

Atomic Structure

Cocept of Acharya Kanada:

Acharya Kanada, also known as Kashyapa, an ancient Indian natural scientist and philosopher, formulated the theory of atoms 2500 years before John Dalton's discovery.

Dalton's Atomic Theory:

John Dalton in 1808 proposed that

- (i) All matter is made of very tiny particles called atoms.
- (ii) Atoms are indivisible particles, which cannot be created or destroyed in a chemical reaction.
- (iii) Atoms of a given element are identical in mass and chemical properties.
- (iv) Atoms of different elements have different masses and chemical properties.

Subatomic Particles

Discovery of subatomic particles in late nineteenth and early twentieth century set a blow to Dalton's atomic model of hard sphere. Three important subatomic particles, namely, proton, electron and neutron which are of concern to Chemistry were discovered.

ELECTRON : (I) J. J. Thomson investigated the cathode rays and found that the cathode rays are a stream of very small, negatively charged particles which are 1837 times lighter than a hydrogen atom and are present in all atoms. Later these particles were named as electrons.

(II) Charge : It was determined by Mullikan by oil drop method as -1.602×10^{-19} coulombs or 4.803×10^{-10} e.s.u.

(III) Mass : It was found by J. J. Thomson as 9.11×10^{-28} g

(IV) Specific charge : e/m ratio is called specific charge and was determined by Thomson as 1.76×10^8 coulombs/gm

(V) Radius : It is of the order 10^{-15} cm.

(VI) Density : 2.17×10^{17} g/cc.

(VII) Mass of electron at speed v is $m =$

PROTON:

In the year 1911, Ernest Rutherford found in the experiment of scattering of α -particles by thin gold foil (see Fig. 4.2) that a few α -particles bounce back. From this he inferred the presence of massive and positively charged nucleus inside the atom. Following the discovery of nucleus in an atom, Rutherford found (1919) that fast moving α particles transmuted nitrogen into oxygen with simultaneous liberation of hydrogen.



He further showed that other elements could also be transmuted, but hydrogen was always emitted..

On this basis Rutherford proposed that the hydrogen nucleus must be contained inside nuclei of all the elements. Hence, the hydrogen nucleus was renamed as proton.

- (I) Mass : It was found to be 1.672×10^{-24} g or 1.672×10^{-27} kg or 1.00728 amu. It is about 1837 times heavier than an electron.
- (II) Charge : It carries unit positive charge 1.602×10^{-19} coulombs or 4.803×10^{-10} esu.
- (III) Specific charge : It is 9.58×10^4 coulomb/gm. It varies with nature of gas and is maximum if H_2 is used.
- (IV) Charge on 1 mole of proton is 96500 coulomb or 1 Faraday.
- (V) Volume : The volume for proton is approximately $1.5 \times 10^{-38} \text{ cm}^3$.

NEUTRON

Discovered by Sir James Chadwick in 1932 by bombarding Be or B atoms (sheet) with high speed α -particles



- (i) Mass : Its mass is 1.675×10^{-24} gm or 1.675×10^{-27} kg or 1.00866 amu.
- (II) It is heavier than proton by 0.18%.
- (III) Density : Its density is $1.5 \times 10^{14} \text{ g/cm}^3$.
- (IV) Specific Charge : It is zero.
- (V) Stability : It is least stable of all elementary particles present in an atom.
- (VI) Disintegration : Isolated neutron is unstable and disintegrates into electron, proton and neutrino.
- (VII) Among all elementary particles neutron is the heaviest and least stable.

THOMSON'S ATOMIC MODEL:

According to Thomson's atomic model, also known as plum pudding model, an atom is made up of a positively charged sphere into which negatively charged electrons are embedded.

RUTHERFORD'S NUCLEAR MODEL:

It is based upon alpha particles scattering experiment.

Only a few (one in 10,000) α -particles were returned back from the gold foil (10^{-4} mm thick).

Scattering of α -particles $\propto \frac{1}{\sin^4(\frac{\theta}{2})}$

Conclusion : Atom consists of two parts –

- (a) Nucleus
- (b) Extra nuclear part

Drawbacks - This model fails to explain

- (a) the stability of the atoms
- (b) line spectrum of hydrogen

BLACK BODY RADIATION

A black body is one that absorbs all the electromagnetic radiation that strikes it. To stay in thermal equilibrium, it must emit radiation at the same rate as it absorbs it so a black body also radiates well. Radiation from a hot object is familiar to us. If we heat an object up to about 1500 degrees we will begin to see a dull red glow and we say the object is red hot. If we heat something up to about 5000 degrees, near the temperature of the sun's surface, it radiates well throughout the visible spectrum and we say it is white hot. The frequency of radiation increases with temperature. At a given temperature the intensity of radiation emitted increases with decrease of wavelength, reaches a maximum value and then starts decreasing with further decrease of wavelength.

PLANCK QUANTUM THEORY

In the year 1900, Max Planck put forth his quantum theory to explain black-body radiation

According to Max Planck (1901) radiant energy is emitted or absorbed only in discrete units in the form of bundle or packets of energy called photon

(quantum). Photon is not a material body. It is massless bundle of energy.
Energy associated with each photon (quantum)

$$E \propto \nu$$

$$\therefore E = h\nu = hc/\lambda$$

[h = Planck's constant = 6.626×10^{-34} Js in S.I.]

Thus a body can radiate energy in multiples of quantum $h\nu, 2h\nu, 3h\nu \dots nh\nu$ where n is an integer.

PHOTOELECTRIC EFFECT:

Phenomenon of ejection of electrons from the surface of a metal when light of suitable frequency strikes on it is called photoelectric effect.

Threshold frequency (ν_0) : The minimum frequency of incident radiation to cause the photoelectric effect is called threshold frequency.

Work function (ϕ) : A part of the photons energy that is absorbed by the metal surface to release the electron is known as work function of the surface denoted by ϕ . The remaining part of the energy of photons goes into the Kinetic energy of the electron emitted.

Kinetic energy of photo electron $KE = (E - \phi) = (h\nu - h\nu_0)$

Characteristics of photoelectric effect:

Number of photoelectrons \propto Intensity of light

K.E. is directly proportional to frequency of incident light

$E = K.E. + \phi$ is known as Einstein's photoelectric equation.

Energy required to stop the ejection of electrons is given by eV_0 where e is the electric charge and V_0 is stopping potential.

ATOMIC SPECTRUM

when an atom is excited by heating, passing current or electric discharge then it emits electromagnetic radiations of definite frequencies .

Arrangement of these radiations in decreasing order of frequencies is called atomic spectrum.

DISPERSION OF LIGHT: Phenomenon of splitting of beam of light into radiations of different frequencies after passing through a prism is called dispersion.

CONTINUOUS SPECTRUM : It contains radiations of all the frequencies.

LINE SPECTRUM : It consists of a number of bright lines separated by dark bands. Atomic Spectra of most elements is line spectrum.

ABSORPTION SPECTRUM : It is obtained by passing white light through solutions or vapours of chemical substance and then is analysed by spectroscope. It has few dark lines in otherwise continuous spectrum.

EMISSION SPECTRUM : It is obtained by passing radiations from the atoms through prism. It has few bright lines against a dark back ground.

HYDROGEN SPECTRUM : It is obtained by passing light being emitted from discharge tube containing hydrogen at low pressure through spectrograph. Hydrogen Spectrum has six Series:

Lyman, Balmer, Paschen, Brackett, Pfund and Humphreys series.

<i>Spectral series</i>	<i>Values of</i>		<i>Region of radiation</i>
	n_1	n_2	
Lyman	1	2,3,4, . . .	ultraviolet
Balmer	2	3,4,5, . . .	Visible
Paschen	3	4,5,6, . . .	Near infrared
Brackett	4	5,6, . . .	Infrared
Pfund	5	6,7, . . .	Far infrared

BOHR'S MODEL OF ATOM

Postulates of Bohr atomic theory

- Electrons revolve around nucleus only in certain selected circular orbits. These orbits are associated with definite energies and are called stationary orbits or Bohr orbits.
- Electrons can move only in those circular orbits where angular momentum is a whole number and multiple of $h/2\pi$. i.e. $mvr = nh/2\pi$
- Energy of electron remains constant as long as it revolves in a particular orbit..
- Lowest energy state is called ground state and when electron absorbs energy and jumps to higher state, it is called excited state .

i)Energy of electron in n^{th} orbit

$$E_n = -\frac{2\pi^2 m z^2 e^4}{n^2 h^2} = -\frac{13.6 z^2}{n^2} \text{ eV atom}^{-1}$$

(ii) The radius of n^{th} orbit

$$r_n = \frac{n^2 h^2}{4\pi^2 m z e^2} = \frac{0.53 n^2}{z} \text{ \AA}$$

(iii) The velocity of electron in n^{th} orbit

$$V_n = \frac{2\pi ze^2}{nh} = \frac{2.19 \times 10^8 Z}{n} \text{ cm/s}$$

Electronic energy is negative because at infinite distance there is no interaction between electron and nucleus thus energy is zero. While when close to nucleus, attraction takes place, energy is released and it becomes negative as it was already zero. The energy of electron increases with the value of n , but the difference of energy between two successive orbits decreases. Thus $E_2 - E_1 > E_3 - E_2 > E_4 - E_3 \dots\dots\dots$ etc

Limitations of Bohr model

1. Bohr's atomic model failed to account for fine lines of the hydrogen atom spectrum observed in sophisticated spectroscopic experiments.
2. Bohr model was unable to explain the spectrum of atoms other than hydrogen having more than one electron.
3. Bohr theory could not explain the splitting of spectral lines in the presence of a magnetic field (Zeeman effect) or electric field (Stark effect).
4. It goes against the Heisenberg's uncertainty principle.
5. In Bohr model an electron is regarded as a charged particle moving in well defined circular orbits about the nucleus. In contrast to this de Broglie proposed in 1924 that electron should exhibit a dual behaviour, that is, both particle and wave like properties.

Sommerfeld theory

In order to explain the observed fine structure of spectrum, Sommerfeld introduced two main modifications in Bohr's theory.

- (i) According to Sommerfeld, the path of an electron around the nucleus, in general, is elliptical with the nucleus at one of its foci.
- (ii) The velocity of the electron moving in an elliptical orbit varies at different parts of the orbit. This causes the relativistic variation in the mass of the moving electron.

Now an elliptical orbit has two variables:

- (i) The varying distance of the electron from the nucleus (r).
- (ii) The varying angular position of the electron with respect to the nucleus i.e the azimuthal angle (ϕ)

To deal with these two variables, two quantum numbers are introduced (i) The principal quantum number n of Bohr's theory, which determines the energy of the electrons, and

- (ii) a new quantum number called orbital (or azimuthal) quantum number (l) which has been introduced to characterize the angular momentum in an orbit i.e., it determines the orbital angular momentum of the electron. Its values vary from zero to (n-1) in steps of unity.

de- BROGLIE PRINCIPLE (1924)

According to de Broglie's theory of matter waves, each particle of matter with linear momentum is also a wave. The amount of a particle's linear momentum is inversely proportional to the wavelength of a matter wave associated with that particle.

de- BROGLIE equation:

$$\lambda = \frac{h}{p}$$

Derivation: de Broglie was the first to apply Einstein's famous equation for the relationship between matter and energy: $E = mc^2$

Planck's equation: $E = h\nu \therefore mc^2 = h\nu$

De Broglie proposed velocity (v) for the speed of light since real particles do not travel at the speed of light (c).

$$mv^2 = h\nu$$

$$\lambda = \frac{h}{mv}$$

Davission and Germer's experiment confirms the wave nature of electrons. Scintillation method and photoelectric effect confirms the particle nature. This principle is applicable only for microscopic particles.

Heisenberg uncertainty principle

It states that the position and the momentum of an object cannot both be measured exactly, at the same time, even in theory

Mathematical form:

$$\Delta x \cdot \Delta p \gg \frac{h}{4\pi}$$

Where Δx = uncertainty in position

Δp = uncertainty of momentum, h = Planck's constant

It is hard to imagine not being able to know exactly where a particle is at a given moment. It seems intuitive that if a particle exists in space, then we can point to where it is; however, the Heisenberg Uncertainty Principle clearly shows otherwise. This is because of the wave-like nature of a particle. A particle is spread out over space so that there

simply is not a precise location that it occupies, but instead occupies a range of positions. Similarly, the momentum cannot be precisely known since a particle consists of a packet of waves, each of which have their own momentum so that at best it can be said that a particle has a range of momentum.

QUANTUM MECHANICAL MODEL OF ATOM: Schrodinger wave equation
Based on de Broglie's and Heisenberg's principle, behaviour of electron was described in terms of equation known as Schrodinger wave equation:

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

Wave function, ψ , as such does not have any physical meaning. The probability of finding an electron at a point within an atom is proportional to ψ^2 ($\psi^* \psi$) in the neighbourhood of that point (within a tiny volume element) around it.

Many solutions for this equation are possible for hydrogen but only certain solutions are permissible and are called eigen values

The solution must be single valued, should satisfy the relation

$$\int_0^\infty \psi^* \psi d\tau = 1 \quad \text{and it must be finite and continuous}$$

Schrodinger equation or wave equation can also be written as $\hat{H}\psi = E\psi$,
Here \hat{H} is a mathematical operator called Hamiltonian operator, ψ is wave function and E is total energy of system.

QUANTUM NUMBERS

When Schrodinger equation is solved for hydrogen atom, the possible values of energy of electron and corresponding wave function (ψ) are obtained.

As a natural consequence of solving this equation, a set of three quantum numbers characteristic of the quantized energy levels and the corresponding wave functions are obtained. These are : Principal quantum number (n), azimuthal quantum number (l) and magnetic quantum number (m_l).

The solution of Schrodinger wave equation successfully predicted features of hydrogen atom emission spectrum.

Splitting of spectral lines in multi-electron atomic emission spectra could not be explained through such model. These were explained by George

Uhlenbeck and Samuel Goudsmit (1925) who proposed the presence of the fourth quantum number called electron spin quantum number, m_s .

1. **principal quantum number (n):** It is a positive integer with values of n being 1, 2, 3, 4, It describes size of orbit. Angular momentum of electron in an orbit is given by

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

2. **Azimuthal quantum number (l):** It is also called subsidiary quantum number. Different values of 'l' defines subshells for a particular shell. The values of 'l' range from 0 to $(n - 1)$. The subshells having 'l' equal to 0, 1, 2, 3, are represented by the symbols s, p, d, f,, respectively. It describes shape of suborbit.

Orbital angular momentum L is given by

$$L = \sqrt{l(l + 1)} \frac{h}{2\pi}$$

3. **The magnetic orbital quantum number (m_l)** gives information about the relative spatial orientation of the orbitals in a given subshell.

For any subshell (defined by 'l' value) $(2l + 1)$ values of m_l are possible which range through :

$$m_l = -l, -(l - 1), -(l - 2), \dots, 0, \dots, (l - 2), (l - 1), l.$$

Z-component of orbital angular momentum is given by:

$$L_z = m_l \cdot \frac{h}{2\pi}$$

4. **Electron spin quantum number (m_s)** specifies the spin state of the electron in an orbital. An electron spins around its axis. This imparts intrinsic spin angular momentum, to the electron.

Possible value of m_s are $+\frac{1}{2}$ and $-\frac{1}{2}$

SHAPE OF ORBITALS

s orbitals are spherically symmetrical.

p orbitals are dumbbell shaped.

d orbitals have five different orientation. Three of them d_{xy} , d_{yz} , d_{xz} are identical in shape but have different orientation.

The plane passing through nucleus where probability of finding the electron is zero is called a nodal plane. Number of nodal planes in an orbital = l .

Orbitals of a sub shell having same energy are called degenerated orbitals.

Spherical surface within an orbital where probability of finding an electron is zero is called spherical or radial node.

Number of spherical nodes = $(n - l - 1)$.

Angular or non spherical nodes = (l) .

Thus total nodes = $(n - 1)$.

Boundary surface is drawn in space to describe the shape of an orbital in such a way that the value of probability density ψ^2 is constant and encloses a region where the probability of finding electron is typically more than 90%. Such a boundary surface diagram is a good representation of shape of an orbital

Energies of orbitals

The energy of an electron in the hydrogen atom or hydrogen like species (one electron system) is determined by the principal quantum number alone. This is because the only interaction in these species is attraction between the electron and nucleus.

Increasing order of energies of orbitals in the hydrogen atom is given by $1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < \dots$

In multi-electron atoms there is mutual repulsion among the electrons.

Thus the energy of an electron depends both on the principal quantum number, n , and the azimuthal quantum number, l .

The lower the sum $(n + l)$ for an orbital, the lower is its energy. If two orbitals have the same $(n + l)$ values then orbital with the lower value of n is of lower energy. This is called the $(n + l)$ rule. From the $(n + l)$ rule the increasing order of energy of orbitals in multi-electron atoms can be written as:

$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s \dots$

Electronic Configuration of Atoms

Aufbau principle : 'Aufbau' is a German word meaning 'building up'. The building up of orbital means filling up of orbitals with electrons in the ground state of an atom. According to this principle, electrons are added to orbitals in increasing order of energies. The order of energies for orbitals for multielectron atoms/ions is

$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s \dots$

The order of energies can be calculated by $(n + l)$ rule. i.e. orbitals are filled in order of increasing $(n+l)$ values the one with lower n value is filled first.

(ii) The energy of atomic orbitals for H-atom depends on the value of n only.

$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f$$

Hund's rule of maximum spin multiplicity: The pairing of electrons in orbitals of a subshell does not take place until all orbitals of sub shell are singly occupied.

(i) This arrangement leads to lower energy level.

(ii) Singly occupied orbitals should have same spins giving rise to lower energies

Pauli's exclusion principle: No two electrons in an atom can have same values for all the four quantum numbers.

It is not possible to accommodate more than two electrons in an orbital. In other words, s sub shell can have maximum of 2 electrons p sub shell can have maximum of 6 electrons, d subshell 10 electron and f subshell 14 electrons.

Electronic Configuration (Atomic Number: 1 – 15)

<u>Atomic Number</u>	<u>Element</u>	<u>Electronic configuration</u>
1	Hydrogen	$1s^1$
2	Helium	$1s^2$
3	Lithium	$[\text{He}] 2s^1$
4	Beryllium	$[\text{He}] 2s^2$
5	Boron	$[\text{He}] 2s^2 2p^1$
6	Carbon	$[\text{He}] 2s^2 2p^2$
7	Nitrogen	$[\text{He}] 2s^2 2p^3$
8	Oxygen	$[\text{He}] 2s^2 2p^4$
9	Fluorine	$[\text{He}] 2s^2 2p^5$
10	Neon	$[\text{He}] 2s^2 2p^6$

11	Sodium	$[\text{Ne}]3s^1$
12	Magnesium	$[\text{Ne}]3s^2$
13	Aluminium	$[\text{Ne}]3s^2 3p^1$
14	Silicon	$[\text{Ne}]3s^2 3p^2$
15	Phosphorous	$[\text{Ne}]3s^2 3p^3$
Atomic Number	Element	Electronic configuration
16	Sulfur	$[\text{Ne}]3s^2 3p^4$
17	Chlorine	$[\text{Ne}]3s^2 3p^5$
18	Argon	$[\text{Ne}]3s^2 3p^6$
19	Potassium	$[\text{Ar}] 4s^1$
20	Calcium	$[\text{Ar}] 4s^2$
21	Scandium	$[\text{Ar}] 3d^1 4s^2$
22	Titanium	$[\text{Ar}] 3d^2 4s^2$
23	Vanadium	$[\text{Ar}] 3d^3 4s^2$
24	Chromium	$[\text{Ar}] 3d^5 4s^1$
25	Manganese	$[\text{Ar}] 3d^5 4s^2$
26	Iron	$[\text{Ar}] 3d^6 4s^2$
27	Cobalt	$[\text{Ar}] 3d^7 4s^2$
28	Nickel	$[\text{Ar}] 3d^8 4s^2$
29	Copper	$[\text{Ar}] 3d^{10} 4s^1$

Electronic configurations of Cu and Cr

Chromium : Atomic number of chromium is 24. Expected electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^2$; here one 4s electron enter into one of empty 3d orbitals, thereby both 4s and 3d orbitals become half-filled so that chromium atom acquires extra stability. Its actual electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$.

Copper : Atomic number of copper is 29. The expected electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$.Here one 4s electron to enter

into 3d which makes it completely filled with 4s being half-filled. Hence copper atom acquires extra stability. So the actual electronic configuration of Cu is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$.

Causes of Stability of Completely Filled and Half-filled Subshells: The completely filled and completely half-filled subshells are stable due to the following reasons:

1. **Symmetrical distribution of electrons:** The completely filled or half filled subshells have symmetrical distribution of electrons in them and are therefore more stable.
2. **Exchange Energy :** The stabilizing effect arises whenever two or more electrons with the same spin are present in the degenerate orbitals of a subshell. These electrons tend to exchange their positions and the energy released due to this exchange is called exchange energy. The number of exchanges that can take place is maximum when the subshell is either half filled or completely filled .As a result the exchange energy is maximum and so is the stability.

RADIAL PROBABILITY DISTRIBUTION CURVES

The electron density is directly proportional to ψ^2 . The larger the value of ψ^2 more is the probability of finding the electrons. Schrodinger wave

equation may be separated into a product of three functions dependent on r, θ, ϕ

$$\psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi)$$

$R(r)$ = Radial wave

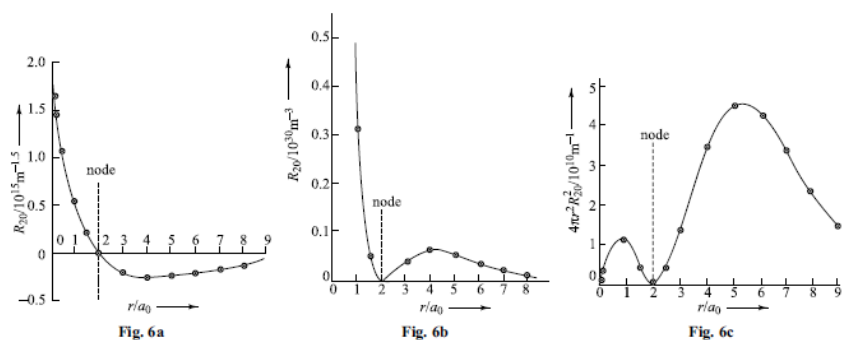
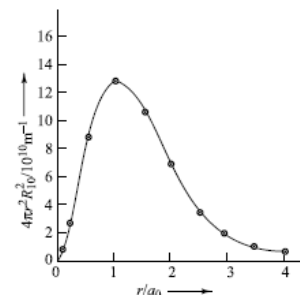
function

$\Theta(\theta)\Phi(\phi)$ = Angular part of wave function.

R^2 = Radial density in per unit volume of spherical shell. It is always positive.

$P(r) = 4\pi r^2 \cdot dr \cdot R^2$ = Radial probability. It is defined as maximum density of electrons in the volume of spherical shell having small thickness dr .

Note : $4\pi r^2 \cdot dr$ is the volume of spherical shell having small thickness dr .



Part-II (Question/Answer)

1. The number of angular and radial nodes in 3p orbital respectively are

- (a) 3,1 (b) 2,1 (c) 1,1 (d) 2,3

Ans.(c) Number of angular nodes = $l = 1$

Number of radial nodes = $n-l-1 = 3-1-1=1$

2. The correct order of number of unpaired electrons is

- (a) $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Cr}^{3+} > \text{Fe}^{3+}$ (b) $\text{Ni}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+} > \text{Cr}^{3+}$
 (c) $\text{Fe}^{3+} > \text{Cr}^{3+} > \text{Ni}^{2+} > \text{Cu}^{2+}$ (d) $\text{Cr}^{3+} > \text{Fe}^{3+} > \text{Ni}^{2+} > \text{Cu}^{2+}$

Ans. (c) Cu^{2+} : $[\text{Ar}]3d^9$ unpaired electron = 1

Ni^{2+} : $[\text{Ar}]3d^8$ unpaired electron = 2

Cr^{3+} : $[\text{Ar}]3d^3$ unpaired electron = 3

Fe^{3+} : $[\text{Ar}]3d^5$ unpaired electron = 5

3. Find out the number of waves made by a Bohr electron in one complete revolution in its 3rd orbit of hydrogen atom.

- (a) 4 (b) 3 (c) 6 (d) 8

Ans.(b) Number of waves = $n=3$

4. In Bohr model of atom, radius of hydrogen atom in ground state is r_1 and radius of He^+ ion in ground state is r_2 . Which of the following is correct?

- (a) $\frac{r_1}{r_2} = 4$ (b) $\frac{r_1}{r_2} = \frac{1}{2}$ (c) $\frac{r_2}{r_1} = \frac{1}{4}$ (d) $\frac{r_2}{r_1} = \frac{1}{2}$

Ans.(d) $r_n \propto \frac{n^2}{z}$; $\therefore \frac{r_2}{r_1} = \frac{1}{2}$

5. Which one of the following is the correct set of four quantum numbers (n, l, m, s)?

- (a) $(3, 0, -1, +\frac{1}{2})$ (b) $(4, 3, -2, -\frac{1}{2})$ (c) $(3, 1, -2, -\frac{1}{2})$ (d) $(4, 2, -3, +\frac{1}{2})$

Ans. (b)

6. The de-Broglie wavelength (λ) for electron (e), proton (p) and He^{2+} ion (a) are in the following order. Speed of e, p and α are the same.

- (a) $\alpha > p > e$ (c) $e > \alpha > p$ (b) $e > p > \alpha$ (d) $\alpha < p > e$

Ans.(b) $\lambda = \frac{h}{mv}$, or, $\lambda \propto \frac{1}{m}$ (as speed is same)

7. The electrons, identified by quantum number n and l

- (i) $n = 4, l = 1$ (ii) $n = 4, l = 0$ (iii) $n = 3, l = 2$ (iv) $n = 3, l = 1$

can be placed in order of increasing energy, from the lowest to highest, as

- (a) (iv) < (ii) < (iii) < (i) (b) (ii) < (iv) < (i) < (iii)
 (c) (i) < (iii) < (ii) < (iv) (d) (iii) < (i) < (iv) < (ii)

Ans. (a) $E_n \propto (n+l)$, when $(n+l)$ is same then the one having higher n will have higher energy.

8. Photoelectric emission is observed from a metal surface with incident frequencies ν_1 and ν_2 , where $\nu_1 > \nu_2$. If the kinetic energies of the photoelectrons emitted in the two cases are in the ratio 2 : 1, then the threshold frequency ν_0 of the metal is

- (a) $\frac{\nu_1 - \nu_2}{h}$ (b) $(\nu_1 - \nu_2)$ (c) $\frac{2\nu_1 - \nu_2}{h}$ (d) $2\nu_2 - \nu_1$

Ans. (d)

$h\nu_1 = h\nu_0 + 2E$; $h\nu_2 = h\nu_0 + E$; Solving the two equations we get $\nu_0 = 2\nu_2 - \nu_1$

9. What is the work function of the metal if the light of wavelength 4000 Å generates photoelectrons of velocity $6 \times 10^5 \text{ m s}^{-1}$ from it?

(Mass of electron = $9 \times 10^{-31} \text{ kg}$, Velocity of light = $3 \times 10^8 \text{ m s}^{-1}$, Planck's constant = $6.626 \times 10^{-34} \text{ J s}$, charge on electron = $1.6 \times 10^{-19} \text{ J eV}^{-1}$)

- (a) 4.0 eV (c) 0.9 eV (b) 2.1 eV (d) 3.1 eV

Ans. (b)

$$\frac{hc}{\lambda} = w + \frac{1}{2}mv^2; \text{ here, } h=6.626 \times 10^{-34} \text{ J s, } c=3 \times 10^8 \text{ m s}^{-1}$$

$\lambda = 4 \times 10^{-7} \text{ m}$; w = Work function; $m = 9 \times 10^{-31} \text{ kg}$; $v = 6 \times 10^5 \text{ m s}^{-1}$

Using these values we get $w = 3.35 \times 10^{-19} \text{ J} = 2.1 \text{ eV}$.

10. Which set of quantum numbers is possible for the outermost electron of Mg^+ ion?

- (a) $n = 3, l = 2, m = 0, s = +1/2$ (b) $n = 2, l = 3, m = 0, s = +1/2$
 (c) $n = 1, l = 0, m = 0, s = +1/2$ (d) $n = 3, l = 0, m = 0, s = +1/2$

Ans. (d); $\text{Mg}^+ : [\text{Ne}]3s^1$; $\therefore n = 3, l = 0, m = 0, s = +1/2$

11. By estimating the difference in energy between 1st and 2nd Bohr orbit for a hydrogen atom, at what minimum atomic number, a transition from $n = 2$ to $n = 1$ energy level would result in the emission of X-rays with

$\lambda = 3.0 \times 10^{-8} \text{ m}$?

- (a) 4 (b) 2 (c) 3 (d) 1

Ans. (b)

$$E_n = 2.18 \times 10^{-19} Z^2 (1/n_1^2 - 1/n_2^2)$$

Here, $E_n = hc/\lambda = (6.625 \times 10^{-34} \times 3 \times 10^8) / (3.0 \times 10^{-8}) \text{ J} = 6.625 \times 10^{-18} \text{ J}$

$n_1 = 1, n_2 = 2$. Using these values we get $Z = 2$.

12. The energy levels for $A^{+(Z-1)}$ can be given by

(a) E_n for $A^{+(Z-1)} = Z^2 \times E_n$ for H

(b) E_n for $A^{+(Z-1)} = Z \times E_n$ for H

(c) E_n for $A^{+(Z-1)} = 1/Z^2 \times E_n$ for H

(d) E_n for $A^{+(Z-1)} = 1/Z \times E_n$ for H

Ans. (a).

Bohr's theory is applicable for one electron system. For the given ion to be one electron ion, atomic number must be equal to $(Z-1)+1=z$

$\therefore E_n$ for $A^{+(Z-1)} = Z^2 \times E_n$ for H

13. What is the maximum number of electrons in the all possible sub-shells for $n + l = 4$?

(a) 8

(b) 6

(c) 12

(d) 16

Ans. (a)

The possible suborbitals satisfying the above conditions are 4s and 3p. So total number of electrons = 2 + 6 = 8

14. The ground state energy of the hydrogen atom is -13.6 eV and the energy of 1st excited state is 10.2 eV higher than the ground state i.e., at -3.4 eV. If a collection of hydrogen atoms in the ground state is irradiated with monochromatic light of energy 11.9 eV, then

(a) light will not be absorbed

(b) the atoms will absorb 10.2 eV to reach the first excited state and the excess energy will be returned as radiation

(c) the atoms will absorb 10.2 eV and the excess energy will be converted into kinetic energy

(d) for every 6 photons absorbed, 7 atoms will be excited.

Ans. Electronic energy levels in hydrogen atom are quantized. So, only radiation with energy 10.2 eV will be absorbed for the said transition. Thus no radiation will be absorbed here.

15. If n and l are the principal and azimuthal quantum numbers, then the expression for calculating the total number of electrons at an energy level can accommodate is

- (a) $\sum_{l=1}^{l=n} 2(2l + 1)$ (b) $\sum_{l=0}^{l=n+1} 2(2l + 1)$
 (c) $\sum_{l=1}^{l=n-1} 2(2l + 1)$ (d) $\sum_{l=0}^{l=n-1} 2(2l + 1)$

Ans. (d) For a given value of n , sub-orbits with $l=0$ to $l=(n-1)$ are possible.

Now each sub-orbit can accommodate $2(2l+1)$ electrons. So, total number of electrons that can be accommodated for a given value of n is given by the expression (d).

16. Two particles A and B are in motion. If the wavelength associated with the particle A is 5×10^{-8} m, calculate the wavelength of particle B if its momentum is half of A.

- (a) 10^{-8} m (c) 10^{-5} m (b) 10^{-6} m (d) 10^{-7} m

Ans. (d)

$\lambda = h/p$; i.e. $\lambda \propto 1/p$. Thus $\lambda_B = 2 \lambda_A = 2 \times 5 \times 10^{-8}$ m = 10^{-7} m

17. Element with atomic number 115 has electronic configuration as and with most stable cation as

- (a) $[Rn]5f^{14}6d^{10}7s^27p^3$; M^{3+}
 (b) $[Rn]7s^25d^{10}4f^{14}7p^3$; M^{5+}
 (c) $[Rn] 7s^25d^{10}4f^{14}7p^3$; M^+
 (d) $[Rn] 5d^{10}4f^{14}7p^5$; M^{5+}

Ans. (a) : Element with atomic number 115 has electronic configuration

$[Rn]5f^{14}6d^{10}7s^27p^3$. Probable oxidation states are +3, +5. But due to inert pair effect, M^{3+} is the most stable cation.

18. Splitting of spectral lines under the influence of magnetic field is called

- (a) Stark effect (b) Zeeman effect
 (c) photoelectric effect (d) screening effect.

Ans. (b)

19. When a certain metal was irradiated with light of frequency 3.2×10^{16} Hz, photoelectrons emitted had twice the kinetic energy as did photoelectrons emitted when the same metal was irradiated with light of frequency 2.0×10^{16} Hz. Hence, threshold frequency is

- (a) 0.8×10^{15} Hz (c) 0.85×10^{14} Hz
 (b) 8.0×10^{15} Hz (d) 6.4×10^{16} Hz

Ans.(b)

$\nu_0 = (2\nu_2 - \nu_1)$ [Same as problem 8]

$$= (2 \times 2.0 \times 10^{16} - 3.2 \times 10^{16}) = 8.0 \times 10^{15} \text{ Hz}$$

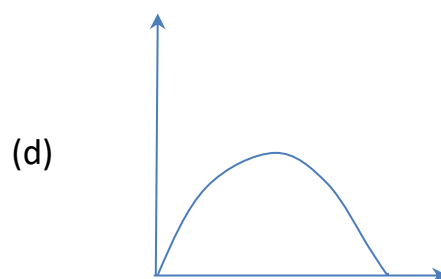
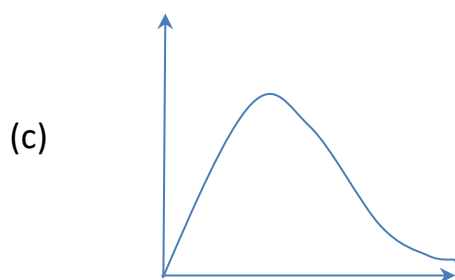
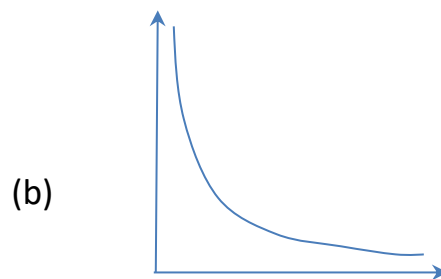
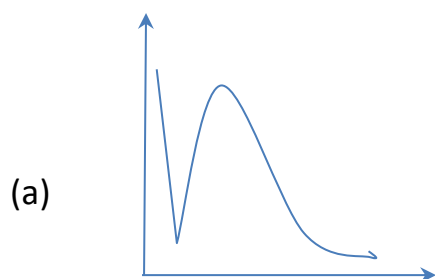
20. The limiting line in Balmer series will have a frequency of

- (a) $6.22 \times 10^{15} \text{ s}^{-1}$ (b) $8.22 \times 10^{14} \text{ s}^{-1}$
 (c) $7.22 \times 10^{14} \text{ s}^{-1}$ (d) $9.22 \times 10^{14} \text{ s}^{-1}$

Ans. (b)

$$\begin{aligned} \underline{\nu} &= R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ [For limiting line of Balmer serie } n_1=2, n_2=\infty \text{]} \\ &= 1.097 \times 10^7 \times \left(\frac{1}{2^2} - \frac{1}{\infty} \right) \text{ m}^{-1} \\ \therefore \nu &= c \underline{\nu} = 3 \times 10^8 \times 1.097 \times 10^7 \times \left(\frac{1}{2^2} - \frac{1}{\infty} \right) \text{ sec}^{-1} = 8.22 \times 10^{14} \text{ s}^{-1} \end{aligned}$$

21. P is the probability of finding the 1s electron of hydrogen atom in a spherical shell of infinitesimal thickness dr , at a distance r from the nucleus. The volume of this shell is $4\pi r^2 dr$. The qualitative sketch of the dependence of P on r is



Ans. (c)

$P = 4\pi r^2 \times R^2$, where $R = 2(1/a_0)^{3/2} e^{-r/a_0}$ [Radial wave function for 1s orbital of H atom]. Thus plot (c) is obtained when P is plotted against r.

22. If the radius of 2nd Bohr orbit of hydrogen atom is r_2 . The radius of 3rd Bohr orbit will be

- (a) $\frac{4}{9} r_2$ (b) $4 r_2$ (c) $\frac{9}{4} r_2$ (d) $9 r_2$

Ans. (c)

$$r_n \propto n^2 \therefore r_3/r_2 = 3^2/2^2 = 9/4, \therefore r_3 = \frac{9}{4} r_2$$

23. Find the quantum no. 'n' corresponding to the excited state of He^+ ion if on transition to the ground state that ion emits two photons in succession with wavelengths 108.5 nm and 30.4 nm.

- (a) 5 (b) 7 (c) 2 (d) 4

Ans. (a)

24. A particular electromagnetic radiation with wavelength 200 nm

- (a) has a higher frequency than radiation with wavelength 400 nm
(b) is in the visible region of the electromagnetic spectrum
(c) has a greater speed in vacuum than does radiation of wavelength 400 nm
(d) has a greater energy content per photon than does radiation with wavelength 100 nm.

25. In the Bohr's orbit, what is the ratio of total kinetic energy and total energy of the electron?

- (a) -1 (b) -2 (c) 1 (d) +2