

DAY THREE

Atomic Structure

Learning & Revision for the Day

- Subatomic Particles
- Atomic Models (Thomson and Rutherford)
- Developments Leading to the Bohr's Model of an Atom
- Bohr's Model of Hydrogen Atom
- Dual Behaviour of Matter
- Elementary Ideas of Quantum Mechanics
- Rules for Filling Electrons in Orbitals
- Quantum Numbers and their Significance

Subatomic Particles

A large number of subatomic particles have been discovered but among them only electron, proton and neutron are of great importance and hence, these three are called **fundamental particles**.

Various experiments that lead to the **discovery of fundamental particles** are as follows:

Discovery of Electron

Cathode rays were discovered by Sir J.J. Thomson. Cathode rays were a stream of fast moving negatively charged particles, called **electrons**. The specific charge is the ratio of charge to mass of an electron, i.e. e/m ratio of electron was found to be same for all gases. Its value is $= 1.758 \times 10^{11}$ C/kg.

Positive Rays or Canal Rays (Discovery of Proton)

Positive rays (canal rays) were discovered by Goldstein. These rays consist of positively charged particles, called **protons**. Unlike cathode rays, their e/m value depends upon the nature of gas taken in the tube. The e/m value is maximum for hydrogen gas.

Discovery of Neutrons

Neutrons are neutral particles and discovered by Chadwick. These are the heaviest particles of the atom.

Masses of electron, proton and neutron respectively, are 9.1×10^{-31} kg, 1.672×10^{-27} kg and 1.674×10^{-27} kg and their charges are 1.6×10^{-19} C, 1.6×10^{-19} C and zero respectively.

Different Types of Atomic Species

1. **Isotopes** Isotopes are the species with same atomic number but different mass numbers. e.g. ${}_1\text{H}^1$, ${}_1\text{H}^2$
2. **Isobars** Isobars are the species with same mass number but different atomic numbers. e.g. ${}_{18}\text{Ar}^{40}$, ${}_{19}\text{K}^{40}$
3. **Isotones** Isotones are the species having same number of neutrons. e.g. ${}_1\text{H}^3$, ${}_2\text{He}^4$

4. **Isodiaphers** Isodiaphers are the species with same isotopic number. e.g. ${}_{19}\text{K}^{39}$, ${}_{9}\text{F}^{19}$

Isotopic number = mass number - 2 × atomic number

Atomic Models

(Thomson and Rutherford)

The atomic model which describe the atomic structure are given below

1. Thomson Model of an Atom

Thomson model of an atom proposed that an atom is a sphere of positive charges uniformly distributed, with the electrons scattered as points throughout the sphere. This was also known as **plum pudding model**.

Limitations of Thomson Model

Thomson's model was able to explain the overall neutrality of the atom, but it could not satisfactorily explain the results of scattering.

2. Rutherford Atomic Model

Rutherford bombarded a thin foil of gold with high speed positively charged α -particles and made the following observations and conclusions :

- Most of the α -particles passed through the foil undeflected, it means that most of the space in atom is empty.
- Some of them were deflected, but only at small angles. This shows that there is something positively charged at the centre.
- A very few α -particles were deflected by nearly 180° , it means that the positively charged solid thing (called nucleus) is very small.
- The electrons present in empty space, around the nucleus, revolve around with a very high speed.

Limitations of Rutherford Model

Rutherford's model cannot explain the stability of an atom. When a charge is subjected to acceleration around an opposite charge, it emits radiation continuously.

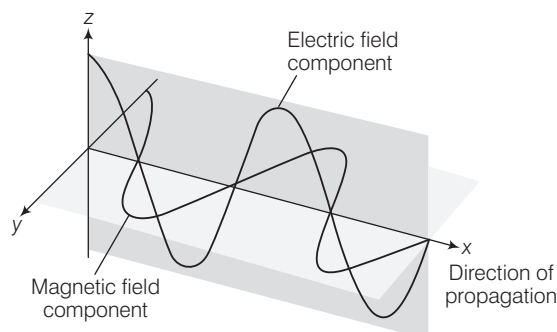
Developments Leading to the Bohr's Model of an Atom

Nature of electromagnetic radiations and spectrum play an important role in the development of Bohr's model.

Wave Nature of Electromagnetic Radiation

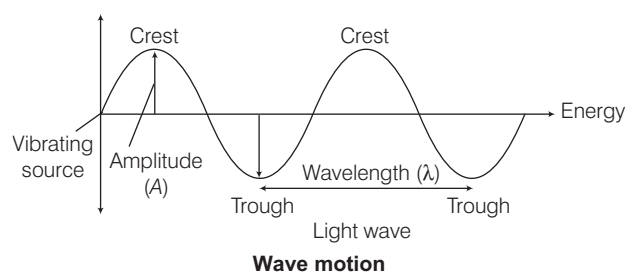
- James Maxwell explains the interaction between the charged bodies and the behaviour of electrical and magnetic fields on macroscopic level.
- He suggested that when electrically charged particle moves under acceleration, alternating electrical and magnetic fields are produced and transmitted.

These fields are transmitted in the form of waves called **electromagnetic waves**.



Simplified picture of electromagnetic waves

- A wave is a periodic disturbance in space or in a medium that involves elastic displacement of material particles or a periodic change in some physical quantities such as temperature, pressure, electric potential, electromagnetic field. Thus, wave motion represents propagation of a periodic disturbance carrying energy.



Characteristics of Wave

The waves are characterised in terms of their wavelength (λ), frequency (ν), velocity (c), amplitude and wave number ($\bar{\nu}$). These characteristics are related as

$$c = \lambda \times \nu$$

$$\text{or } \nu = \frac{c}{\lambda} \quad \text{and} \quad \frac{1}{\lambda} = \bar{\nu}$$

$$\therefore \nu = c\bar{\nu}$$

Particle Nature of Electromagnetic Radiation (Planck's Quantum Theory)

The radiant energy which is emitted or absorbed in the form of small discrete packets of energy known as **quantum** and in case of light, the quantum of energy is called **photon**.

$$E = h\nu \quad (c = \nu\lambda)$$

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

where, h = Planck's constant = 6.63×10^{-34} Js

E = energy of photon or quantum

If n is the number of quanta of a particular frequency and E_T be the total energy, then $E_T = nh\nu$.

The energy possessed by one mole of quanta (or photon), i.e. Avogadro's number (N_0) of quanta, is called one Einstein of energy, i.e. 1 Einstein of energy.

$$E = N_0 h\nu = N_0 \frac{hc}{\lambda}$$

Photoelectric Effect

The phenomenon of ejection of electrons from a metal surface when a light of certain frequency strikes on its surface is called **photoelectric effect**.

- The minimum energy required to eject electrons from a surface is called **work function** (W_0)

$$\text{Work function } (W_0) = h\nu_0 = \frac{hc}{\lambda_0}$$

Here ν_0 is called **threshold frequency**, the minimum frequency of incident radiation to eject electrons from the metal surface.

λ_0 is **threshold wavelength**, the maximum wavelength in incident radiation below which, electrons can be emitted from metal surface.

- If a photon of energy E is incident of a metallic surface, then it is absorbed by the surface and electrons are emitted. The energy (E) is consumed in two ways; in during work function and providing kinetic energy to emitted electrons.

$$\begin{aligned} \therefore E &= W_0 + \text{KE} \\ h\nu &= h\nu_0 + \text{KE} \\ \therefore \text{KE} &= h(\nu - \nu_0) \end{aligned}$$

If velocity of ejected electrons is v , then $\frac{1}{2}mv^2 = h(\nu - \nu_0)$

Spectrum of Hydrogen Atom

The pictorial representation of arrangement of various types of EMR in their increasing order of wavelength (or decreasing order of frequency) is known as **spectrum**. The order of radiation would be:

$$\gamma\text{-rays} < \text{X-rays} < \text{UV-rays} < \text{Visible} < \text{IR} < \text{Microwave} < \text{Radiowave}$$

In vacuum, all types of electromagnetic radiation regardless of their wavelength, travel at the same speed, i.e. $3 \times 10^8 \text{ ms}^{-1}$.

The two most common spectra are as follows:

- The arrangement of the radiation emitted by an atom of an element on the absorption of energy in the increasing order of the wavelengths or decreasing frequencies is called **emission spectrum**.
- The arrangement of absorbed radiation by an atom of element on the emission of energy in the increasing wavelength is **absorption spectrum**.

If $\Delta E = E_{n_2} - E_{n_1}$; $n_2 > n_1 \Rightarrow$ emission spectra

If $\Delta E = E_{n_2} - E_{n_1}$; $n_2 < n_1 \Rightarrow$ absorption spectra

Here, n = energy levels

- When an electric discharge is passed through gaseous hydrogen, the H_2 molecules dissociate and the energetically excited hydrogen atoms produced, emit electromagnetic radiation of discrete frequencies.
- The line spectra of hydrogen lies in three regions of electromagnetic spectrum viz, infrared, visible and UV region. The set of lines in the visible region is known as **Balmer series**, that in ultraviolet region as **Lyman series** and there are three sets of lines in infrared region namely **Paschen, Brackett and Pfund series**.

- Wave number** ($\bar{\nu}$) is defined as reciprocal of the wavelength, i.e. $\bar{\nu} = \frac{1}{\lambda} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

where, λ = wavelength, R = Rydberg constant = 109677 cm^{-1}

For Lyman series $n_1 = 1$ and $n_2 = 2, 3, 4, \dots$

For Balmer series $n_1 = 2$, $n_2 = 3, 4, 5, \dots$

For Paschen series $n_1 = 3$, $n_2 = 4, 5, 6, \dots$ and so on.

- Wave number ($\bar{\nu}$) and frequency (ν) of radiations emitted when electron drops from n_2 to n_1 are obtained by the following expressions

$$\bar{\nu} = 109678 [\text{cm}^{-1}] \times Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ (For hydrogen, } Z = 1)$$

$$\nu = 3.289 \times 10^{15} (\text{s}^{-1}) \times Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

- The number of spectral lines in the spectrum when the electron comes from n th level to the ground level will be $\frac{n(n-1)}{2}$. The intensities of spectral lines decreases with increase in the value of n . e.g. the intensity of first Lyman series ($2 \rightarrow 1$) is greater than second line ($3 \rightarrow 1$) and so on.

Bohr's Model of Hydrogen Atom

Bohr's model is applicable only for one electron system like H, He^+ , Li^{2+} etc.

Postulates of Bohr's Atomic Model

Its main postulates are :

- Electrons revolve around the nucleus only in stationary path, called energy levels or **orbits** or shells. Each energy level has a definite energy associated with it. As one moves away from the nucleus, the energy of the states increases.
- Angular momentum of an electron is an integral multiple of

$$\frac{h}{2\pi}, \text{ i.e. } mvr = n \frac{h}{2\pi}$$

where, m = mass of the electron, v = velocity of the electron, r = radius of the orbit, n = number of orbit

- Energy is emitted or absorbed, only when an electron jumps from higher energy level to lower energy level and *vice-versa*. $\Delta E = E_2 - E_1 = h\nu = \frac{hc}{\lambda}$

- The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE , $\nu = \frac{\Delta E}{\lambda}$

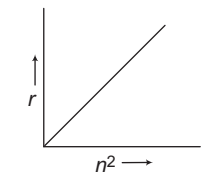
Derivation of the Relations for Energy of the Electron and Radii of Different Orbitals

From Bohr's model, energy and radius of an electron in n^{th} orbit are calculated as:

1. Radius of n^{th} Bohr Orbit

$$r_n = \frac{n^2 h^2}{4\pi^2 m e^2 Z} = \frac{r_0 n^2}{Z}$$

where, $r_0 = 52.9 \text{ pm}$



Variation of r with n^2

The above relation suggests that with an increase of energy levels (n), the radius of atom also increases.

$$\text{Thus, } \frac{r_1}{r_2} = \frac{n_1^2}{n_2^2}$$

This was derived by equating

electrostatic force of attraction $\left(F = \frac{kZe^2}{r^2}\right)$ and

centrifugal force $\left(\frac{mv^2}{r}\right)$ when both of them are equal

and opposing to each other.

2. Energy of an Electron in n^{th} Orbit

$$E_n = -\frac{2\pi^2 m Z^2 e^4}{n^2 h^2} k^2 = -\frac{21.78 \times 10^{-19} Z^2}{n^2} \text{ J/atom}$$

$$\Delta E = -2.178 \times 10^{-18} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) Z^2 \text{ J/atom}$$

where, n = number of shell, Z = atomic number

Thus was derived by considering sum of kinetic energy $\left(\frac{1}{2} mv^2\right)$ and potential energy $\left(\frac{-kZe^2}{r}\right)$ and then substituting in equation of radius.

NOTE • Velocity of an Electron in n^{th} Bohr Orbit

$$v_n = \frac{2\pi e^2 Z}{nh} = v_0 \times \frac{Z}{n}$$

where, $v_0 = 2.188 \times 10^8 \text{ cm s}^{-1}$

Limitations of Bohr's Model

Bohr left the following facts unexplained.

- Fine structure of atom.
- Spectrum of multielectron system.
- Zeeman effect and Stark effect (i.e. splitting of spectral lines under the influence of magnetic and electric field respectively).
- Three dimensional existence of atom.
- Dual nature of electron.

Dual Behaviour of Matter

Concept of movement of an electron in an orbit was replaced by the concept of probability of finding electron in an orbital due to **de-Broglie concept** of dual nature of electron and **Heisenberg uncertainty principle**.

de-Broglie Principle (Dual Nature of Matter)

According to de-Broglie, moving particles behave like wave and matter both i.e. show dual behaviour. The wavelength of wave associated with moving particle is given by

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

where, λ = wavelength, v = velocity of particle
 m = mass of particle, P = momentum

Heisenberg's Uncertainty Principle

It states that it is impossible to determine at any given instant, both the momentum and the position of subatomic particles like electron, simultaneously.

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

Since, $p = mv$

Hence $\Delta p = m\Delta v$

$$\text{So, } (m \cdot \Delta v) \Delta x \geq \frac{h}{4\pi}$$

where, Δx = uncertainty in position,

ΔP = uncertainty in momentum.

The effect of Heisenberg uncertainty principle is significant only for motion of microscopic objects and is negligible for that of macroscopic objects.

Elementary Ideas of Quantum Mechanics

On the basis of dual nature of matter and Heisenberg's uncertainty principle, Erwin Schrodinger developed a new branch of science, called quantum mechanics.

Quantum Mechanical Model of Atom

Quantum mechanical model of atom is the picture of the structure of atom, which energies from the application of the Schrodinger equation to atoms.

Schrödinger Wave Equation

- Schrödinger derived an equation for an electron which describes the wave motion of an electron along any of three axis, i.e. x , y and z .

This Schrödinger wave equation is given as

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

where, ψ = wave function, m = mass of electron,
 E = permissible total energy of electron,
 U = potential energy of electron = $-\frac{Ze^2}{r}$,

h = Planck's constant.

- For H-atom, the equation is solved on the basis of $\hat{H}\psi = E\psi$, where, \hat{H} is the total energy operator, called Hamiltonian; the sum of kinetic energy operator (\hat{T}) and potential energy operator (\hat{V}), is the total energy, E of the system,

$$\therefore \begin{aligned} \hat{H} &= \hat{T} + \hat{V} \\ (\hat{T} + \hat{V})\psi &= E\psi \end{aligned}$$

Important Features of the Quantum Mechanical Model of Atom

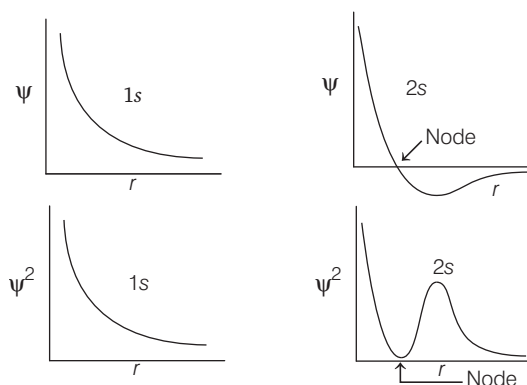
- The energy of electrons in atoms is quantised.
- The existence of quantised electronic energy levels is a direct consequence of the wave like properties of electrons and allowed solutions of Schrodinger wave equation.

Concept of Atomic Orbitals as One Electron Wave Function

The atomic orbitals or orbital wave functions can be represented by the product of two wave functions, radial and angular wave function.

Significance of ψ and ψ^2

- The orbital wave function ψ has no significance but ψ^2 measures the electron probability density at a point in an atom.
- Variation of ψ and ψ^2 with distance from nucleus for 1s and 2s-orbitals.
- Wave function ψ and ψ^2 can be plotted against distance 'r' from the nucleus as:



Plot of ψ and ψ^2 for 1s and 2s orbitals

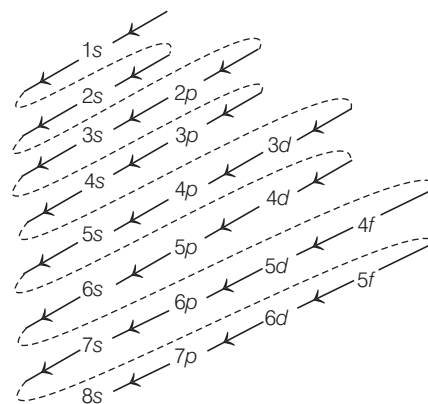
- A node is a region of space, where probability of finding an electron is zero. Different nodes can be calculated as
 - $(n - l - 1)$ = radial nodes
 - l = angular nodes
 - $(n - 1)$ = total number of nodes

Rules for Filling Electrons in Orbitals

There are some rules for filling the electrons in orbitals are given below:

- Aufbau Principle** It states that "electrons are filled to the various orbitals, in their order of increasing energy starting with the orbital of lowest energy".

As a working rule, a new electron enters in an empty orbital for which the value of $(n + l)$ is minimum, if the value of $(n + l)$ is same for two or more orbitals, the new electron enters in an orbital having lower value of 'n'.



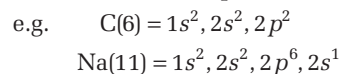
Order of filling of orbitals

The energy of atomic orbitals for H-atom varies as :
 $1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f$

- Hund's Rule of Maximum Multiplicity** It states that "Electrons never pair up until each orbital of a given sub-shell contains one electron or is singly occupied.

Electronic Configuration of Elements

The arrangement of electrons in various shells, sub-shells and orbitals in an atom is termed as **electronic configuration**. It is written as nl^x , where n = order of shell, l = sub-shell and x = number of electrons present.



Extra Stability of Completely Filled one Half-Filled Orbitals

When a set of equivalent orbitals (degenerate orbitals) is either **fully filled** or **half-filled**, i.e. each containing one or a pair of electrons, the atom gain more stability. This effect is more dominant in d and f -sub-shells. Therefore, the outer shell configuration for Cr is $3d^5 4s^1$ and for Cu is $3d^{10} 4s^1$.

Quantum Numbers and their Significance

The term quantum number is used to identify the various energy and levels that are available to an electron.

There are four types of quantum numbers which are given below:

- 1. Principal Quantum Number (n)** It gives an idea about the position and energy of an orbital. Principal quantum number also identifies the shell number.
- 2. Azimuthal Quantum Number (l)** Represents the sub-shells (s, p, d, f) present in the main shell and angular momentum of the electron. It tells about the three dimensional shape of sub-shells. It is also called the orbital angular momentum.

For values n, l can have n values ranging from 0 to $n-1$.

Value for l : 0 1 2 3 4.....

$s p d f g \dots$

- 3. Magnetic Quantum Number (m_l)** It gives information about the spatial orientation of the orbital with respect to standard set of coordinate axis.

$$m = -l \text{ to } +l$$

Number of sub-shells = $2l + 1$

Number of orbitals = n^2

s -sub-shell contains only one orbital. p -sub-shell has three orbitals p_x, p_y, p_z (axis perpendicular to each other). d -sub-shell has 5 orbitals, i.e. $d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}, d_{z^2}$. In f -sub-shell, there are seven orbitals.

Maximum number of electrons in a sub-shell is equal to $2(2l + 1)$.

- 4. Spin Quantum number (m_s)** These are distinguished by the two orientations of an electron in an orbital which can take values of $+\frac{1}{2}$ and $-\frac{1}{2}$. These are called two spin states of the electron and are generally represented by two arrows \uparrow (spin up) and \downarrow (spin down) respectively. Maximum number of electrons in a main energy level = $2n^2$ and total spin = $\pm\left(\frac{1}{2} \times n\right)$.

NOTE

- **Pauli's Exclusion Principle** states that "No two electrons in an atom can have the same set of all the four quantum numbers."
- The pairing of electrons will start in that p, d and f orbitals with the entry of 4th, 6th and 8th electron.
- Number of sub-shells in main energy level = n
- Orbital angular momentum of electron in an orbital

$$= \left(\frac{h}{2\pi}\right) \sqrt{l(l+1)}$$
- Spin angular momentum = $\left(\frac{h}{2\pi}\right) \sqrt{s(s+1)}$
- Shapes of s, p, d and f -orbitals

s -orbital	—	spherical
p -orbital	—	dumbell
d -orbital	—	double-dumbell
f -orbital	—	complicated

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

- The radii of an atom and atomic nucleus is of the order of
 - 10^{-12} m and 10^{-10} m
 - 10^{-10} cm and 10^{-8} cm
 - 10^{-10} m and 10^{-15} m
 - 10^{-15} m and 10^{-10} m
- Atom consists of electrons, protons and neutrons. If the mass attributed to neutron is halved and that attributed to the electrons is doubled, the atomic mass of ${}^6\text{C}^{12}$ would be approximately
 - same
 - doubled
 - halved
 - reduced by 25
- Many elements have non-integral atomic masses because
 - their isotopes have same number of neutrons
 - their isotopes have non-integral masses
 - they exist as isotopes
 - their constituents neutrons, protons and electrons combine to give fractional masses
- Rutherford's α -particle scattering experiment eventually concluded that
 - mass and energy are related
 - neutrons are buried deep in the nucleus
 - electrons occupy space around the nucleus
 - the point of impact with matter can be precisely determined
- A photon of light of wavelength 6000 Å has energy E . What will be the wavelength of photon of a light which has energy of photon $4E$?
 - 1500 Å
 - 6000 Å
 - 2000 Å
 - 750 Å
- Calculate the wavelength of a helium atom whose speed is equal to root mean square speed at 293 K.

$$\left(\text{rms} = \sqrt{\frac{3RT}{M}}\right)$$
 - 6.51×10^{-5} nm
 - 7.38×10^{-5} nm
 - 7.96×10^{-5} nm
 - None of these



- 7 The work function (ϕ) of some metals is listed below. The number of metals which will show photoelectric effect when light of 300 nm wavelength falls on the metals is

→ AIEEE 2011

Metal	ϕ (eV)
Li	2.4
Na	2.3
K	2.2
Mg	3.7
Cu	4.8
Ag	4.3
Fe	4.7
Pt	6.3
W	4.75

- (a) 2 (b) 4 (c) 6 (d) 8
- 8 A 25 Watt bulb emits monochromatic yellow light of wavelength of 0.57 μm . What will be the rate of emission of quanta per second?
 (a) 7.17×10^{19} (b) 0.717×10^{-19}
 (c) 71.7×10^{19} (d) 7.17×10^{-19}
- 9 The critical wavelength for producing the photoelectric effect in tungsten metal is 2600 \AA . What wavelength would be necessary to produce photoelectrons from tungsten having twice the kinetic energy of those produced at 2200 \AA ?
 (a) 1800 \AA (b) 1907 \AA (c) 1926 \AA (d) 2015 \AA
- 10 Energy required to stop the ejection of electrons from Cu plate is 0.24 eV. If radiation of $\lambda = 253.7 \text{ nm}$ strikes the plate, the work function is
 (a) 4.65 eV (b) 4.89 eV
 (c) 4.24 eV (d) 3.0 eV
- 11 When an electron is excited from ground level to 5th orbit, the number of spectral lines obtained in Bohr spectrum of H-atom is
 (a) 5 (b) 8 (c) 10 (d) 15
- 12 How many times does the electron go round the first Bohr's orbit of hydrogen in one second?
 (a) 0.657×10^{15} (b) 6.57×10^{15}
 (c) 6.57×10^{10} (d) 65.7×10^{12}
- 13 Which hydrogen like species will have same radius as that of Bohr orbit of hydrogen atom?
 (a) $n = 2, \text{Li}^{2+}$ (b) $n = 2, \text{Be}^{3+}$ (c) $n = 2, \text{He}^+$ (d) $n = 3, \text{Li}^{2+}$
- 14 In Bohr's series of lines of hydrogen spectrum, the third line from the red end corresponds to which one of the following inter-orbit jumps of the electron for Bohr's orbit in an atom of hydrogen?
 (a) $5 \rightarrow 2$ (b) $4 \rightarrow 1$ (c) $2 \rightarrow 5$ (d) $3 \rightarrow 2$
- 15 When the electron of a hydrogen atom jumps, from the $n = 4$ to the $n = 1$ state, the number of spectral lines emitted is
 (a) 15 (b) 6 (c) 3 (d) 4

- 16 The wave number of first line of Balmer series of hydrogen is 15200 cm^{-1} . The wave number of first Balmer line of Li^{2+} ion is

- (a) 15200 cm^{-1} (b) 60800 cm^{-1}
 (c) 76000 cm^{-1} (d) 136800 cm^{-1}

- 17 The wave number of the first emission line in the Balmer series of H-spectrum is ($R = \text{Rydberg constant}$)

→ JEE Main (Online) 2013

- (a) $\frac{5}{36}R$ (b) $\frac{9}{400}R$
 (c) $\frac{7}{6}R$ (d) $\frac{3}{4}R$

- 18 If the shortest wavelength of H-atom in Lyman series is X , the longest wavelength in Balmer series of He^+ is

- (a) $\frac{9X}{5}$ (b) $\frac{36X}{5}$
 (c) $\frac{X}{4}$ (d) $\frac{5X}{9}$

- 19 If the speed of an electron in the Bohr's first orbit of hydrogen atom be x , speed of the electron in 3^{rd} orbit is
 (a) $x/9$ (b) $x/3$ (c) $3x$ (d) $9x$

- 20 The ionisation enthalpy of hydrogen atom is $1.312 \times 10^6 \text{ J mol}^{-1}$. The energy require to excite the electrons in an atom from $n = 1$ to $n = 2$ is

- (a) $7.56 \times 10^5 \text{ J mol}^{-1}$ (b) $9.84 \times 10^5 \text{ J mol}^{-1}$
 (c) $8.51 \times 10^5 \text{ J mol}^{-1}$ (d) $6.56 \times 10^5 \text{ J mol}^{-1}$

- 21 Ionisation energy of He^+ is $19.6 \times 10^{-18} \text{ J atom}^{-1}$. The energy of the first stationary state ($n = 1$) of Li^{2+} is

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- (a) $4.41 \times 10^{-16} \text{ J atom}^{-1}$ (b) $-4.41 \times 10^{-17} \text{ J atom}^{-1}$
 (c) $-2.2 \times 10^{-15} \text{ J atom}^{-1}$ (d) $8.82 \times 10^{-17} \text{ J atom}^{-1}$

- 22 The wavelength of a neutron with a translatory kinetic energy equal to kT at 300 K is

- (a) 17.8 pm (b) 20.0 pm
 (c) 200 pm (d) 178 pm

- 23 Energy of an electron is given by

$$E = -2.178 \times 10^{-18} \times \frac{Z^2}{n^2}$$

Wavelength of light required to excite an electron in the hydrogen atom from level $n = 1$ to $n = 2$ will be

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- (a) $2.816 \times 10^{-7} \text{ m}$ (b) $6.500 \times 10^{-7} \text{ m}$
 (c) $8.500 \times 10^{-7} \text{ m}$ (d) $1.214 \times 10^{-7} \text{ m}$

- 24 A gas absorbs photon of 355 nm and emits at two wavelengths. If one of the emission is at 680 nm, the other is at

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- (a) 1035 nm (b) 325 nm (c) 743 nm (d) 518 nm

- 25 The energy required to break one mole of Cl—Cl bonds in Cl_2 is 242 kJ mol^{-1} . The longest wavelength of light capable of breaking a single Cl—Cl bond is

→ AIEEE 2010

- (a) 594 nm (b) 640 nm
 (c) 700 nm (d) 494 nm



26 A photon of 300 nm is absorbed by a gas which then re-emits two photons. One re-emitted photon has wavelength of 496 nm. Wavelength of other re-emitted photon is

- (a) 300 nm (b) 496 nm
(c) 759 nm (d) 550 nm

27 Which of the following is the energy of a possible excited state of hydrogen? → JEE Main 2015

- (a) +13.6 eV (b) -6.8 eV
(c) -3.4 eV (d) +6.8 eV

28 The radius of the second Bohr orbit for hydrogen atom is (Planck's constant (h) = 6.6262×10^{-34} Js; mass of electron = 9.1091×10^{-31} kg; charge of electron (e) = 1.60210×10^{-19} C; permittivity of vacuum (ϵ_0) = 8.854185×10^{-12} kg $^{-1}$ m $^{-3}$ A 2) → JEE Main 2017

- (a) 1.65 Å (b) 4.76 Å
(c) 0.529 Å (d) 2.12 Å

29 The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom is [a_0 is Bohr radius] → AIEEE 2011

- (a) $\frac{h^2}{4\pi^2 ma_0^2}$ (b) $\frac{h^2}{16\pi^2 ma_0^2}$
(c) $\frac{h^2}{32\pi^2 ma_0^2}$ (d) $\frac{h^2}{64\pi^2 ma_0^2}$

30 The de-Broglie wavelength of a car of mass 1000 kg and velocity 36 km/h is ($h = 6.63 \times 10^{-34}$ Js) → JEE Main 2013

- (a) 6.626×10^{-34} m (b) 6.626×10^{-38} m
(c) 6.626×10^{-31} m (d) 6.626×10^{-30} m

31 A stream of electrons from a heated filament was passed between two charged plates kept at a potential difference V esu. If e and m are charge and mass of an electron, respectively, then the value of h/λ (where, λ is wavelength associated with electron wave) is given by → JEE Main 2016

- (a) $2 meV$ (b) \sqrt{meV}
(c) $\sqrt{2meV}$ (d) meV

32 The uncertainty in the position of an electron moving with a velocity of 300 ms $^{-1}$ along with an accuracy of 0.001% is

- (a) 3.84×10^{-2} m (b) 5.76×10^{-2} m
(c) 1.93×10^{-2} m (d) 19.3×10^{-2} m

33 A dust particle has mass equal to 10^{-11} g, diameter 10^{-4} cm and velocity 10^{-4} cm s $^{-1}$. The error in measurement of velocity is 0.1%. What will be the uncertainty in its position?

- (a) 0.527×10^{-10} m (b) 5.27×10^{-9} cm
(c) 0.527×10^{-15} m (d) 0.527×10^{-9} cm

34 The uncertainty involved in the measurement of velocity of an electron within a distance of 0.1 Å is

- (a) 5.79×10^8 ms $^{-1}$
(b) 5.79×10^5 ms $^{-1}$
(c) 5.79×10^6 ms $^{-1}$
(d) 5.79×10^7 ms $^{-1}$

35 In an atom, an electron is moving with a speed of 600 m/s with an accuracy of 0.005%. Certainty with which the position of the electron can be located is

($h = 6.6 \times 10^{-34}$ kg m 2 s $^{-1}$, mass of electron, $e_m = 9.1 \times 10^{-31}$ kg)

- (a) 1.52×10^{-4} m (b) 5.10×10^{-3} m
(c) 1.92×10^{-3} m (d) 3.84×10^{-3} m

36 Amongst the following set of quantum numbers, the impossible set is

- | n | l | m | s | n | l | m | s |
|-------|-----|-----|------|-------|-----|-----|-----|
| (a) 3 | 2 | -3 | 1/2 | (b) 4 | 0 | 0 | 1/2 |
| (c) 5 | 3 | 0 | -1/2 | (d) 3 | 2 | -2 | 1/2 |

37 In an atom how many orbital(s) will have the quantum numbers $n=3, l=2$ and $m_l = +2$? → JEE Main (Online) 2013

- (a) 5 (b) 3 (c) 1 (d) 7

38 The correct set of four quantum numbers for the valence electrons of rubidium atom ($Z = 37$) is → JEE Main 2014

- (a) 5, 0, 0, $+\frac{1}{2}$ (b) 5, 1, 0, $+\frac{1}{2}$
(c) 5, 1, 1, $+\frac{1}{2}$ (d) 5, 0, 1, $+\frac{1}{2}$

39 Which of the following is not possible for 4p or 3d electrons?

- (a) $n = 3, l = 2, m = +1, s = +1/2$
(b) $n = 4, l = 1, m = 0, s = +1/2$
(c) $n = 3, l = 3, m = +3, s = +1/2$
(d) $n = 4, l = 1, m = -1, s = +1/2$

40 Given, (i) $n = 5, m_l = +1$

(ii) $n = 2, l = 1, m_l = -1, m_s = -1/2$

The maximum number of electron(s) in an atom that can have the quantum numbers as given in (i) and (ii) respectively are → JEE Main 2013

- (a) 25 and 1 (b) 8 and 1 (c) 2 and 4 (d) 4 and 1

41 The electrons identified by quantum numbers 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 the order of increasing energy as

→ AIEEE 2012

- (a) (III) < (IV) < (II) < (I) (b) (IV) < (II) < (III) < (I)
(c) (II) < (IV) < (I) < (III) (d) (I) < (III) < (II) < (IV)

42 The orbital diagram in which Aufbau principle is violated is

- (a) $\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow \uparrow (b) \uparrow $\uparrow\downarrow$ \uparrow \uparrow
(c) $\uparrow\downarrow$ \uparrow \uparrow \uparrow (d) $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow

Direction (Q Nos. 43-45) In the following questions assertion (A) followed by reason (R) is given. Choose the correct answer out of the following choices.

- (a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) Both A and R are false.

43 Assertion (A) All isotopes of a given element show the same type of chemical behaviour.

Reason (R) The chemical properties of an atom are controlled by the number of electrons in the atom.

44 Assertion (A) The path of an electron in an atom is clearly defined.

Reason (R) It is impossible to determine the exact position and exact momentum of an electron simultaneously.

45 Assertion (A) On heating a solid for a longer time, radiations become white and then blue as the temperature becomes very high.

Reason (R) Radiations emitted go from a lower frequency to higher frequency as the temperature increases.

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 The atomic numbers of elements x , y and z are 19, 21 and 25 respectively. The number of electrons present in M -shell of these elements follow the order

(a) $z > x > y$ (b) $x > y > z$ (c) $z > y > x$ (d) $y > z > x$

2 The uncertainties in the velocities of two particles A and B are 0.05 and 0.02 m s^{-1} respectively. The mass of B is five times to that of mass A . What the ratio of

uncertainties $\left(\frac{\Delta x_A}{\Delta x_B}\right)$ in their positions.

(a) 2 (b) 0.25 (c) 4 (d) 1

3 I_2 molecule dissociates into atoms after absorbing light of 4500 \AA . If one quantum of energy is absorbed by each molecule, the KE of iodine atoms will be (BE of $\text{I}_2 = 240 \text{ kJ/mol}$)

(a) $240 \times 10^{-19} \text{ J}$ (b) $0.216 \times 10^{-19} \text{ J}$
(c) $2.16 \times 10^{-19} \text{ J}$ (d) $2.40 \times 10^{-19} \text{ J}$

4 In a Bohr's model of atom when an electron in H-atom jumps from $n = 1$ to $n = 3$, how much energy will be emitted or absorbed?

(a) $2.15 \times 10^{-11} \text{ erg/atom}$ (b) $1.936 \times 10^{-11} \text{ erg/atom}$
(c) $2.389 \times 10^{-12} \text{ erg/atom}$ (d) $0.239 \times 10^{-10} \text{ erg/atom}$

5 The total mass of neutrons in 7 mg of C^{14} (assume mass of a neutron $= 1.675 \times 10^{-27} \text{ kg}$) is

(a) 1.25×10^{-9} (b) 2.40×10^{-8}
(c) 4.03×10^{-6} (d) 5.36×10^{-7}

6 The frequency of light emitted for the transition $n = 4$ to $n = 2$ of He^+ is equal to the transition in H atom corresponding to which of the following?

(a) $n = 3$ to $n = 1$ (b) $n = 2$ to $n = 1$
(c) $n = 3$ to $n = 2$ (d) $n = 4$ to $n = 3$

7 To move an electron in one H-atom from the ground state to the second excited state, 12.084 eV are needed. How much energy is needed to cause 1 mole of H-atoms to undergo this transition ?

(a) 728 kJ/mol (b) 984 kJ/mol
(c) 1036 kJ/mol (d) 1164 kJ/mol

8 Which of the following statements in relation to the hydrogen atom is correct?

(a) $3s$, $3p$ and $3d$ orbitals all have the same energy
(b) $3s$ and $3p$ orbitals are of lower energy than $3d$ -orbital
(c) $3p$ -orbital is lower in energy than $3d$ -orbital
(d) $3s$ -orbital is lower in energy than $3p$ -orbital

9 The radiation is emitted when a hydrogen atom goes from a higher energy state to a lower energy state. The wavelength of one line in visible region of atomic spectrum of hydrogen is $6.63 \times 10^{-7} \text{ m}$. Energy difference between the two states is

(a) $3.0 \times 10^{-19} \text{ J}$ (b) $1.0 \times 10^{-18} \text{ J}$
(c) $5.0 \times 10^{-10} \text{ J}$ (d) $6.5 \times 10^{-7} \text{ J}$

10 Given the set of quantum numbers for a multi-electron atom $2, 0, 0, \frac{1}{2}$ and $2, 0, 0, -\frac{1}{2}$. What is the next higher allowed set of n and l quantum numbers for this atom in its ground state?

(a) $n = 2, l = 0$ (b) $n = 2, l = 1$
(c) $n = 3, l = 0$ (d) $n = 3, l = 1$

11 In a multielectron atom, which of the following orbitals described by the three quantum numbers will have the same energy in the absence of magnetic and electric fields?

(A) $n = 1, l = 0, m = 0$ (B) $n = 2, l = 0, m = 0$
(C) $n = 2, l = 1, m = 1$ (D) $n = 3, l = 2, m = 1$
(E) $n = 3, l = 2, m = 0$
(a) (D) and (E) (b) (C) and (D)
(c) (B) and (C) (d) (A) and (B)

12. Consider the following sets of quantum numbers.

	n	l	m	s
I.	3	0	0	+1/2
II.	2	2	1	+1/2
III.	4	3	-2	-1/2
IV.	1	0	-1	-1/2
V.	2	3	3	+1/2

Which of the following sets of the quantum number is not possible?

- (a) II, III and IV (b) I, II, III and IV
(c) II, IV and V (d) I and III

13 For the electrons of oxygen atom, which of the following statements is correct?

- (a) Z_{eff} for an electron in a 2s-orbital is the same as Z_{eff} for an electron in a 2p-orbital
(b) An electron in the 2s-orbital has the same energy as an electron in the 2p-orbital
(c) Z_{eff} for an electron in 1s-orbital is the same as Z_{eff} for an electron in a 2s-orbital
(d) The two electrons present in the 2s-orbital have spin quantum numbers m_s but of opposite sign

14 Which of the following statements about electromagnetic spectrum is not correct?

- (a) Infrared radiations have larger wavelength than cosmic rays

(b) The frequency of microwaves is less than that of ultraviolet rays

(c) X-rays have larger wave number than microwaves

(d) The velocity of X-rays is more than that of microwaves

15 Consider the following statements.

- I. $|\psi|^2$ is a measure of electron density at a point in an atom.
II. Radial probability function ($= 4\pi r^2 R^2 \psi^2$) gives the probability of finding the electron at a distance r (atomic radius) from the nucleus regardless of direction.
III. The shape of an orbital is defined as a surface of constant probability density that encloses some large fractions of the probability of finding the electron.

Select the correct statements.

- (a) Both I and II (b) Both II and III
(c) Both I and III (d) All of these

ANSWERS

SESSION 1

- 1** (c) **2** (d) **3** (c) **4** (c) **5** (a) **6** (b) **7** (b) **8** (a) **9** (b) **10** (a)
11 (c) **12** (b) **13** (b) **14** (a) **15** (b) **16** (d) **17** (a) **18** (a) **19** (b) **20** (b)
21 (b) **22** (d) **23** (d) **24** (c) **25** (d) **26** (c) **27** (c) **28** (d) **29** (c) **30** (b)
31 (c) **32** (c) **33** (d) **34** (c) **35** (d) **36** (a) **37** (c) **38** (a) **39** (c) **40** (b)
41 (b) **42** (b) **43** (a) **44** (a) **45** (a)

SESSION 2

- 1** (c) **2** (a) **3** (b) **4** (b) **5** (c) **6** (b) **7** (d) **8** (a) **9** (a) **10** (b)
11 (a) **12** (c) **13** (d) **14** (b) **15** (d)

Hints and Explanations

SESSION 1

- 1** The radii of an atom and atomic nucleus is in the order of 10^{-10} m and 10^{-15} m.
2 No change by doubling mass of electron, however by reducing mass of neutron to half, total atomic mass becomes 6 + 3 instead of 6 + 6.
Now, atomic mass = $\frac{9}{12} \times 100 = 75\%$
 \therefore Reduction in atomic mass = 25%
3 Many elements have several isotopes, for such elements atomic mass is average of the atomic masses of different isotopes, which is usually non-integral.

4 According to Rutherford, extra nuclear part is present around the nucleus in which electrons are contained.

$$\begin{aligned} \mathbf{5} \quad E &= \frac{hc}{\lambda} \quad \text{or} \quad E \propto \frac{1}{\lambda} \\ \therefore \quad E_1 &\propto \frac{1}{6000} \quad \text{and} \quad E_2 \propto \frac{1}{\lambda_2} \\ \therefore \quad \frac{E_1}{E_2} &= \frac{\lambda_2}{6000} \\ \therefore \quad E_1 &= E; E_2 = 4E \\ \therefore \quad \lambda_2 &= 1500 \text{ \AA} \end{aligned}$$

$$\mathbf{6} \quad \text{Mass of one He-atom} = \frac{4}{N_0} = \frac{4}{6.02 \times 10^{23}}$$

$$\begin{aligned} v &= \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.3143 \times 293}{4 \times 10^{-3}}} \text{ ms}^{-1} \\ &= 1351.69 \text{ ms}^{-1} \end{aligned}$$

$$\begin{aligned} \lambda &= \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{4} \times 1351.69 \\ &= \frac{6.626 \times 10^{-34}}{6.02 \times 10^{23}} \times 1351.69 \\ \lambda &= 7.38 \times 10^{-5} \text{ nm} \end{aligned}$$

$$\begin{aligned} \mathbf{7} \quad \text{Energy of photon} &= \frac{hc}{\lambda} \text{ J} = \frac{hc}{e\lambda} \text{ eV} \\ &= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{300 \times 10^{-9} \times 1.602 \times 10^{-19}} \\ &= 4.14 \text{ eV} \end{aligned}$$

For photoelectric effect to occur, energy of incident photons must be greater than work function of metals. Hence, only Li, Na, K and Mg have work function less than 4.14 eV.

$$\begin{aligned} \mathbf{8} \quad E_{\text{photon}} &= \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3.0 \times 10^8}{0.57 \times 10^{-6}} \\ &= 34.86 \times 10^{-20} \text{ J} \end{aligned}$$

Watt = power
= number of photons emitted/s

$$25 = \text{number of photons emitted/s} \times E_{\text{photon}} \times 34.86 \times 10^{-20}$$

$$\therefore \text{Number of photons emitted/s} = \frac{25}{34.86 \times 10^{-20}} = 7.17 \times 10^{19}/\text{s}$$

9 Critical wavelength corresponds to work function.

$$\therefore \text{Work function, } hv_0 = \frac{hc}{\lambda_0}$$

Also, KE at $\lambda_1 = 2$ (KE) at 2200 Å

$$\left(\frac{hc}{\lambda_1} - \frac{hc}{\lambda_0}\right) = 2\left(\frac{hc}{\lambda_2} - \frac{hc}{\lambda_0}\right)$$

$$\left(\frac{1}{\lambda_1} - \frac{1}{2600}\right) = 2\left(\frac{1}{2200} - \frac{1}{2600}\right)$$

$$\frac{1}{\lambda_1} = \frac{1}{1100} - \frac{1}{2600}$$

$$\frac{1}{\lambda_1} = \frac{1500}{1100 \times 2600}$$

$$\lambda_1 = \frac{2600 \times 11}{15} = 1907 \text{ Å}$$

10 Energy of photon (E_{photon})

= work function + kinetic energy absorbed
= $W_0 + eV_0$
where, e = electric charge,
 V_0 = stopping potential and eV_0 = KE,
i.e. energy required to stop the ejection of electrons.

$$E_{\text{photon}} = \frac{hc}{\lambda}$$

$$= \frac{6.626 \times 10^{-34} \times 3.0 \times 10^8}{253.7 \times 10^{-9}}$$

$$= 7.835 \times 10^{-19} \text{ J}$$

$$= \frac{7.835 \times 10^{-19}}{1.602 \times 10^{-19}} \text{ eV}$$

$$= 4.89 \text{ eV}$$

$$\therefore E_{\text{photon}} = W_0 + 0.24 \text{ eV}$$

$$\therefore W_0 = 4.65 \text{ eV}$$

11 Number of spectral lines from ground state is

$$\frac{n(n-1)}{2} = \frac{5 \times 4}{2} = 10$$

12 For H-atom, $v_1 = \frac{2\pi e^2}{h}$, $r_1 = \frac{h^2}{4\pi^2 me^2}$

$$\therefore \text{Circumference of 1st Bohr orbit} = 2\pi r_1$$

$$= \frac{2\pi h^2}{4\pi^2 me^2} = \frac{h^2}{2\pi me^2}$$

\therefore Number of rounds by electron in 1st orbit

$$= \frac{v_1}{2\pi r_1} = \frac{2\pi e^2 \times 2\pi me^2}{h \times h^2} = \frac{4\pi^2 me^4}{h^3}$$

$$= \frac{4 \times (3.14)^2 \times 9.108 \times 10^{-28} \times (4.8 \times 10^{-10})^4}{(6.626 \times 10^{-27})^3}$$

$$= 6.57 \times 10^{15} \text{ round/s}$$

13 Radius of orbit (r) = $\frac{n^2 h^2}{4\pi^2 me^2} \times \frac{1}{Z}$

$$= \frac{0.529}{Z} n^2 \text{ Å}$$

For H atom, $r_H = \frac{0.529 n^2}{1} \text{ Å}$

$r_{\text{Be}^{3+}} = 0.529 n^2 / 4 \text{ Å}$ and $r_n = r_{\text{Be}^{3+}}$

$$\therefore n = 2$$

14 As red colour is sun, so the line lies in visible region and obviously only Balmer series corresponds to the visible region. For Balmer series $n_1 = 2$ and red end means low energy or third end from red end means $n_2 = 5$. So, jump is involved from $5 \rightarrow 2$.

15 N = Number of lines emitted = $\frac{1}{2}n(n-1)$

$$= \frac{1}{2} \times 4(4-1) = 6$$

16 For H, $\bar{\nu} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

For other atoms/ions, $\bar{\nu}$

$$= R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) Z^2$$

\therefore For Li^{2+} ,

$$\bar{\nu} = 15200 \times 3^2 = 136,800 \text{ cm}^{-1}$$

17 For Balmer series, $n_1 = 2$ and

$n_2 = (n_1 + 1)$ for first emission line

$$= (2 + 1) = 3$$

We know that,

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

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

$$= R \left(\frac{1}{4} - \frac{1}{9} \right) = \frac{5R}{36}$$

18 For the shortest wavelength in Lyman series of H-atom, $n_1 = 1$, $n_2 = \infty$

$$\therefore \frac{1}{\lambda_{\text{min}}} = R_H \times 1^2 \left(\frac{1}{1^2} - \frac{1}{\infty^2} \right)$$

or $\frac{1}{\lambda} = R_H$... (i)

For the longest wavelength in Balmer series; $n_1 = 2$, $n_2 = 3$ and $Z = 2$ for He^+ ion.

$$\frac{1}{\lambda_{\text{max}}} = R_H \times 2^2 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = R_H \cdot \frac{5}{9} \dots \text{(ii)}$$

For He^+ , $\frac{1}{\lambda_{\text{max}}} = \frac{1}{X} \cdot \frac{5}{9}$

or $\lambda_{\text{max}} = \frac{9}{5} X$

19 $v_n = k \frac{Z}{n}$

i.e. $v_n \propto \frac{1}{n}$

$\therefore \frac{v_1}{v_3} = \frac{3}{1}$

As $v_1 = x$, $\therefore v_3 = \frac{x}{3}$

20 $\text{IE} = E_{\infty} - E_1 = 0 - E_1 = -E_1$

$$E_1 = -1.312 \times 10^6 \text{ J mol}^{-1}$$

$$= \frac{-1.312 \times 10^6}{1^2} \text{ J mol}^{-1}$$

$$E_2 = \frac{-1.312 \times 10^6}{2^2} \text{ J mol}^{-1}$$

$$\therefore E_2 - E_1 = -1.312 \times 10^6 \left[\frac{1}{2^2} - \frac{1}{1^2} \right] \text{ J mol}^{-1}$$

$$= 1.312 \times 10^6 \times \frac{3}{4} \text{ J mol}^{-1}$$

$$= 9.84 \times 10^5 \text{ J mol}^{-1}$$

21 $\text{IE} = E_1$

$$E_1 \text{ for } \text{He}^+ = -19.6 \times 10^{-18} \text{ J atom}^{-1}$$

$$\frac{(E_1)_{\text{He}^+}}{(E_1)_{\text{Li}^{2+}}} = \frac{(Z_{\text{He}^+})^2}{(Z_{\text{Li}^{2+}})^2}$$

$$\frac{-19.6 \times 10^{-18}}{(E_1)_{\text{Li}^{2+}}} = \frac{4}{9}$$

or $E_{1(\text{Li}^{2+})} = \frac{-19.6 \times 9 \times 10^{-18}}{4}$

$$= -4.41 \times 10^{-17} \text{ J atom}^{-1}$$

22 $\text{KE} = kT = \frac{RT}{N_0}$

$$= \frac{8.3143 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{6.02 \times 10^{23} \text{ mol}^{-1}}$$

$$= 4.143 \times 10^{-21} \text{ J}$$

$$m \text{ (neutron)} = 1.67495 \times 10^{-27} \text{ kg}$$

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2m(\text{KE})}}$$

$$= \frac{6.626 \times 10^{-34}}{\sqrt{2 \times 1.67495 \times 10^{-27} \times 4.143 \times 10^{-21}}}$$

$$= 1.778 \times 10^{-10} \text{ m}$$

$$= 177.8 \text{ pm} \approx 178 \text{ pm}$$

$$23 \quad E = \frac{hc}{\lambda} = 2.178 \times 10^{-18} Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\frac{6.6 \times 10^{-34} \times 3 \times 10^8}{\lambda} = 2.178 \times 10^{-18} \times (1)^2$$

$$\times \left[\frac{1}{(1)^2} - \frac{1}{(2)^2} \right]$$

$$\lambda = 1.214 \times 10^{-7} \text{ m}$$

24 Energy values are always additive.

$$E_{\text{total}} = E_1 + E_2$$

$$\frac{hc}{\lambda} = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2}$$

$$\frac{1}{\lambda} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$$

$$\lambda_2 = 742.94 \text{ nm} \approx 743 \text{ nm}$$

25 Energy required for 1 Cl₂ molecule

$$= \frac{242 \times 10^3 \text{ J}}{N_A}$$

$$E = \frac{hc}{\lambda} \quad \text{or} \quad \lambda = \frac{hc}{E}$$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8 \times 6.02 \times 10^{23}}{242 \times 10^3}$$

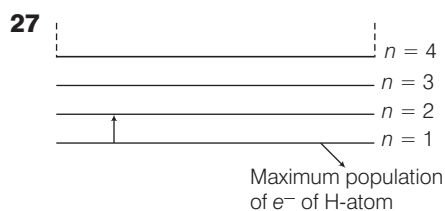
$$= 494 \times 10^{-9} \text{ m} = 494 \text{ nm}$$

26 λ of photon absorbed = 300 nm

λ of I photon re-emitted out = 496 nm
 Let λ of II photon re-emitted out = λ_H
 \therefore Total energy absorbed = Total energy re-emitted out

$$\therefore \frac{hc}{300 \times 10^{-9}} = \frac{hc}{496 \times 10^{-9}} + \frac{hc}{\lambda_H}$$

$$\therefore \lambda_H = 759 \times 10^{-9} \text{ m} = 759 \text{ nm}$$



Since, at $n = 1$, the population of electrons is maximum, i.e. at ground state. So, maximum excitation will take place from $n = 1$ to $n = 2$.

Hence, $n = 2$ is the possible excited state.

Now, we have the formula for energy of H-atom $(E_n)_H = -13.6 \frac{Z^2}{n^2} \text{ eV}$

where, $Z =$ atomic number, Z for H-atom = 1

$$\therefore (E_n)_H = -13.6 \times \frac{1}{2^2} \text{ eV}$$

$$= -\frac{13.6}{4} \text{ eV} = -3.4 \text{ eV}$$

28 Bohr radius (r_n) = $\epsilon_0 n^2 h^2$

$$r_n = \frac{n^2 h^2}{4\pi^2 m e^2 k Z}$$

$$k = \frac{1}{4\pi\epsilon_0}$$

$$\therefore r_n = \frac{n^2 h^2 \epsilon_0}{\pi m e^2 Z} = n^2 \frac{a_0}{Z}$$

where, $m =$ mass of electron
 $e =$ charge of electron
 $h =$ Planck's constant
 $k =$ Coulomb constant

$$r_n = \frac{n^2 \times 0.53 \text{ \AA}}{Z}$$

Radius of n^{th} Bohr orbit for H-atom
 $= 0.53 n^2 \text{ \AA} \quad [Z = 1 \text{ for H-atom}]$

\therefore Radius of 2^{nd} Bohr orbit for H-atom
 $= 0.53 \times (2)^2 = 2.12 \text{ \AA}$

29 According to Bohr's model,

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

$$(mv)^2 = \frac{n^2 h^2}{4\pi^2 r^2}$$

$$\text{KE} = \frac{1}{2} mv^2 = \frac{n^2 h^2}{8\pi^2 r^2 m} \quad \dots(i)$$

$$\text{Radius of the orbit } r_n = \frac{a_0 \times n^2}{Z}$$

For H-atom $Z = 1$

Substituting the value of r in Eq. (i) gives

$$\text{KE} = \frac{h^2}{8\pi^2 n^2 a_0^2 m}$$

When $n = 2$, $\text{KE} = \frac{h^2}{8\pi^2 (2)^2 a_0^2 m}$

$$= \frac{h^2}{32\pi^2 a_0^2 m}$$

30 de-Broglie equation is $\lambda = \frac{h}{mv}$

Given, $m = 1000 \text{ kg}$ and $v = 36 \text{ km/h}$

$$= \frac{36 \times 1000}{60 \times 60} = 10 \text{ m/s}$$

On putting values, $\lambda = \frac{6.626 \times 10^{-34}}{1000 \times 10}$

$$= 6.626 \times 10^{-38} \text{ m}$$

31 As you can see in options, energy term is mentioned hence, we have to find out relation between $\frac{h}{\lambda}$ and energy. For this,

we shall use de-Broglie wavelength and kinetic energy term in eV.

de-Broglie wavelength for an electron

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

$$\Rightarrow p = \frac{h}{\lambda} \quad \dots(i)$$

Kinetic energy of an electron = eV

As we know that, $\text{KE} = \frac{p^2}{2m}$

$$\therefore \text{eV} = \frac{p^2}{2m} \quad \text{or} \quad p = \sqrt{2meV} \quad \dots(ii)$$

From Eqs. (i) and (ii), we get

$$\frac{h}{\lambda} = \sqrt{2meV}$$

$$32 \quad \Delta x \cdot \Delta v \geq \frac{h}{4\pi m} \Rightarrow \Delta x = \frac{h}{4\pi m \times \Delta v}$$

$$= \frac{6.626 \times 10^{-34}}{4 \times \frac{22}{7} \times 9.1 \times 10^{-31} \times 300 \times 0.001 \times 10^{-2}}$$

$$= 1.93 \times 10^{-2} \text{ m}$$

$$33 \quad v = 10^{-4} \text{ cm}^{-1} \text{ s}^{-1}$$

$$\therefore \Delta v = \frac{0.1 \times 10^{-4}}{100} = 1 \times 10^{-7} \text{ cm}^{-1} \text{ s}^{-1}$$

Now, $\Delta v \cdot \Delta x = \frac{h}{4\pi m}$

$$\therefore \Delta x = \frac{6.626 \times 10^{-27}}{4 \times 3.14 \times 10^{-11} \times 10^{-7}}$$

$$= 0.527 \times 10^{-9} \text{ cm}$$

$$34 \quad \Delta v \cdot \Delta x = \frac{h}{4\pi m}$$

$$\therefore \Delta v = \frac{h}{4\pi m \cdot \Delta x}$$

$$= \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 9.11 \times 10^{-31} \times 0.1 \times 10^{-10}}$$

$$= 5.79 \times 10^6 \text{ ms}^{-1}$$

35 By Heisenberg's uncertainty principle

$$\Delta m \Delta v = \frac{h}{4\pi} \Rightarrow \Delta v = 0.005\%$$

or $600 \text{ m/s} = \frac{600 \times 0.005}{100} = 0.03$

$$\Delta x \times 9.1 \times 10^{-31} \times 0.03 = \frac{6.6 \times 10^{-34}}{4 \times 3.14}$$

Hence,

$$\Delta x = \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 0.03 \times 9.1 \times 10^{-31}}$$

$$= 1.92 \times 10^{-3} \text{ m}$$

36 For each value of l , m is $-l$ to $+l$. For $l = 2$, $m = -3$ is not possible.

37 Quantum numbers $n = 3$, $l = 2$, $m_l = +2$ represents only one orbital.

38 Given, atomic number of Rb, $Z = 37$

Thus, its electronic configuration is $[\text{Kr}] 5s^1$. Since, the last electron or valence electron enter in $5s$ -sub-shell.

So, the quantum numbers are $n = 5, l = 0$, (for s -orbital)

$m = 0$ ($\because m = +l$ to $-l$), $s = +1/2$ or $-1/2$

39 For $4p$ orbital, $n = 4$ and $l = 1$

and for $3d$ orbital, $n = 3$ and $l = 2$

So, option (c) doesn't show $4p$ and $3d$ orbital, it indicates $3f$ -orbital which is not possible.

40 (i) When $n = 5, l = 0, 1, 2, 3, 4$

When $l = 0, m_l = 0$

When $l = 1, m_l = 0, +1, -1$ (two e^-)

When $l = 2, m_l = 0, \pm 1, \pm 2$ (two e^-)

When $l = 3, m_l = 0, \pm 1, \pm 2, \pm 3$ (two e^-)

When $l = 4, m_l = 0, \pm 1, \pm 2, \pm 3, \pm 4$

(two e^-)

(Because each orbital can accommodate a maximum of $2e^-$.)

\therefore Total electrons having $n = 5$

and $m_l = \pm 1 = 2 + 2 + 2 + 2 = 8$

(ii) Only one electron is associated with $n = 2, l = 1, m_l = -1$

and $m_s = -1/2$ because Pauli's principle states that no two electrons can have same value for all the four quantum numbers.

41

n	l	nl (sub-orbit)	$n + 1$
4	1	$4p$	5
4	0	$4s$	4
3	2	$3d$	5
3	1	$3p$	4

Higher the value of $(n + l)$, higher the energy. If $(n + l)$ are same, sub-orbit with lower value of n has lower energy.

Thus, $3p < 4s < 3d < 4p$

Hence correct order is (iv) < (ii) < (iii) < (i).

42 Aufbau principle states that electrons are filled in the increasing order of energy. Hence, $2s$ -orbital should be filled first before filling $2p$ -orbitals.

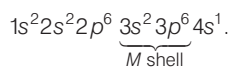
43 Isotopes have the same atomic number i.e. same number of electrons which are responsible for their chemical behaviour. Hence, these exhibit similar chemical properties.

44 According to Heisenberg's uncertainty principle, the exact position and exact momentum of an electron cannot be determined simultaneously. Thus, the path of electron in an atom is not clearly defined. Hence (a) option is correct.

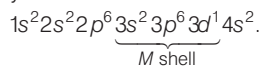
45 On heating a solid for a longer time, radiations become white and then blue as the temperature becomes very high because radiations emitted go from a lower frequency to higher frequency as the temperature increases.

SESSION 2

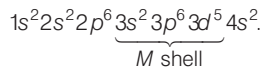
1 $x = 19 \Rightarrow$ The electronic configuration is



$y = 21 \Rightarrow$ The electronic configuration is



$z = 25 \Rightarrow$ The electronic configuration is



\therefore The number of electrons present in M shell of these element follow the order

$$z > y > x.$$

2 From Heisenberg uncertainty principle

$$= \Delta x \cdot \Delta p = \frac{h}{4\pi} = \Delta x \cdot m \Delta v = \frac{h}{4\pi}$$

For two particle A and B the ratio can be written as:

$$= \frac{\Delta x_A \Delta v_A}{\Delta x_B \Delta v_B} = \frac{m_B}{m_A}$$

$$\frac{\Delta x_A \times 0.05}{\Delta x_B \times 0.02} = \frac{5}{1}$$

$$\frac{\Delta x_A}{\Delta x_B} = \frac{5 \times 0.02}{1 \times 0.05} = \frac{2}{1}$$

3 Energy given to I_2 molecule = $\frac{hc}{\lambda}$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{4500 \times 10^{-10}}$$

$$= 4.4 \times 10^{-19} \text{ J}$$

Energy of I_2 molecule = $240 \times 10^3 \text{ J/mol}$

$$= \frac{240 \times 10^3}{6.023 \times 10^{23}} \text{ J/atom}$$

$$= 3.98 \times 10^{-19} \text{ J/atom}$$

$$\text{KE} = (4.4 \times 10^{-19}) - (3.98 \times 10^{-19})$$

$$= 0.42 \times 10^{-19} \text{ J/atom}$$

KE of I atoms

$$= \frac{0.42}{2} \times 10^{-19} = 0.21 \times 10^{-19}$$

4 The amount of energy required by an electron to excite or jump from $n = 1$ (ground state) to $n = 3$ (excited state)

$$\Delta E = E_3 - E_1$$

According to Bohr's model

$$E = \frac{-13.6}{n^2} \text{ eV/atom}$$

$$\therefore \Delta E = \frac{-13.6}{3^2} - \left(\frac{-13.6}{1^2} \right)$$

$$= \frac{-13.6}{3^2} + \frac{13.6}{1}$$

$$= \frac{-13.6 + 122.4}{9}$$

$$= \frac{108.8}{9} \text{ eV/atom}$$

$$= 12.08 \text{ eV/atom}$$

$$= 12.08 \times 1.602 \times 10^{-12}$$

$$(1 \text{ eV} = 1.602 \times 10^{-12} \text{ erg})$$

$$= 19.36 \times 10^{-12}$$

or 1.936×10^{-11}

5 1 mole of C-14

$$= 14 \text{ g} = 6.022 \times 10^{23} \text{ carbon atoms}$$

Number of neutrons in 1 carbon atom

= mass number - atomic number

$$= 14 - 6 = 8 \text{ neutrons}$$

6.023×10^{23} carbon atoms will contain

$$6.023 \times 10^{23} \times 8 \text{ neutrons}$$

$$\therefore 14 \text{ g C-14 have } 6.023 \times 10^{23} \times$$

8 neutrons

Hence, $7 \times 10^{-3} \text{ g C-14}$ will have

$$= \frac{7 \times 10^{-3} \times 6.023 \times 10^{23} \times 8}{14} \text{ neutrons}$$

$$= 24.092 \times 10^{20} \text{ neutrons}$$

$$= 2.4092 \times 10^{21} \text{ neutrons}$$

Mass of 1 neutron = $1.675 \times 10^{-27} \text{ kg}$

\therefore Mass of 2.4092×10^{21} neutrons

$$= 2.4092 \times 10^{21} \times 1.675 \times 10^{-27} \text{ kg}$$

$$= 4.0354 \times 10^{-6} \text{ kg}$$

$$\mathbf{6} \quad v = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

For He^+ , $Z = 2, n_1 = 2, n_2 = 4$

$$v = R(2)^2 \left[\frac{1}{2^2} - \frac{1}{4^2} \right]$$

$$= 4R \left[\frac{3}{16} \right]$$

... (i)

$$= \frac{3R}{4}$$

For H, $Z = 1$, as the frequency of light emitted for the transition $n = 4$ to

$n = 2$ of He^+ is equal to the transition in H-atom corresponds to $n = 2$ to $n = 1$.

$$v = R(1)^2 \left[\frac{1}{1^2} - \frac{1}{2^2} \right]$$

$$= R \left[\frac{3}{4} \right] = \frac{3R}{4}$$

7 $\Delta E = 12.084 \text{ eV}$

$$= 12.084 \times 1.6 \times 10^{-19} \text{ J/atom}$$

$$= 12.084 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{23} \text{ J mol}^{-1}$$

$$= 1164 \text{ kJ}$$

8 For any atom the order of energy for the orbitals can be given as:

$$1s < 2s < 2p < 3s < 3p < 3d$$

Hence, statement (a) is an incorrect statement.

9 $\Delta E = \frac{hc}{\lambda}$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{6.63 \times 10^{-7}}$$

$$= 2.9 \times 10^{-19} \text{ J} \approx 3 \times 10^{-19} \text{ J}$$

10 For any orbital set of quantum number possible are,

$$l = n - 1$$

$$m = -l \text{ to } l$$

$$s = \frac{-1}{2}, \frac{1}{2}$$

For given set of quantum numbers for a multi-electron atom $2, 0, 0, \frac{1}{2}$ and $2, 0,$

$0, \frac{-1}{2}$. The next higher allowed set of n

and l quantum number for this atom in its ground state is $n = 2, l = 1$.

11 Orbitals having quantum number $n = 3, l = 2, m = 1$ and $n = 3, l = 2, m = 0$ represents $3d$ -orbitals which are degenerate in the absence of magnetic and electric field.

12 For any orbital, set of quantum number possible are

$$l = n - 1$$

$$m = -l \text{ to } l$$

$$s = \frac{-1}{2}, \frac{1}{2}$$

Thus, in case (II) $n = l = 2$ hence this set of quantum number is not possible.

In case (IV) $n = 1$ to $l = 0, m = -1$ but it should be 0 hence, this is not possible.

In case (V) $n = 2, l = 3$ which is greater than n thus this is also not possible.

13 (a) Electrons in $2s$ and $2p$ -orbitals have different screening effect. Hence, their Z_{eff} is different. Z_{eff} of $2s$ -orbital $>$ Z_{eff} of $2p$ -orbital. Therefore, it is not correct.

(b) Energy of $2s$ -orbital $<$ energy of $2p$ -orbital.

Hence, it is not correct.

(c) Z_{eff} of $1s$ -orbital \neq Z_{eff} of $2s$ -orbital. Hence, it is incorrect.

(d) For the two electrons of $2s$ -orbital, the value of m_s is $+\frac{1}{2}$ and $-\frac{1}{2}$. Hence, it is correct.

14 The order of frequency of radiation is given as γ -rays $<$ X-rays $<$ UV rays $>$ Visible $<$ IR $<$ Microwave $<$ Radiowave

Thus, statement (b) is incorrect.

15 I. $|\psi|^2$ is a measure of electron density at a point in an atom. Thus, the statement is correct.

II. Radial probability function $4\pi^2 R^2 \psi^2$ gives the probability of finding the electron at a distance r from the nucleus regardless of direction. Thus, the statement is correct.

III. The shape of an orbital is defined as a surface of constant probability density that encloses some large fractions of the probability of finding the electron. Thus, the statement is correct.