JEE Main Chemistry

Short Notes

Atomic Structure

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Atomic Structure

1. DISCOVERY OF FUNDAMENTAL PARTICLES

Discovery of electron (Cathode rays): Electrons were discovered by JJ Thomson in 1897 by the study of electrical discharge in cathode ray tubes. On applying a sufficiently high voltage, the stream of particles move from cathode to anode. These particles are called cathode rays.

Discovery of proton (Anode rays or Canal rays): Protons were discovered by Goldstein after the discovery of electrons to maintain electrical neutrality of an atom. Electrical discharge was carried out in a modified cathode ray tube also termed as canal rays or anode rays that carries positively charged particles

Properties of cathode and anode rays:

S. No.	CATHODE RAYS	ANODE RAYS
1	travel in a straight line	travel in a straight line
2	deflected by electric and magnetic field	deflected by electric and magnetic field
3	particles are negatively charged	Particles are positively charged.
4	particles in cathode rays move towards positively charged plate	particles in anode rays move towards negatively charged plate
5	possess kinetic energy	possess kinetic energy
6	possess the capacity to penetrate through thin foil of solid material	possess the capacity to penetrate through thin foil of solid material
7	produce ionization of gases	produce ionization of gases

Charge to mass (e/m) ratio of electron:

From the deflection study of cathode rays in electric and magnetic field, JJ Thomson determined the e/m value of electrons. The value of e/m has been found to be -1.7588×10^{8} coulomb/g .This value is independent of the gas taken and is always the same.

Discovery of neutrons: Neutron was discovered by Chadwick in 1932 by bombarding a thin sheet of beryllium by alpha particles. This resulted in the emission of electrically neutral particles with a mass slightly higher than proton. These particles were termed as neutrons.

The discovery of these fundamental particles led to the atomic model concept which describes about the arrangement of these particles in an atom.

Charge and mass of the fundamental particles in an atom:

Name of particle	symbol	Absolute charge(C)	Mass/kg
electron	e	-1.602×10^{-19}	9.1×10^{-31}
proton	p	1.602×10^{-19}	1.672×10^{-27}
neutron	n	0	1.675×10^{-27}

Along with these three fundamental particles, some more subatomic particles are also present in an atom.

1. **Positron:** Positron is a subatomic particle which possess mass equal to electron but the charge is positive.
2. **Antiproton:** Antiproton is a subatomic particle possess mass equal to proton but the charge is negative.
3. **Neutrino and antineutrino:** These are subatomic particles with no mass and only spin.
4. **Π-mesons and μ-mesons**: These are subatomic particles which are responsible for nuclear stability.
5. **Antineutrino:** Antineutrino is a subatomic particle identical to neutrons but with opposite spin.

ATOMIC STRUCTURE:

Mass number: Mass number of the element is the sum of number of neutrons and protons.

Atomic number: it is the number of protons present in the nucleus. It is also termed as nuclear charge.

For a neutral atom, number of proton = number of electron

For charged atom, number of electron = Z – (charge on atom) where Z = number of protons.

Number of neutrons = mass number – atomic number

Atomic weight: it is the average weight of all the isotopes of the element present.

$$\text{Average weight} = \frac{\sum(\text{isotopic weight})\times(\text{percentage of occurence})}{\sum \text{percentage of occurance}}$$

Isotopes: Isotopes are atoms of those elements which possess same atomic number but different mass number.

Example: $_{17}Cl^{35}$ and $_{17}Cl^{37}$

Isobars: Isobars are atoms of those elements which possess same mass number but different atomic number.

Example: $_{1}H^{3}$ and $_{2}He^{3}$

Isotones: Isotones are atoms of different elements with same number of neutrons.

Example: $_{1}H^{3}$ and $_{2}He^{4}$; number of neutrons for H = 3-1 =2 and for He = 4 – 2 = 2

Isoelectronic species: Isoelectronic species are atoms or molecules with similar number of electrons.

Example: Cl^{-} and Ar possess 18 electrons respectively.

2. EARLIER ATOMIC MODELS:

Thomson model of atom:

Thomson proposed that atoms consist of a uniform sphere of positive charge in which electrons are unevenly distributed in the sphere.

Drawback: The theory considers the mass of the atoms to be uniformly distributed over the whole atom. Moreover it does not show the movement of electron.

Rutherford's model: Based on the alpha scattering experiment, Rutherford gave the nuclear model of an atom. The features of this model are:

1. The mass and positive charge is located centrally in a space called nucleus of an atom.

2. Protons and neutrons are altogether termed as nucleons.

3. The radius of atom is 10^5 times that of the radius of nucleus.

4. The revolving electrons surround the nucleus like the solar system in which nucleus acts as sun and electrons as planets.

Drawbacks:

1. Unable to explain the stability of atom

2. The spectrum should be continuous if electrons loss energy continuously, but the spectrum observed is discontinuous with lines of definite frequencies. This means that the loss of energy by electron in an atom is not continuous.

Millikan's oil drop method:

In this method, oil droplets are produced in the form of a mist by the atomizer and were allowed to enter through a tiny hole in the upper plate of electrical condenser. The downward movement was viewed with a telescope equipped with a micrometre eye piece. Measuring the rate of fall he measured the mass of droplets. The air inside was ionized by passing beam of X-rays. The electrical charge on the droplets was acquired by collision with gaseous ion. The fall of the charge droplets can be increased or decreased depending upon the polarity, charge and voltage applied. By measuring the effects of electric field strength on the motion of droplets of oil, Millikan made the conclusion that the magnitude of electrical charge 'q' on the droplets is always an integral multiple of electrical charge i.e q=ne where n=1,2,3..

3. DUAL NATURE OF RADIATION:

Electromagnetic radiation: Wave nature of electromagnetic radiations According to James Maxwell, the radiant energy travels with the velocity of light in the form of wave in space.

Characteristics of wave motion:

Wavelength (λ): distance between two nearest crest or trough. It is expressed in Angstrom, meters, centimetres etc.

1 Angstrom = 10^{-10} meter

Frequency (v): the number of times a wave passes a given point in one second .it is expressed in Hertz or sec^{-1}

Wave number (1/ λ): the reciprocal of wavelength is termed as wave number.

Velocity(c): distance travelled by a wave in one second. It is expressed as ms^{-1}.

Velocity 'c' in terms of frequency 'v' and wavelength (λ) can be written as:

$$c = v\lambda$$

or $$\frac{1}{\lambda} = \frac{v}{c}$$

Amplitude: height of crest or depth of trough of a wave.it helps to determine the brightness of light beam.

Particle nature of electromagnetic radiation or Planck's quantum theory:

According to this theory,

The radiant energy emitted or absorbed by a body discontinuously in small packets of energy is called quanta.

In case of light, the smallest packet of energy is termed as photon.

Energy of each quanta is proportional to frequency of radiation

i.e. $E \propto v$

or E = hv ; h is the Planck's constant and h= 6.626×10^{-34} J.sec

Black body radiation: A black body is an ideal body that emits and absorbs radiations of all frequencies. The radiation emitted by such a body is known as black body radiation.

Photoelectric effect: When a suitable frequency of light is incident on a metal surface, electrons are ejected from the metal surface. This phenomenon of ejection of electrons due to radiation is called photoelectric effect. Greater the energy possessed by photon, greater is the energy transfer and hence more is the kinetic energy.

From photoelectric effect,

Energy of incident photon = threshold energy (work function) + kinetic energy of ejected electron

$$E = W + K$$

$$hv = hv_0 + \frac{1}{2} m_e v^2$$

ATOMIC SPECTRA:

Emission and absorption spectra: The spectrum of radiation emitted by a body that has absorbed energy is called emission spectrum whereas absorption spectrum is the continuum of radiation absorbed by a body when an incident radiation falls on it.

Line spectrum of hydrogen: The series of line in hydrogen spectrum is as follows:

Series	n_1	n_2	**Spectral region**
Lyman	1	2, 3…	Ultraviolet
Balmer	2	3, 4…	visible
Paschen	3	4, 5…	infrared
Brackett	4	5, 6…	infrared
Pfund	5	6, 7…	infrared
Humphrey	6	7, 8…	Far infrared

If the spectral lines are expressed in terms of wave number ($\frac{1}{\lambda}$) according to Balmer, the visible lines of hydrogen spectrum obeys the formula:

$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) cm^{-1}$, where R is the Rydberg's constant, R=109677cm^{-1} n_1=2, n_2 =3 or greater than 3.

4. BOHR'S MODEL:

Bohr's model for hydrogen atom: Bohr extended Rutherford's work and succeeded in explaining the structure and spectrum of H atom. According to Bohr, electrons can revolve only in orbits whose angular momentum (mvr) is integral multiple of $\frac{h}{2\pi}$.

i.e mvr = $\frac{nh}{2\pi}$; n= whole number, h = Planck's constant.

The radii of various orbits of hydrogen or hydrogen like atom are given by:

$r_n = 0.529 \frac{n^2}{Z} \overset{0}{A}$; n =nth orbit, Z = atomic number.

Also, the energy expression for various orbits of hydrogen or hydrogen like atom is given as:

$E_n = -13.6 \frac{Z^2}{n^2} eV$ per atom.

Limitations of Bohr's model:

1. It does not explain the spectrum of multi electron atom.

2. It does not explain why mvr = $\frac{nh}{2\pi}$.

3. Interrelation between quantum theory of radiation and classical law of physics without any theoretical explanation was the biggest drawback.

4. Fine structure and splitting of spectral lines cannot be explained by Bohr's Model.

5. QUANTUM MECHANICAL MODEL OF ATOM:

Dual behaviour of matter:

De Broglie in 1924 proposed that matter too should exhibit wave like and particle like properties. He gave an expression for the wavelength (λ) and momentum (p) of material particles.

So, $\lambda = \frac{h}{p}$ where h = Planck's constant.

or $\lambda = \frac{h}{mv}$ [since, p =mv]

or $\lambda = \frac{h}{\sqrt{2(K.E)m}}$ in terms of kinetic energy (K.E)

Particle nature of matter was confirmed when an electron produced an spot of light on ZnS screen whereas the wave nature was confirmed from the diffraction pattern obtained.

Heisenberg's uncertainty principle: It states that the uncertainty in position (Δx) and uncertainty in momentum (Δp_x) of a microscopic moving particle can't be determined with accuracy or certainty.
Mathematically,

$\Delta x.\Delta p_x \geq \frac{h}{4p}$; h is the Planck's constant.

or $\Delta x.m\Delta v_x \geq \frac{h}{4\pi}$; m = mass, Δv_x = uncertainty in velocity.

Hydrogen atom and Schrodinger's equation:

Solution of Schrodinger's equation gives the possible energy levels an electron can occupy and the wave function (Ψ) associated with each energy level. The quantized energy state and the wave function characterized by the set of three quantum numbers, principal quantum number 'n', azimuthal quantum number 'l' and magnetic quantum number 'm' arises as a consequence of the solution of Schrodinger's equation. The wave function is a mathematical function and the value does not contain physical meaning. When an electron in any energy state, the wave function corresponding to that energy state contains all information about the electron. Such wave function of hydrogen and hydrogen like species are called atomic orbitals.

Orbitals and Quantum numbers:

The principal quantum number ‘n’ denotes the size and energy of the orbital.

The azimuthal quantum number ‘l’ denotes the shape of the orbital.’l’ can have values from 0 to (n-1) i.e. l=0 corresponds to s subshell, l=1 corresponds to p subshell, l=3 corresponds to d subshell.

The magnetic quantum number ‘m’ gives information about the orientation of the orbitals. Its value ranges from ‘-l’ to ‘+l’.

Orbital angular momentum = $\sqrt{l(l+1)}\,\frac{h}{2\pi}$

The value of ‘m’ can be determined from ‘l’ value as m=2l + 1

Another quantum number‘s’, the spin quantum number denotes the spin of electron. For clockwise s =+1/2 and for anti-clockwise‘s’= -1/2

Principal Quantum number (n)	azimuthal quantum number (l)	Subshell notation
1	0	1s
2	1	2p
3	0	3s
4	2	4d
4	3	4f

Important points:

Number of subshell in nth shell =n

Number of orbitals in nth shell =n^2

Number of electrons in nth shell =$2n^2$

Number of orbitals in subshell =2(2l+1)

Total number of nodes=n-1

Radial nodes = n-l-1

Angular nodes = l

Nodal plane = l

n= principal quantum number, l=azimuthal quantum number

Shapes and energy of orbitals:

s orbitals: they are of spherical shape and unidirectional orientation. The 'l' and 'm' value for s orbital is 0 which means they have only one unidirectional orientation.

Size and energy of s orbital increases with increasing value of principal quantum number 'n'. Hence, 1s <2s <3s <4s…..

p orbitals: they are dumb-bell shaped. For p subshell 'l'=1. So 'm' can have value ranging from

' –l' to '+l' i.e m= -1, 0, +1 value. This means that three p-orbitals axis are mutually perpendicular. They are designated as p_x, p_y, p_z.

Size and energy of these orbitals follow the trend: 2p <3p <4p

d orbitals: d orbitals have double dumb-bell shape except d_{z^2} which is baby soother like shape. It possesses directional properties. There are five d orbitals d_{xy} , $d_{yz}, d_{xz}, d_{x^2-y^2}, d_{z^2}$ as l =2 for d orbital. The 'm' values will therefore be respectively -2,-1,0,+1,+2.

In the case of d orbitals, as the principal quantum number 'n' increases, the shapes remain same but differ in energy

Orbital filling rules in an atom:

The filling of orbitals takes place in accordance to Aufbau's principle which is based on Pauli's exclusion principle and Hund's rule of maximum multiplicity.

Aufbau's principle: It states that in the ground state of an atom, the orbitals are filled in order of increasing energy. The lower orbitals are filled first and the order of filling orbitals is as follows:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 4f, 5d…..

(n+l) rule: The various subshell that are filled can be determined using (n+l) rule where n and l denotes the principal and azimuthal quantum numbers.

Pauli's exclusion principle:

It states that no two electrons in an atom can have the same set of four quantum numbers or it can be stated that only two electrons may exist in the same orbital and these electrons must have opposite spin.

Hund's rule of maximum multiplicity:

It states that pairing of electrons in the orbitals does not take place until each orbital belonging to the same subshell has got one electron each i.e. it is singly occupied.

Stability of half-filled and completely filled subshells:

The ground state electronic configuration of the atom of an element corresponds to the state of lowest total electronic energy. In the case of Cr and Cu, the valence shell electronic configurations are $3d^5 4s^1$ and $3d^{10} 4s^1$ and not $3d^4 4s^2$ and $3d^9 4s^2$.There is an extra stability associated with these half filled and fully filled orbitals.

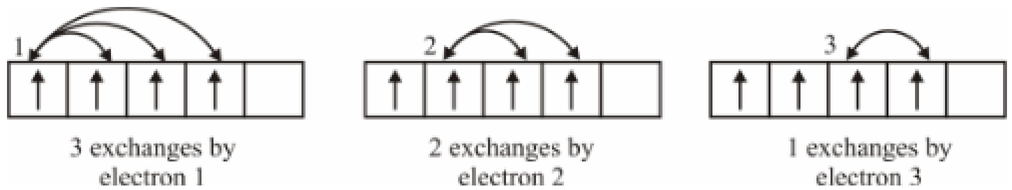
Magnetic moment value can be determined as: $\mu = \sqrt{n(n+2)}$ where n= number of unpaired electrons.

The stability of half-filled and completely filled subshells are due to:

Symmetrical distribution of electrons: symmetry leads to stability, so half filled and fully filled orbitals are symmetrical and hence stable.

Exchange energy: Electrons with similar spin possess the tendency to exchange their positions when present in degenerate orbitals of a subshell. The energy released during this exchange is the exchange energy.

If the electronic configuration of chromium was $[Ar]3d^4 4s^2$, then electrons could be exchanged in only (3+2+1) =6 ways as shown below.



But the actual configuration of chromium is $[Ar]3d^5 4s^1$, then possible exchange can be done in

(4+3+2+1) =10 ways as shown below: