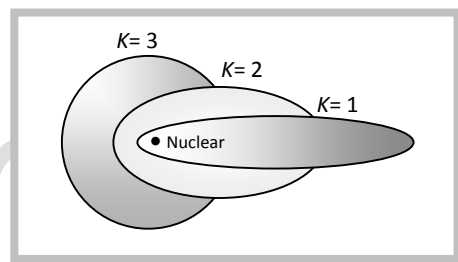Angular momentum = $(n_r + n_\phi)\dfrac{h}{2\pi}$

(5) Shape of elliptical orbit depends on,

$$\dfrac{\text{Length of major axis}}{\text{Length of minor axis}} = \dfrac{n}{n_\phi} = \dfrac{n_r + n_\phi}{n_\phi}$$

(6) n^ϕ can take all integral values from l to 'n' values of n_r depend on the value of n^ϕ. For n = 3, n $^\phi$ can have values 1, 2, 3 and n_r can have (n −1) to zero i.e. 2,1 and zero respectively.

Thus for n = 3, we have 3 paths

n	n^ϕ	n^r	Nature of path
3	1	3	elliptical
	2	1	elliptical
	3	0	circular

The possible orbits for n = 3 are shown in figure.

Thus Sommerfield showed that Bohr's each major level was composed of several sub-levels. Therefore it provides the basis for existence of subshells in Bohr's shells (orbits).

(7) Limitation of Bohr Sommerfield model:

(I) This model could not account for, why electrons does not absorb or emit energy when they are moving in stationary orbits.

(ii) When electron jumps from inner orbit to outer orbit or vice –versa, then electron run entire distance but absorption or emission of energy is discontinuous.

(iii) It could not explain the attainment of expression of $\dfrac{nh}{2\pi}$ for angular momentum. This model could not explain Zeeman Effect and Stark effect.

10. Dual nature of electron.

(1) In 1924, the French physicist, Louis de Broglie suggested that if light has both particle and wave like nature, the similar duality must be true for matter. Thus an electron, behaves both as a material particle and as a wave.

(2) This presented a new wave mechanical theory of matter. According to this theory, small particles like electrons when in motion possess wave properties.

(3) According to de-Broglie, the wavelength associated with a particle of mass m, moving with velocity v is given by the relation

$$\lambda = \frac{h}{mv},$$ Where h = Planck's constant.

(4) This can be derived as follows according to Planck's equation, $E = h\nu = \frac{h.c}{\lambda} \quad \left(\because \nu = \frac{c}{\lambda}\right)$

Energy of photon (on the basis of Einstein's mass energy relationship), $E = mc^2$

Equating both $\frac{hc}{\lambda} = mc^2 \ or \ \lambda = \frac{h}{mc}$ which is same as de-Broglie relation. $(\because mc = p)$

(5) This was experimentally verified by Davisson and Germer by observing diffraction effects with an electron beam. Let the electron is accelerated with a potential of V than the Kinetic energy is

$$\frac{1}{2}mv^2 = eV \quad \therefore \quad m^2v^2 = 2eVm$$

$$mv = \sqrt{2eVm} = P \ ; \quad \lambda = \frac{h}{\sqrt{2eVm}}$$

(6) If Bohr's theory is associated with de-Broglie's equation then wave length of an electron can be determined in Bohr's orbit and relate it with circumference and multiply with a whole number

$$2\pi r = n\lambda \ or \ \lambda = \frac{2\pi r}{n}$$

From de-Broglie equation, $\lambda = \frac{h}{mv}$. Thus $\frac{h}{mv} = \frac{2\pi r}{n}$ or $mvr = \frac{nh}{2\pi}$

Note: For a proton, electron and an α-particle moving with the same velocity have de-Broglie wavelength in the following order: Electron > Proton > α - particle.

(7) The de-Broglie equation is applicable to all material objects but it has significance only in case of microscopic particles. Since, we come across macroscopic objects in our everyday life, de-Broglie relationship has no significance in everyday life.

11. Heisenberg's uncertainty principle.
12.

(1) One of the important consequences of the dual nature of an electron is the uncertainty principle, developed by Warner Heisenberg.

(2) According to uncertainty principle "It is impossible to specify at any given moment both the position and momentum (velocity) of an electron".

Mathematically it is represented as , $\boxed{\Delta x . \Delta p \geq \dfrac{h}{4\pi}}$

Where $\Delta x =$ uncertainty is position of the particle, $\Delta p =$ uncertainty in the momentum of the particle

Now since $\Delta p = m \Delta v$

So equation becomes, $\Delta x . m \Delta v \geq \dfrac{h}{4\pi}$ or $\Delta x \times \Delta v \geq \dfrac{h}{4\pi m}$

The sign $\geq$ means that the product of Δx and Δp (or of Δx and Δv) can be greater than, or equal to but never smaller than $\dfrac{h}{4\pi}$. If Δx is made small, Δp increases and vice versa.

(3) In terms of uncertainty in energy, ΔE and uncertainty in time Δt, this principle is written as,

$\Delta E . \Delta t \geq \dfrac{h}{4\pi}$

Note: Heisenberg's uncertainty principle cannot we apply to a stationary electron because its velocity is 0 and position can be measured accurately.

13. Schrödinger wave equation.

(1) Schrodinger wave equation is given by Erwin Schrödinger in 1926 and based on dual nature of electron.

(2) In it electron is described as a three dimensional wave in the electric field of a positively charged nucleus.

(3) The probability of finding an electron at any point around the nucleus can be determined by the help of Schrodinger wave equation which is,

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\Psi = 0$$

Where x, y and z are the 3 space co-ordinates, m = mass of electron, h = Planck's constant,

E = Total energy, V = potential energy of electron, Ψ = amplitude of wave also called as wave function.

∂ = stands for an infinitesimal change.

(4) The Schrodinger wave equation can also be written as:

$$\nabla^2 \Psi + \frac{8\pi^2 m}{h^2}(E - V)\,\Psi = 0$$

Where ∇ = laplacian operator.

(5) Physical Significance of Ψ and Ψ^2

(I)The wave function Ψ represents the amplitude of the electron wave. The amplitude Ψ is thus a function of space co-ordinates and time i.e. $\Psi = \Psi(x, y, z......times)$

(ii)For a single particle, the square of the wave function (Ψ^2) at any point is proportional to the probability of finding the particle at that point.

(iii) If Ψ^2 is maximum than probability of finding e^- is maximum around nucleus. And the place where probability of finding e^- is maximum is called electron density, electron cloud or an atomic orbital. It is different from the Bohr's orbit.

(iv) The solution of this equation provides a set of number called quantum numbers which describe specific or definite energy state of the electron in atom and information about the shapes and orientations of the most probable distribution of electrons around the nucleus.

14. Quantum numbers and Shapes of orbitals.

Quantum numbers

(1) Each orbital in an atom is specified by a set of three quantum numbers (n, l, and m) and each electron is designated by a set of four quantum numbers (n, l, m and s).

(2) Principle quantum number (n)

(I) It was proposed by Bohr's and denoted by 'n'.

(ii) It determines the average distance between electron and nucleus, means it is denoted the size of atom.

$$r = \frac{n^2}{Z} \times 0.529 \mathring{A}$$

(iii) It determine the energy of the electron in an orbit where electron is present.

$$E = -\frac{Z^2}{n^2} \times 313.3 \, Kcal \, per \, mole$$

(iv) The maximum number of an electron in an orbit represented by this quantum number as $2n^2$. No energy shell in atoms of known elements possess more than 32 electrons.

(v) It gives the information of orbit K, L, M, N------------.

(vi) The value of energy increases with the increasing value of n.

(vii) It represents the major energy shell or orbit to which the electron belongs.

(viii) Angular momentum can also be calculated using principle quantum number

$$mvr = \frac{nh}{2\pi}$$

(3) Azimuthal quantum number (l)

(I) Azimuthal quantum number is also known as angular quantum number. Proposed by Sommerfield and denoted by 'l'.

(ii) It determines the number of sub shells or sublevels to which the electron belongs.

(iii) It tells about the shape of subshells.

(iv) It also expresses the energies of subshells $s < p < d < f$ (increasing energy).

(v) The value of $l = (n - 1)$ always where 'n' is the number of principle shell.

(vi)   Value of l = 0, 1, 2, 3..........(n-1)

Value of l	=	0	1	2	3..........(n-1)
Name of subshell	=	s	p	d	f
Shape of subshell	=	Spherical	Dumbbell	Double dumbbell	Complex

(vii) It represent the orbital angular momentum. Which is equal to $\dfrac{h}{2\pi}\sqrt{l(l+1)}$

(viii) The maximum number of electrons in subshell $= 2(2l + 1)$

$$s - \text{subshell} \rightarrow 2 \text{ electrons} \quad d - \text{subshell} \rightarrow 10 \text{ electrons}$$

$$p - \text{subshell} \rightarrow 6 \text{ electrons} \quad f - \text{subshell} \rightarrow 14 \text{ electrons.}$$

(ix) For a given value of 'n' the total value of 'l' is always equal to the value of 'n'.

(x) The energy of any electron is depend on the value of n & l because total energy = (n + l). The electron enters in that sub orbit whose (n + l) value or the value of energy is less.

(4) Magnetic quantum number (m)

(I) It was proposed by Zeeman and denoted by 'm'.

(ii) It gives the number of permitted orientation of subshells.

(iii) The value of m varies from –l to +l through zero.

(iv) It tells about the splitting of spectral lines in the magnetic field i.e. this quantum number proved the Zeeman effect.

(v) For a given value of 'n' the total value of 'm' is equal to n^2.

(vi) For a given value of 'l' the total value of 'm' is equal to $(2l + 1)$.

(vii) Degenerate orbitals: Orbitals having the same energy are known as degenerate orbitals. E.g. for p subshell p_x p_y p_z

(viii) The number of degenerate orbitals of s subshell $= 0$.
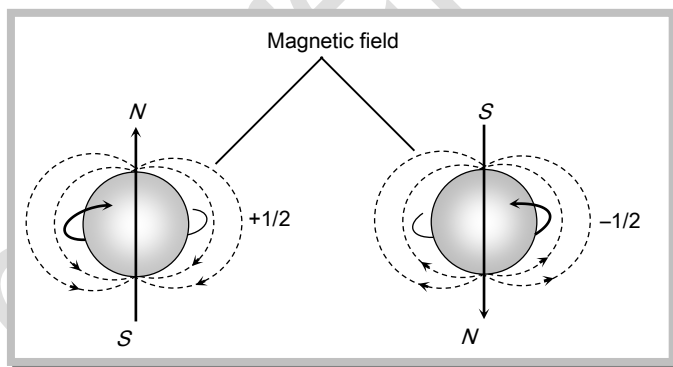
(5) Spin quantum numbers (s)

(I) It was proposed by Goldshmidt & Ulen Back and denoted by the symbol of 's'.

(ii) The value of $'s'$ is $+1/2$ and $-1/2$, which is signifies the spin or rotation or direction of electron on its axis during movement.

(iii) The spin may be clockwise or anticlockwise.

(iv) It represents the value of spin angular momentum is equal to $\dfrac{h}{2\pi}\sqrt{s(s+1)}.$

(v) Maximum spin of an atom $= 1/2 \times$ number of unpaired electron.

(vi) This quantum number is not the result of solution of Schrodinger equation as solved for H-atom.

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Distribution of electrons among the quantum levels

| n	l	m	s	Designation of orbitals	Electrons present	Total no. of electrons
1 (K shell)	0	0	+1/2, −1/2	1s	2	2
2 (L shell)	0	0	$+1/2, -1/2$	2s	2 ⎤	8
	1	+1	$+1/2, -1/2$	2p		
		0	$+1/2, -1/2$		6 ⎦	
		−1	$+1/2, -1/2$			
3 (M shell)	0	0	$+1/2, -1/2$	3s	2 ⎤	18
		+1	$+1/2, -1/2$			
	1	0	$+1/2, -1/2$	3p	6	
		−1	$+1/2, -1/2$			
		+2	$+1/2, -1/2$			
		+1	$+1/2, -1/2$	3d		
	2	0	$+1/2, -1/2$			
		−1	$+1/2, -1/2$			
		−2	$+1/2, -1/2$		10 ⎦	
	0	0	$+1/2, -1/2$	4s	2 ⎤	32
		+1	$+1/2, -1/2$			
	1	0	$+1/2, -1/2$	4p	6	
		−1	$+1/2, -1/2$			
		+2	$+1/2, -1/2$			
		+1	$+1/2, -1/2$			
	2	0	$+1/2, -1/2$	4d		
		−1	$+1/2, -1/2$			
4 (N shell)		−2	$+1/2, -1/2$		10	
		+3	$+1/2, -1/2$			
		+2	$+1/2, -1/2$			
		+1	$+1/2, -1/2$			
	3	+0	$+1/2, -1/2$	4f		
		−1	$+1/2, -1/2$			
		−2	$+1/2, -1/2$			
		−3	$+1/2, -1/2$		14 ⎦	

Shape of orbitals

(1) Shape of 's' orbital

(I) For 's' orbital l=0 & m=0 so 's' orbital have only one unidirectional orientation i.e. the probability of finding the electrons is same in all directions.

(ii) The size and energy of 's' orbital with increasing 'n' will be $1s < 2s < 3s < 4s$.

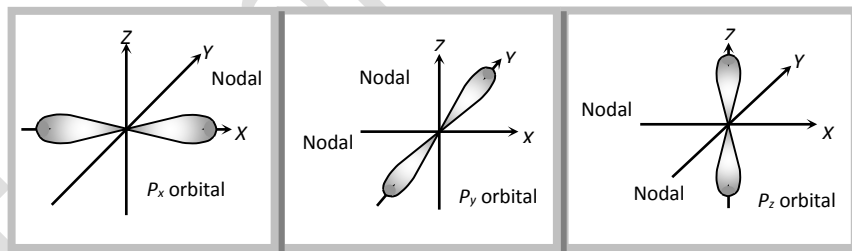(iii) It does not possess any directional property. S orbital has spherical shape.
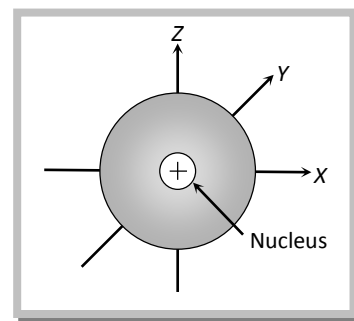
(2) Shape of 'p' orbitals

(I) For 'p' orbital l=1, & m=+1,0,–1 means there are three 'p' orbitals, which is symbolized as p_x, p_y, p_z.

(ii) Shape of 'p' orbital is dumb bell in which the two lobes on opposite side separated by the nodal plane.

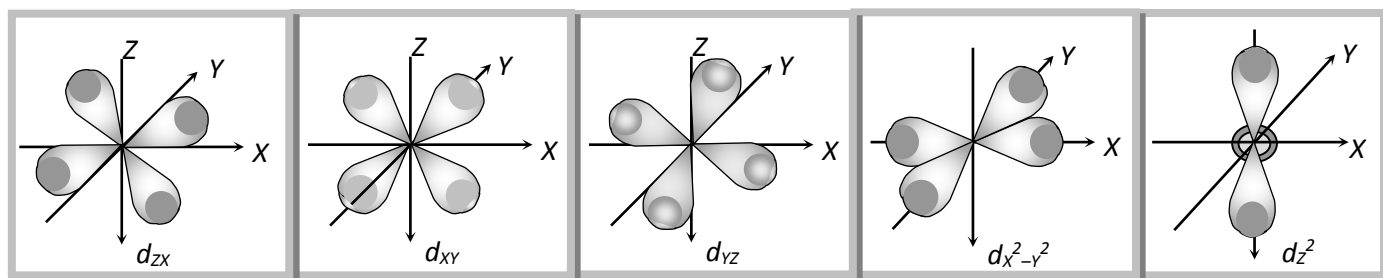(iii) p-orbital has directional properties.

(3) Shape of 'd' orbital

(I) For the 'd' orbital l =2 then the values of 'm' are –2,–1,0,+1,+2. It shows that the 'd' orbitals has five orbitals as $d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{z^2}.$

(ii) Each 'd' orbital identical in shape, size and energy.

(iii) The shape of d orbital is double dumb bell.

(iv) It has directional properties.

(4) Shape of 'f' orbital

(I) For the 'f' orbital l=3 then the values of 'm' are –3, –2, –1,0,+1,+2,+3. It shows that the 'f' orbitals have seven orientation as $f_{x(x^2-y^2)}, f_{y(x^2-y^2)}, f_{z(x^2-y^2)}, f_{xyz}, f_{z^3}, f_{yz^3}$ and f_{xz^2}.

(ii) The 'f' orbital is complicated in shape.

15. Electronic configuration principles.

The distribution of electrons in different orbitals of atom is known as electronic configuration of the atoms.

Filling up of orbitals in the ground state of atom is governed by the following rules:

(1) Aufbau principle

(I) Auf bau is a German word, meaning 'building up'.

(ii) According to this principle, "In the ground state, the atomic orbitals are filled in order of increasing energies i.e. in the ground state the electrons first occupy the lowest energy orbitals available".

(iii) In fact the energy of an orbital is determined by the quantum number n and l with the help of (n+l) rule or Bohr Bury rule.

(iv) According to this rule

(a) Lower the value of n + l, lower is the energy of the orbital and such an orbital will be filled up first.

(b) When two orbitals have same value of (n+l) the orbital having lower value of "n" has lower energy and such an orbital will be filled up first.

Thus, order of filling up of orbitals is as follows:

$$1s < 2s < 2p < 3s < 3p < 4s < 4p < 5s < 4d < 5p < 6s < 6f < 5d$$

(2) Pauli's exclusion principle

(I) According to this principle, "No two electrons in an atom can have same set of all the four quantum numbers n, l, m and s .

(ii) In an atom any two electrons may have three quantum numbers identical but fourth quantum number must be different.

(iii) Since this principle excludes certain possible combinations of quantum numbers for any two electrons in an atom, it was given the name exclusion principle. Its results are as follows:

(a) The maximum capacity of a main energy shell is equal to $2n^2$ electron.

(b) The maximum capacity of a subshell is equal to 2(2l+1) electron.

(c) Number of sub-shells in a main energy shell is equal to the value of n.

(d) Number of orbitals in a main energy shell is equal to n^2.

(e) One orbital cannot have more than two electrons.

(iv) According to this principle an orbital can accommodate at the most two electrons with spins opposite to each other. It means that an orbital can have 0, 1, or 2 electron.

(v) If an orbital has two electrons they must be of opposite spin.

| ⇅ | ⇅ |

Correct

| ⇈ | ⇊ |

Incorrect
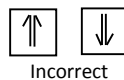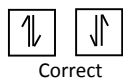
(3) Hund's Rule of maximum multiplicity

(I) This rule provides the basis for filling up of degenerate orbitals of the same sub-shell.

(ii) According to this rule "Electron filling will not take place in orbitals of same energy until all the available orbitals of a given subshell contain one electron each with parallel spin".

(iii) This implies that electron pairing begins with fourth, sixth and eighth electron in p, d and f orbitals of the same subshell respectively.

(iv) The reason behind this rule is related to repulsion between identical charged electrons present in the same orbital.

(v) They can minimize the repulsive force between them serves by occupying different orbitals.

(vi) Moreover, according to this principle, the electron entering the different orbitals of subshell have parallel spins. This keep them farther apart and lowers the energy through electron exchange or resonance.

(vii) The term maximum multiplicity means that the total spin of unpaired e^- is maximum in case of correct filling of orbitals as per this rule.

Energy level diagram

The representation of relative energy levels of various atomic orbital is made in the terms of energy level diagrams.

One electron system: In this system $1s^2$ level and all orbital of same principal quantum number have same energy, which is independent of (l). In this system l only determines the shape of the orbital.

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Multiple electron system: The energy levels of such system not only depend upon the nuclear charge but also upon the electron present in them.
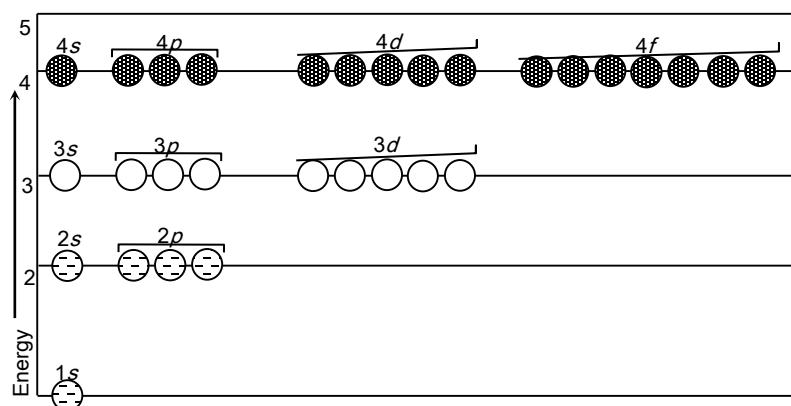
Energy level diagram of one electron system

Energy level diagram of multiple electron system

Diagram of multi-electron atoms reveals the following points:

(i)   As the distance of the shell increases from the nucleus, the energy level increases. For example energy level of 2 > 1.

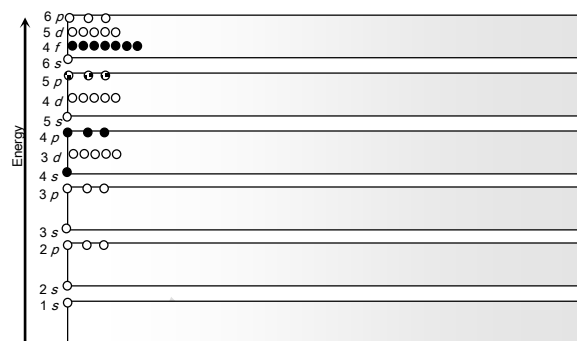(ii)   The different sub shells have different energy levels which possess definite energy. For a definite shell, the subshell having higher value of l possesses higher energy level. For example in 4th shell.

Energy level order   4f   >   4d   >   4p   >   4s

               l= 3   l = 2   l = 1   l= 0

(iii)   The relative energy of sub shells of different energy shell can be explained in the terms of the (n+l) rule.

(a)   The sub-shell with lower values of (n + l) possess lower energy.

For   3d   n = 3   l= 2   ∴ n + l = 5

For   4s   n = 4   l = 0   n + l = 4

(b)   If the value of (n + l) for two orbitals is same, one with lower values of 'n' possess lower energy level.

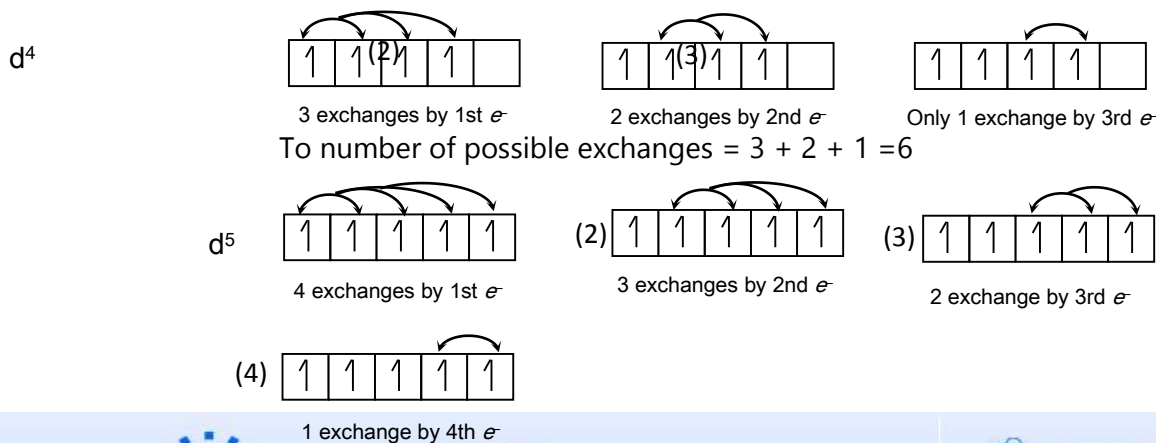Extra stability of half-filled and completely filled orbitals

Half-filled and completely filled sub-shell have extra stability due to the following reasons:

(I) Symmetry of orbitals

(a)   It is a well-known fact that symmetry leads to stability.

(b)   Thus, if the shift of an electron from one orbital to another orbital differing slightly in energy results in the symmetrical electronic configuration. It becomes more stable.

(c)   For example p^3, d^5, f^7 configurations are more stable than their near ones.

(ii) Exchange energy

(a)   The electron in various subshells can exchange their positions, since electron in the same subshell have equal energies.

(b)   The energy is released during the exchange process with in the same subshell.

(c)   In case of half-filled and completely filled orbitals, the exchange energy is maximum and is greater than the loss of orbital energy due to the transfer of electron from a higher to a lower sublevel e.g. from 4s to 3d orbitals in case of Cu and Cr .

(d)   The greater the number of possible exchanges between the electrons of parallel spins present in the degenerate orbitals, the higher would be the amount of energy released and more will be the stability.

(e)   Let us count the number of exchange that are possible in d^4 and d^5 configuration among electrons with parallel spins.

d⁴

3 exchanges by 1st e⁻   2 exchanges by 2nd e⁻   Only 1 exchange by 3rd e⁻

To number of possible exchanges = 3 + 2 + 1 = 6

d⁵

4 exchanges by 1st e⁻   (2) 3 exchanges by 2nd e⁻   (3) 2 exchange by 3rd e⁻

(4) 1 exchange by 4th e⁻

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To number of possible exchanges = 4 + 3 + 2 +1 = 10

16. Electronic configurations of Elements.

(1) On the basis of the electronic configuration principles the electronic configuration of various elements are given in the following table:
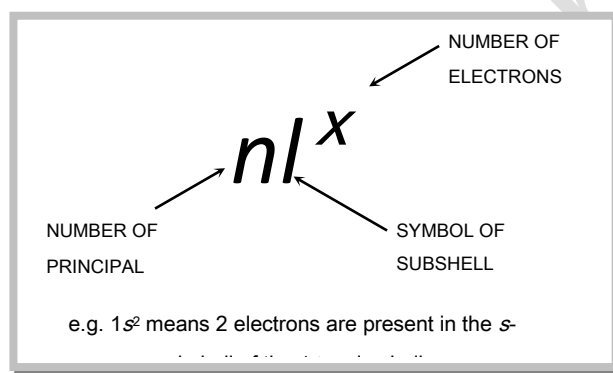
Electronic Configuration (E.C.) of Elements Z=1 to 36

Element	Atomic Number	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f
H	1	1									
He	2	2									
Li	3	2	1								
Be	4	2	2								
B	5	2	2	1							
C	6	2	2	2							
N	7	2	2	3							
O	8	2	2	4							
F	9	2	2	5							
Ne	10	2	2	6							
Na	11	2	2	6	1						
Mg	12				2						
Al	13				2	1					
Si	14	10			2	2					
P	15	electrons			2	3					
S	16				2	4					
Cl	17				2	5					
Ar	18	2	2	6	2	6					
K	19	2	2	6	2	6		1			
Ca	20							2			
Sc	21						1	2			
Ti	22						2	2			
V	23						3	2			
Cr	24						5	1			
Mn	25						5	2			
Fe	26						6	2			

Element	Z	1s	2s	2p	3s	3p	3d	4s	4p
Co	27	18					7	2	
Ni	28	electrons					8	2	
Cu	29						10	1	
Zn	30						10	2	
Ga	31						10	2	1
Ge	32						10	2	2
As	33						10	2	3
Se	34						10	2	4
Br	35						10	2	5
Kr	36	2	2	6	2	6	10	2	6

(2) The above method of writing the electronic configurations is quite cumbersome. Hence, usually the electronic configuration of the atom of any element is simply represented by the notation.

$$nl^x$$

NUMBER OF ELECTRONS

NUMBER OF PRINCIPAL

SYMBOL OF SUBSHELL

e.g. $1s^2$ means 2 electrons are present in the s-

(3)   (I) Elements with atomic number 24(Cr), 42(Mo) and 74(W) have $ns^1(n-1)d^5$ configuration and not $ns^2(n-1)d^4$ due to extra stability of these atoms.

(ii) Elements with atomic number 29(Cu), 47(Ag) and 79(Au) have $ns^1(n-1)d^{10}$ configuration instead of $ns^2(n-1)d^9$ due to extra stability of these atoms.

Cr (24)   [Ar] $4s^1$ $3d^5$ Cu (29)   [Ar] $4s^1$ $3d^{10}$
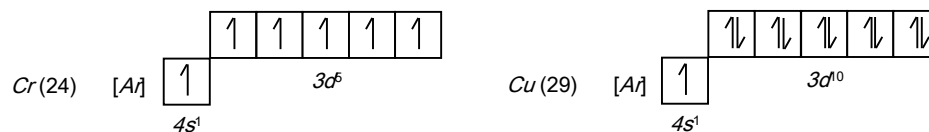
(4) In the formation of ion, electrons of the outer most orbit are lost. Hence, whenever you are required to write electronic configuration of the ion, first write electronic configuration of its atom and take

electron from outermost orbit. If we write electronic configuration of $Fe^{2+}(Z = 26,\ 24\,e^-)$, it will not be similar to Cr (with $24\,e^-$) but quite different.
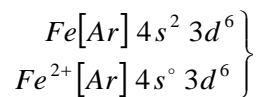
$$\left.\begin{array}{l} Fe[Ar]\,4s^2\,3d^6 \\ Fe^{2+}[Ar]\,4s^\circ\,3d^6 \end{array}\right\}$$ Outer most orbit is 4th shell hence, electrons from 4s have been removed to make Fe^{2+}.

(5) Ion/atom will be paramagnetic if there are unpaired electrons. Magnetic moment (spin only) is $\mu = \sqrt{n(n+2)}$ BM (Bohr Magneton). $(1BM = 9.27 \times 10^{-24}\,J/T)$ Where n is the number of unpaired electrons.

(6) Ion with unpaired electron in d or f orbital will be colored. Thus, Cu^+ with electronic configuration $[Ar]3d^{10}$ is colorless and Cu^{2+} with electronic configuration $[Ar]3d^9$ (one unpaired electron in 3d) is colored (blue).

(7) Position of the element in periodic table on the basis of electronic configuration can be determined as,

> (I) If last electron enters into s-subshell, p-subshell, penultimate d-subshell and anti-penultimate f-subshell then the element belongs to s, p, d and f – block respectively.
>
> (ii) Principle quantum number (n) of outermost shell gives the number of period of the element.
>
> (ii) If the last shell contains 1 or 2 electrons (i.e. for s-block elements having the configuration ns^{1-2}), the group number is 1 in the first case and 2 in the second case.
>
> (iv) If the last shell contains 3 or more than 3 electrons (i.e. for p-block elements having the configuration $ns^2\,np^{1-6}$), the group number is the total number of electrons in the last shell plus 10.
>
> (v) If the electrons are present in the (n −1) d orbital in addition to those in the ns orbital (i.e. for d-block elements having the configuration (n −1)$d^{1-10}ns^{1-2}$), the group number is equal to the total number of electrons present in the (n −1) d orbital and ns orbital.