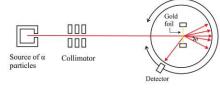
#### 2020 - 2021

## **ATOM MOLECULE**

#### GEIGER - MARSEN EXPERIMENT: (Read)

A narrow beam of α – particles from a radioactive source was incident on a gold foil. The scattering was detected by the detector fixed on a rotating



stand. Detector has a Zinc Sulphide screen and microscope. The whole setup is enclosed in an evacuated chamber. The number of  $\alpha$  particles and their scattering angles ( $\theta$ ) are observed.

The observation showed most of the alpha particles passed undeviated. About 0.14% scattered more than 0.1°. Few got deflected slightly. Very few (1 in 8000) deflected by more than 90°. Some particles even bounced back with  $180^{\circ}$ .

#### **RUTHERFORD'S MODEL of an Atom:**

>>The atom has tiny positively charged core called nucleus >> The total positive charge and the entire mass (99.9%) of the atom is confined in nucleus

>> The nucleus is surrounded by negatively charged electrons, orbiting round the nucleus in circular orbits

>>As an atom is electrically neutral, the positive charge on nucleus is equal to the total negative charge of all the orbiting electrons

>> As the size of the nucleus  $(10^{-15}m)$ , about 100000 times smaller than the size of atom. Thus atom mostly consists of empty space.

>>The revolution of electrons was necessary else the electron would have fallen into the positively charged nucleus. The space between the orbits of electrons and the nucleus is mostly empty (thus most alpha particles when trough undeflected)

#### Failures:

>> Accelerated charge(magnitude of velocity constant but direction changing) radiates energy. Hence, the energy of accelerated electron should continuously decrease and follow inward spiral path and finally fall into the nucleus. Thus no stable atom could exist.

>> If the electron spirals inwards, their angular velocity and hence frequency would increase continuously. Thus, they would emit energy with continuously increasing frequency (decreasing wavelength) and hence we would get a continuous spectra. In which case no atom would have a line spectra, which we know is incorrect (e.g. Hydrogen)

#### BOHR's postulates or BOHR'S MODEL:

**Postulate 1:** The electron in atom revolves in circular orbit around the nucleus with nucleus at the centre of orbit. The necessary centripetal force for circular motion is provided by electrostatic force of attraction between the positively charged nucleus and negatively charged electron.

Centripetal force = Electrostatic Force of Attraction

 $\frac{mv^2}{r} = \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r^2}$ 

**Postulate 2:** The electron revolves around the nucleus only in those orbits for which the angular momentum is equal to an integral multiple of  $\frac{h}{2\pi}$ , where h is Planck's constant. These orbits are called stable or stationary (or permitted or quantized or Bohr orbits) and electron does not radiate energy while revolving in these orbits.

Angular Momentum = mvr =  $n \frac{h}{2\pi}$ , where n = 1,2,3,4,.... n is called the principle quantum number.

**Postulate 3:** When electron jumps from orbit of higher energy to an orbit of lower energy, it radiates energy in the form of quanta or photons. The energy of emitted photon is equal to the difference between energies of two orbits in which transition is taking place.

Suppose an electron from n<sup>th</sup> higher orbit, jumps to p<sup>th</sup> lower orbit. Let  $E_n$  and  $E_p$  be the energies of electron in n<sup>th</sup> and p<sup>th</sup> orbit respectively, then Energy radiated =  $E_n - E_p = hv$  Radius of Bohr's orbit:

Consider an electron revolving around the nucleus in circular orbit of radius r. According to Bohr's first postulate

Centripetal force = electrostatic force of attraction

$$\frac{mv^2}{r} = \frac{1}{4\pi\varepsilon_o} \frac{Ze^2}{r^2} \qquad thus \ v^2 = \frac{Ze^2}{4\pi\varepsilon_o mr} \dots \dots$$

Angular momentum 
$$mvr = n \frac{n}{2\pi}$$
 thus  $v = \frac{nn}{2\pi mr} \dots \dots \dots (II)$ 

Comparing (I) and (III) we get

$$\frac{Ze^2}{4\pi\varepsilon_o mr} = \frac{n^2h^2}{4\pi^2m^2r^2}$$
  
Thus,  $r = \frac{\varepsilon_o n^2h^2}{\pi m Ze^2}$ 

This is the equation of the radius of n<sup>th</sup> Bohr orbit

For Hydrogen Z=1 and for n=1,  $r_1=\frac{\varepsilon_0 h^2}{\pi m e^2}$  = 0.537 Å

In general  $r_n = r_1 n^2$ , thus  $r \alpha n^2$ 

The radius of Bohr orbit is directly proportional to the square of principle quantum number.

NOTE: speed of the electron can be got by substituting r in (II) we get

$$v = \frac{Ze^2}{2\varepsilon_o nh}$$
, thus  $v \alpha \frac{Z}{n}$ 

**NOTE:** angular velocity  $\omega$  can be got using  $v = r\omega$  & freq f using  $\omega = 2\pi f$ **NOTE:** Linear momentum = mv and angular momentum =  $\frac{n\hbar}{2\pi}$ 

#### ENERGY of electron in Bohr's orbit:

According to Bohr's postulate, electron revolves around in circular orbit. It has two energies; potential energy and kinetic energy. Therefore total energy possessed by an electron is given by Total energy E = PE + KE

The electric potential V =  $\frac{1}{4\pi\varepsilon_o}\frac{Ze}{r}$ 

The PE of an electron in the field of nucleus is (PE) = potential x charge pE =  $\frac{1}{2e} \frac{Ze}{(-a)} = -\frac{Ze^2}{2e}$ 

$$\mathsf{PE} = \frac{1}{4\pi\varepsilon_o} \frac{\pi}{r} \quad (-e) = -\frac{\pi c}{4\pi\varepsilon_o}$$

By Bohr's first postulate,  $\frac{mv^2}{r} = \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r^2}$  thus  $mv^2 = \frac{Ze^2}{4\pi\varepsilon_0 r}$ Therefore,  $KE = \frac{1}{2}mv^2 = \frac{Ze^2}{8\pi\varepsilon_0 r}$ Thus,  $E = PE + KE = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{Ze^2}{8\pi\varepsilon_0 r} = -\frac{Ze^2}{8\pi\varepsilon_0 r}$ Substituting r we get,  $E = -\frac{mZ^2e^4}{8\varepsilon_0^2n^2h^2}$ 

Minus sign signifies that the electron is bound to the nucleus by the force of attraction and hence one has to do work on the electron to make it free from the atom.

$$E_n \alpha \frac{Z^2}{n^2}$$

Energy of electron in the n<sup>th</sup> Bohr orbit is inversely proportional to the square of principal quantum number.

For Hydrogen Z=1 and for n=1 , E<sub>1</sub> = -13.6 eV . Thus for the n<sup>th</sup> Bohr orbit En =  $\frac{-13.6}{n^2} eV$ 

Thus the valid energies of electrons in hydrogen atom are -13.6 eV, -13.6 eV, -13.6 eV in the 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup> orbit respectively.

The Binding Energy of electron or *ionization energy* of hydrogen atom is minimum energy required to be given to an electron in ground state to make it free from the nucleus.

For electron in n<sup>th</sup> orbit it is  $\frac{me^4}{8\varepsilon_o^2n^2h^2}$  and 0 for n= $\infty$ 

NOTE: Excitation energy is the energy required to take an electron from ground state to an excited state

VIII•IX•X ICSE • XI(Sc) • XII(Sc) • HSc/CET/JEE/NEET • CBSE • IGCSE•IB•A LEVEL/AS/HL/SL • Engineering Telephone: 9820246760 / 9769479368 • Websites: navlakhi.com –or– navlakhi.education Navlakhi®

Email: abhishek@navlakhi.com –or– kunal@navlakhi.com

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#### **DERIVATION of Wave Number for Spectral Lines of Hydrogen**

In a normal, unexcited hydrogen atom, an electron resides in innermost orbit (n=1). This is called ground state. The energy of an electron in the ground state is - 13.6 eV. If the atom is subjected to external energy equal or greater than 13.6eV, electron becomes free. This process is called ionization.

Suppose an electron jumps from  $n^{th}$  higher orbit to  $p^{th}$  lower orbit and  $E_n$ and  $E_p$  be their energies in their respective orbits, then

$$E_n = -\frac{me^4}{8\varepsilon_o^2 n^2 h^2}$$
 and  $E_p = -\frac{me^4}{8\varepsilon_o^2 p^2 h^2}$ 

According to Bohr's 3rd postulate

Energy emitter = 
$$hv = E_n - E_p = -\frac{me^4}{8\varepsilon_o^2 n^2 h^2} + \frac{me^4}{8\varepsilon_o^2 p^2 h^2}$$
  
 $hv = \frac{me^4}{8\varepsilon_o^2 h^2} \left(\frac{1}{p^2} - \frac{1}{n^2}\right)$   
Thus,  $v = \frac{me^4}{8\varepsilon_o^2 h^3} \left(\frac{1}{p^2} - \frac{1}{n^2}\right)$   
 $\frac{c}{\lambda} = \frac{me^4}{8\varepsilon_o^2 h^3} \left(\frac{1}{p^2} - \frac{1}{n^2}\right)$   
 $\frac{1}{\lambda} = \frac{me^4}{8\varepsilon_o^2 h^3 c} \left(\frac{1}{p^2} - \frac{1}{n^2}\right) = R \left(\frac{1}{p^2} - \frac{1}{n^2}\right)$   
where  $R = Rydberg's constant = 1.093 X 10^7 m^{-1}$   
 $\frac{1}{\lambda}$  is called wave number also denoted as  $\overline{v}$ 

NOTE: The wavelength emitted by each element are unique, and hence can be used to identify the element

#### HYDROGEN SPECTRUM / HYDROGEN SPECTRAL LINES / ENERGY LEVEL DIAGRAM OF HYDROGEN ATOM:

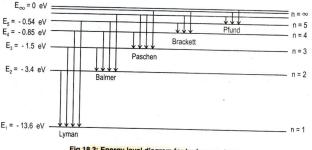


Fig 18.3: Energy level diagram for hydrogen atom

A series of spectral lines is radiated due to transition of electrons from different outer orbits to fixed inner orbit. The spectral series observed for hydrogen are:

Lyman Series: Due to transition of electrons from different outer orbits to first Bohr orbit (p=1)

$$\frac{1}{\lambda} = R \left( \frac{1}{1^2} - \frac{1}{n^2} \right), where \ n = 2,3,4,5 \dots$$

This series lies in the ultraviolet region of the spectrum.

Balmer Series: Due to transition of electrons from different outer orbits to second Bohr orbit (p=2)

$$\frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right), where \ n = 3,4,5,6 \dots$$

This series lies in the VISIBLE region of the spectrum.

The lines are named H $_{\alpha}$ , H $_{\beta}$ , H $_{\gamma}$  and H $_{\delta}$ 

Paschen Series: Due to transition of electrons from different outer orbits to third Bohr orbit (p=3)

$$\frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$$
, where  $n = 4,5,6,7...$ 

This series lies in the infrared region of the spectrum.

Brackett Series: Due to transition of electrons from different outer orbits to fourth Bohr orbit (p=4)

# $\frac{1}{\lambda} = R\left(\frac{1}{4^2} - \frac{1}{n^2}\right)$ , where $n = 5, 6, 7, 8 \dots$

This series lies in the near - infrared region of the spectrum. Pfund Series: Due to transition of electrons from different outer orbits to fifth Bohr orbit (p=5)

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$$\frac{1}{\lambda} = R\left(\frac{1}{5^2} - \frac{1}{n^2}\right)$$
, where  $n = 6,7,8,9...$ 

This series lies in the far – infrared region of the spectrum.

Lyman Series limit:  $\frac{1}{\lambda} = R \left( \frac{1}{1^2} - \frac{1}{m^2} \right) = \frac{R}{1}$ , thus  $\lambda_{min} = \frac{1}{R}$ Balmer Series limit:  $\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{m^2}\right) = \frac{R}{4}$ , thus  $\lambda_{min} = \frac{4}{R}$ Paschen Series limit:  $\frac{1}{2} = R \left( \frac{1}{2^2} - \frac{1}{m^2} \right) = \frac{R}{2}$ , thus  $\lambda_{min} = \frac{9}{R}$ Brackett Series limit:  $\frac{1}{1} = R\left(\frac{1}{t^2} - \frac{1}{t^2}\right) = \frac{R}{t^2}$ , thus  $\lambda_{min} = \frac{16}{R}$ Pfund Series limit:  $\frac{1}{\lambda} = R \left( \frac{1}{5^2} - \frac{1}{cs^2} \right) = \frac{R}{25}$ , thus  $\lambda_{min} = \frac{25}{R}$ 

#### Limitations of Bohr's Model:

>>It could not explain the line spectra of atoms other than hydrogen >>The intensities of the emission lines seemed to differ and Bohr's model had no explanation

>>It assumed arbitrarily a particular condition to be stable. There was no theoretical basis.

#### De BROGLIE'S HYPOTHESIS (Matter Waves):

In 1924, Louis de Broglie suggested that if radiant energy has both wave and particle nature, then particle (matter) must have a wave associated with it. The wavelength associated with a particle of mass m moving with a speed v is given by

 $\lambda = \frac{h}{p} = \frac{h}{mv}$ , where h is planck's constant and p is momentum

This explain dual nature of matter. On left side, it has wavelength  $\lambda$  of wave and on right side the momentum p of particle and Planck's constant relates them.

As  $v \rightarrow 0$ ,  $\lambda \rightarrow \infty$  and as  $v \rightarrow \infty$ ,  $\lambda \rightarrow 0$ 

This implies that matter are associated with material particles only if they are moving. Greater the momentum of the particle, the shorter the wavelength. The velocity of matter waves is not constant because it depends upon the velocity of particle. The de Broglie wavelength is independent of the charge of particle.

Proof: According to Planck's quantum theory energy of photon E =  $hv = \frac{hc}{2}$ According to Einstein's mass energy relation E = mc<sup>2</sup> Thus  $mc^2 = \frac{hc}{\lambda}$ , or  $\lambda = \frac{h}{mc} = \frac{h}{mc}$ 

#### Verification of 2<sup>nd</sup> Postulate by De Broglie's:

For an electron moving in the n<sup>th</sup> orbit or radius  $r_n$  , the distance traveled is  $2\pi r_n$  and that should be an integral multiple of wavelength.  $2\pi r_n = n\lambda$  where n=1.2.3.4

But by de Broglie's 
$$\lambda = \frac{h}{p} = \frac{h}{mv_n}$$
  
Thus,  $2\pi r_n = n \frac{h}{mv_n}$  or  $mv_n r_n =$ 



2π This is the quantum condition proposed by Bohr for angular momentum of the electron in 2<sup>nd</sup> postulate.

#### Wavelength of an accelerated electron:

If an electron of mass m is accelerated by potential V, the work done on electron increases its KE

Work done = E = eV = ½ mv² = ½ m²v²/m = 
$$\frac{p^2}{2m}$$
 .Thus  $p = \sqrt{2mE} = \sqrt{2meV}$ 

substitute in de Broglie's equation  $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2meV}} = \frac{12.27}{\sqrt{V}}$  Å

(DASISSON GERMER EXPERIMENT REFER 14.6 / NEXT SHEET)

### VIII•IX•X ICSE • XI(Sc) • XII(Sc) • HSc/CET/JEE/NEET • CBSE • IGCSE•IB•A LEVEL/AS/HL/SL • Engineering

Telephone: 9820246760 / 9769479368 • Websites: navlakhi.com –or– navlakhi.education Navlak Email: abhishek@navlakhi.com -or- kunal@navlakhi.com