CHAPTER 2

Atomic Structure

IMPORTANT DEFINITIONS

Proton (m_P)/anode rays	Neutron (m_n)	Electron (m_e) /cathode rays
mass = 1.67×10^{-27} kg	mass = 1.67×10^{-27} kg	mass = 9.1×10^{-31} kg
mass = 1.67×10^{-24} g	mass = 1.67×10^{-24} g	mass = 9.1×10^{-28} g
mass = 1.00750 amu	mass = 1.00850 amu	mass = 0.000549 amu
e/m value is dependent on the nature of gas taken in discharge tube.		e/m of electron is found to be independent of nature of gas & electrode used.

REPRESENTATION OF AN ELEMENT

$$\text{Mass number} \rightarrow \boxed{{}^{A}_{Z}X} \leftarrow \text{Symbol of the element}$$

Atomic number → Z

Terms associated with elements:

- Atomic Number (Z): = No. of protons

  Electron = Z–C (charge on atom)
- Mass number (A) = Total number of neutron and proton present

  A = Number of proton + Number of Neutrons
- **Isotopes:** Same atomic number but different mass number

  Example: ${}_6C^{12}$, ${}_6C^{13}$, ${}_6C^{14}$
- **Isobars:** Same mass number but different atomic number

  Example: ${}_1H^3$, ${}_2He^3$
- **Isodiaphers:** Same difference of number of Neutrons & protons

  Example: ${}_5B^{11}$, ${}_6C^{13}$

- **Isotones:** Having same number of neutron

  Example: ${}_1H^3$, ${}_2He^4$
- **Isosters:** They are the molecules which have the same number of atoms & electrons

  Example: CO_2, N_2O
- **Isoelectronic:** Species having same no. of electrons

  Example: Cl^-, Ar

ATOMIC MODELS

- **Thomson:** An atom considered to be positively charged sphere where e^- is embedded inside it.
- **Drawback:** Cannot explain stability of an atom.
- **Rutherford Model of an Atoms:**

  Electron is revolving around the nucleus in circular path.

  $R_N = R_0(A)^{1/3}$, $R_0 = 1.33 \times 10^{-13}$ cm

  [A = mass number, R_N = Radius of nucleus]

SIZE OF NUCLEUS

- The volume of the nucleus is very small and is only a minute fraction of the total volume of the atom. Nucleus has a diameter of the order of 10^{-12} to 10^{-13} cm and the atom has a diameter of the order of 10^{-8} cm.
- Thus, diameter (size) of the atom is 1,00,000 times the diameter of the nucleus.

ELECTROMAGNETIC SPECTRUM

- RW → MW → IR → Visible → UV → X-ryas → CR (Radiowaves → Microwaves → Infrared rays → Visible rays → Ultraviolet rays → X-rays → Cosmic rays)
- Wavelength decreases →
- Frequency increases →
- $c = \nu\lambda$ $\qquad \lambda = \dfrac{c}{\nu}$ $\qquad \bar{\nu} = \dfrac{1}{\lambda} = \dfrac{\nu}{c}$

  $T = \dfrac{1}{\nu}$ $\qquad E = \dfrac{hc}{\sqrt{\nu}} = h\nu$, $h = 6.626 \times 10^{-34}$ Js

  $E(ev) = \dfrac{12400}{\lambda(\text{Å})}$
- Total amount of energy transmitted $E = nh\nu = \dfrac{nhc}{\lambda}$

BOHR'S ATOMIC MODEL

Theory based on quantum theory of radiation and the classical laws of physics

- $\frac{K(Ze)(e)}{r^2} = \frac{mv^2}{r}$
- Electron remains in stationary orbit where it does not radiate its energy.
- **Radius:** $r = 0.529 \times \frac{n^2}{Z}$ Å
- **Velocity:** $v = 2.188 \times 10^6 \frac{Z}{n} ms^{-1}$
- Energy (KE + PE) = Total energy $= -13.6 \times \frac{Z^2}{n^2}$ eV/atom
- $TE = -\frac{KZe^2}{2r}, PE = \frac{-KZe^2}{r}, KE = \frac{KZe^2}{2r}$

  PE = –2KE, KE = –TE, PE = 2TE
- Revolutions per sec $= \frac{v}{2\pi r}$
- Time for one revolution $= \frac{2\pi r}{v}$
- Energy difference between n_1 and n_2 energy level

  $$\Delta E = E_{n_2} - E_{n_1} = 13.6Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \frac{eV}{atom} = IE \times \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

  where IE = ionization energy of single electron species.
- Ionization energy = $E_\infty - E_{G.S.} = 0 - E_{G.S.}$

  $E_{G.S.}$ = Energy of electron in ground state.

  $$E = 21.8 \times 10^{-12} \frac{z^2}{n^2} \text{ erg per atom}$$

  $$= -21.8 \times 10^{-19} \frac{z^2}{n^2} \text{ per atom}$$

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

  1 eV = 3.8 3 × 10^{-23} kcal

  1 eV = 1.602 × 10^{-12} erg

  1 eV = 1.602 × 10^{-19} J

  $$E = -313.6 \frac{z^2}{n^2} \text{ kcal/mole (1 cal = 4.18 J)}$$

  $$V = \frac{2\pi kze^2}{nh}$$

$$r = \frac{n^2h^2}{4\pi^2mkze^2}$$

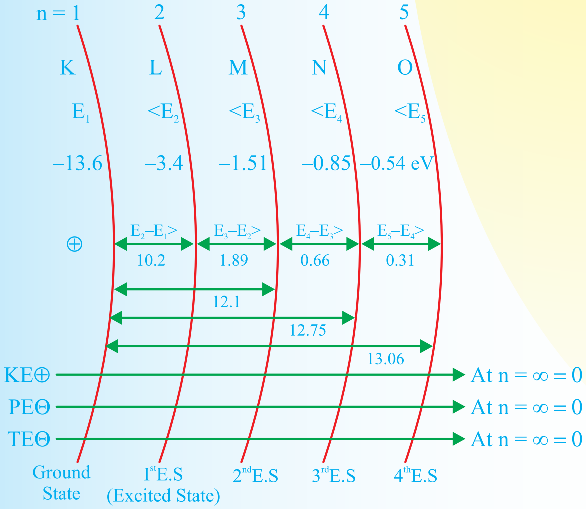
$$E = \frac{2\pi^2mz^2e^4k^2}{n^2h^2}$$

HYDROGEN SPECTRUM

- **Rydberg's Equation:**

  $$\frac{1}{\lambda} = \overline{v} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \times Z^2$$

  $R_H \cong 109700\ cm^{-1}$ = Rydberg constant
- For first line of a series $n_2 = n_1 + 1$
- Limiting spectral line (series limit) means $n_2 = \infty$
- H_α line means $n_2 = n + 1$; also known as line of longest λ, shortest v, least E
- Similarly H_β line means $n_2 = n_1 + 2$
- When electron de-excite from higher energy level (n) to ground state in atomic sample, then number of spectral lines observed in the spectrum $= \frac{n(n-1)}{2}$
- When electrons de-excite from higher energy level (n_2) to lower energy level (n_1) in atomic sample, then number of spectral line observed in the spectrum $= \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$
- No. of spectral lines in a particular series $= n_2 - n_1$.



DE-BROGLIE HYPOTHESIS

- All material particles posses wave character as well as particle character.
- $\lambda = \frac{h}{mv} = \frac{h}{p}$
- The circumference of the n^{th} orbit is equal to n times of wavelength of electron i.e., $2\pi r_n = n\lambda$

  Number of waves = n = principal quantum number
- Wavelength of electron (λ) $\cong \sqrt{\frac{150}{V(vols)}}$Å
- $\lambda = \frac{h}{\sqrt{2mKE}}$

HEISENBERG UNCERTAINTY

- According to this principle, "it is impossible to measure simultaneously the position and momentum of a microscopic particle with absolute accuracy"

  If one of them is measured with greater accuracy, the other becomes less accurate.
- $\Delta x.\Delta p \geq \frac{h}{4\pi}$ or $(\Delta x)(\Delta v) \geq \frac{h}{4\pi m}$

  where Δx = Uncertainty in position

  Δp = Uncertainty in momentum

  Δv = Uncertainty in velocity

  m = mass of microscopic particle
- Heisenberg replaced the concept of orbit by that of orbital.

QUANTUM NUMBER

- **Principal Quantum number (By Bohr)**

  $\Rightarrow$ Indicates = Size and energy of the orbit, distance of e^- from nucleus

  $\Rightarrow$ Values n = 1, 2, 3, 4, 5 …

  $\Rightarrow$ Angular momentum = $n \times \frac{h}{2\pi}$

  $\Rightarrow$ Total number of e^-s in an orbit = $2n^2$

  $\Rightarrow$ Total number of orbitals in an orbit = n^2

  $\Rightarrow$ Total number of subshell in an orbit = n

- **Azimuthal/Secondary/Subsidiary/Angular momentum quantum number (l)**

  $\Rightarrow$ Given by = Sommerfeld

  $\Rightarrow$ Indicates = Sub shells/sub orbit/sub level

  $\Rightarrow$ Vales $\Rightarrow$ 0, 1 … (n–1)

  $\Rightarrow$ Indicates shape of orbital/Sub shell

Value of n	Values of l [Shape]	Initial from word
eg. If n = 4	$l = 0$ (s) [Spherical] $l = 1$ [p] [Dumb bell] $l = 2$ [d] [Double dumb bell] $l = 3$ [f] [Complex]	Sharp Principal Diffused Fundamental

$\Rightarrow$ Total no. of e^-s in a suborbit = 2(2l + 1)

$\Rightarrow$ Total no. of orbital in a suborbit = (2l + 1)

$\Rightarrow$ Orbital angular momentum $= \sqrt{l(l+1)}\dfrac{h}{2\pi} = \sqrt{l(l+1)}\hbar$

h = Planck's constant

$\Rightarrow$ For H & H like species all the subshells of a shell have same energy.

i.e 2s = 2p 3s = 3p = 3d

- **Magnetic Quantum number (m)**

  $\Rightarrow$ Given by Lande

  $\Rightarrow$ Indicates orientation of orbital i.e. direction of electron density.

  $\Rightarrow$ Value of m = $-l$ ....0.............$+l$

  $\Rightarrow$ Maximum no of e's in an orbital = 2

  (with opposite spin)

  m for p sub shell = p_x p_y p_z

  –1 +1 0

  m for d sub shell =

  dxy dyx dz^2 dxz dx^2-y^2

  –2 –1 0 +1 +2

- **Spin Quantum Number (m_s or s)**

  Given by Uhlenback & Goudsmit

  Values of s = ±½

  Total value of spin in an atom = ±½ × number of unpaired electrons

  Spin Angular momentum $= \sqrt{s(s+1)}\dfrac{h}{2\pi}$

RULES FOR FILLING OF ORBITALS

- **Aufbau principle:** The electrons are filled up in increasing order of the energy in subshells.
  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10}$
- **(n + *l*) rule:** The subshell with lowest (n + *l*) value is filled up first, but when two or more subshells have same (n + *l*) value then the subshell with lowest value of n is filled up first.
- **Pauli exclusion principle:** Pauli stated that no two electrons in an atom can have same values of all four quantum numbers.
- **Hund's rule of maximum multiplicity:** Electrons are distributed among the orbitals of subshell in such a way as to give maximum number of unpaired electrons with parallel spin.

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