ATOMIC STRUCTURE

Cathode Rays (Discovery of Electrons)

Cathode rays were for the first time discovered by **Julius Plucker** by discharge tube experiment at very low pressure (0.01mm Hg) and very high voltage (~ 15000V). He observed that, when electric discharge is carried out at very low pressure (0.01mm Hg) and very high voltage (~ 15000V), some invisible rays arise from cathode, move towards anode and produce glow at the wall of discharge tube behind anode. These invisible rays were termed as cathode rays.

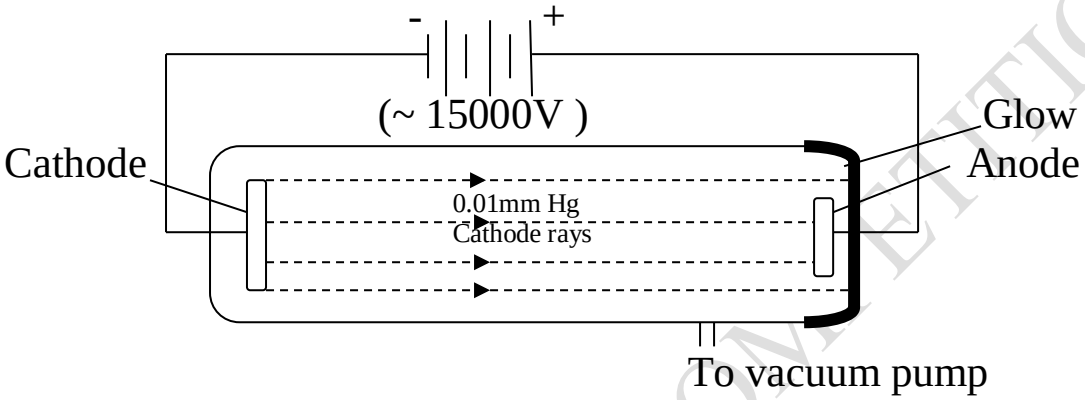


Fig. Production of Cathode Rays

Properties of Cathode Rays - Studied by J.J Thomson

1. When a metallic cross is placed in the path of cathode rays, its shadow is formed at the wall of discharge tube indicating that, cathode rays travel in straight line.

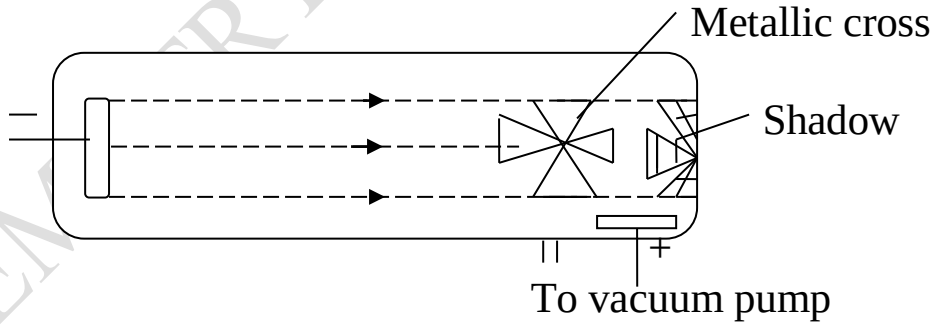


Fig.-Formation of shadow of metallic cross placed in the path of cathode rays

2. When a light paddle wheel is placed in the path of cathode rays, it starts revolving indicating that, cathode rays are consisting of minute particles having sufficient kinetic energy.

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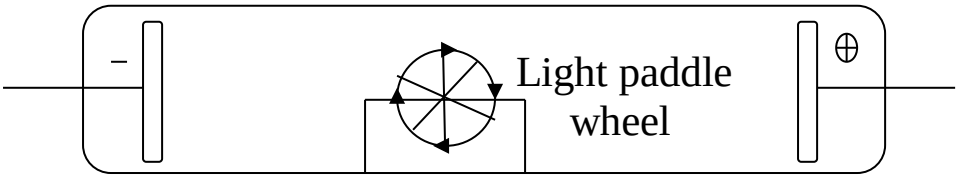


Fig- Revolving of light paddle wheel placed in the path of cathode rays

3. When cathode rays are passed through electric field, they get turned towards positively charged plate, indicating that, cathode rays are consisting of negatively charged particles.

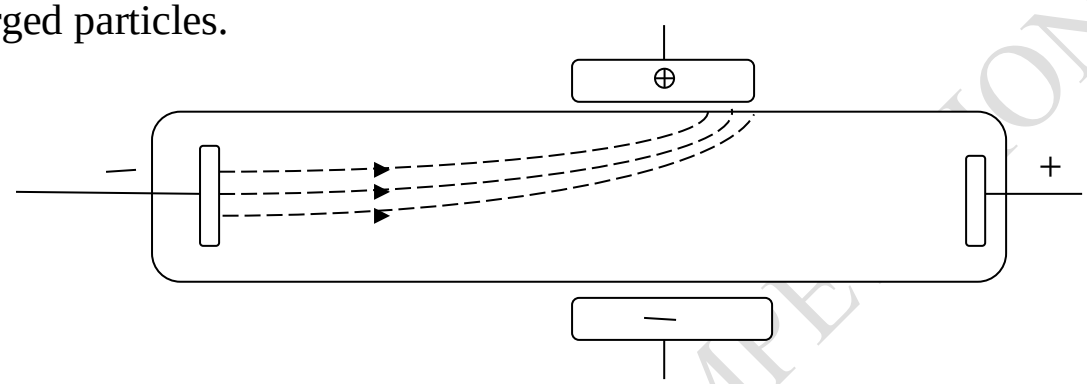


Fig- Deviation of cathode rays in electric field

4. When cathode rays are passed through magnetic field, they get turned towards north pole of the magnet, indicating that, they have magnetic effect.

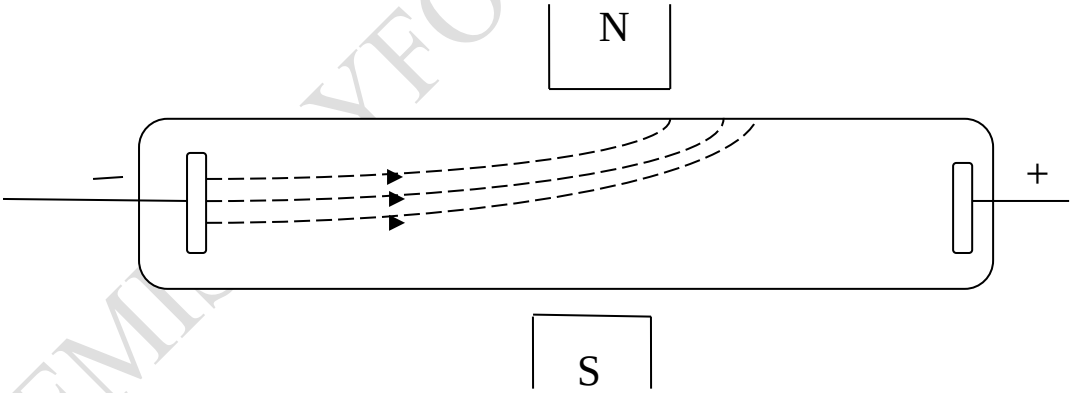


Fig- Deviation of cathode rays in magnetic field

5. Charge to mass ratio (e/m ratio) or specific charge of cathode rays is universal constant and is independent of the nature of gas taken in discharge tube as well as the nature of metal from which the cathode is made.

6. When cathode rays are allowed to fall on the surface of thin aluminium foil, the foil gets heated up, indicating that, the cathode rays have heating effect.

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7.When cathode rays fall on the surface of a metal having very high melting point such as tungsten, they produce X-rays.

Thus, cathode rays are consisting of minute negatively charged particles having sufficient kinetic energy. These particles were ultimately termed as electrons.

Anode Rays (Discovery of Protons)

Anode rays were for the first time discovered by **Goldstein** by discharge tube experiment at very low pressure and very high voltage using perforated cathode. He observed that, when electric discharge is carried out at very low pressure
(0.01mm Hg) and very high voltage (~ 15000V) using perforated cathode, some invisible rays also move towards cathode, pass through its perforations and produce glow at the wall of discharge tube behind cathode. These invisible rays were termed as anode rays.

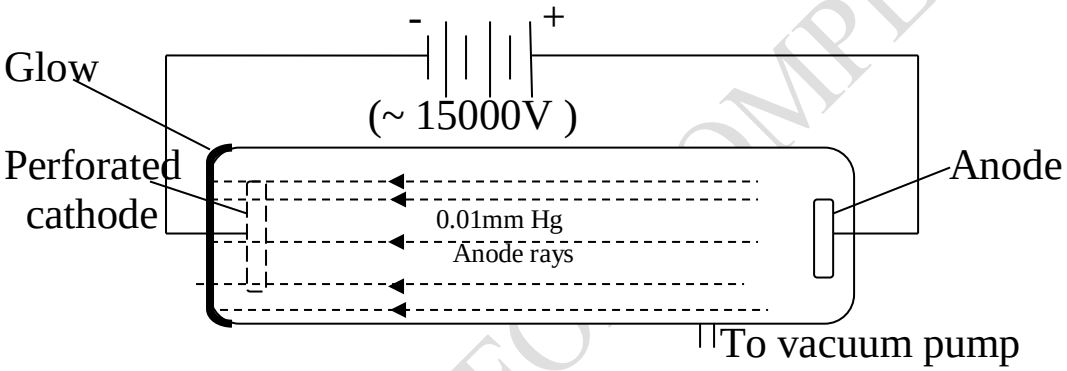


Fig. Production of Anode Rays

Properties of Anode Rays

1. Anode rays travel in straight line.
2. Anode rays are consisting of minute particles having sufficient kinetic energy.
3. When anode rays are passed through electric field, they get turned towards negatively charged plate indicating that, anode rays are consisting of positively charged particles.
4. Anode rays have magnetic effect.
5. Charge to mass ratio (e/m ratio) or specific charge of anode rays is not universal constant, but is dependent on the nature of gas taken in discharge tube as well as nature of metal from which cathode is made.

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Production of Anode Rays

Anode rays are produced by striking of the energetic electrons of cathode rays on the atoms or molecules of the gas taken in discharge tube. When the electrons of cathode rays strike to these atoms or molecules, they eject electrons from them to produce cations. The electrons thus ejected, become the part of cathode rays, while the cations formed move towards cathode as anode rays. Thus, anode rays are not essentially consisting of protons, but they may be consisting of any positively charged particles depending upon the nature of gas taken in discharge tube. It is the reason why e/m ratio anode rays is not universal constant, but depends upon the nature of gas taken in discharge tube.

- e/m ratio or specific charge of cathode rays (electrons) is 1.76×10^{11} C/Kg.
- e/m ratio or specific charge of cathode rays is universal constant. It is because cathode rays are essentially consisting of electrons having fixed value of their charge and mass.
- Anode rays are not essentially consisting of protons, but they may be consisting of any positively charged particles depending upon the nature of gas taken in discharge tube. It is the reason why e/m ratio anode rays is not universal constant but depends upon the nature of gas taken in discharge tube.
- When hydrogen is taken in discharge tube, then anode rays are essentially consisting of protons.
- Amongst positively charged particles, e/m ratio of proton is highest and its value is $9.58\text{x } 10^8$ C/Kg.

Discovery of Neutrons

Neutron was for the first time discovered by **Chadwick.** He bombarded Beryllium nucleus by energetic α - particles and found that, these nuclei got converted into carbon nuclei and a neutral particle ejected. This neutral particle was termed as neutron.

$$_4Be^9 + {}_2He^4 \rightarrow {}_6C^{12} + {}_0n^1$$

Beryllium α-particle Carbon Neutron

- This phenomenon of conversion of the nuclei of one element into that of another element by artificial means is called **artificial transmutation**.
- By artificial transmutation, now a days it has become possible to convert mercury into gold.

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Discovery of Neucleus (Rutherford's Experiment)

Rutherford bombarded energetic α-particles over thin gold foil and found following observations-

(1) Most of the α-particles pass away without any deviation.

(2) A few α-particles passing near the centre of atom, got deviated making certain angles.

(3) A very few α-particles passing just centre of atom, bounced back following same path.

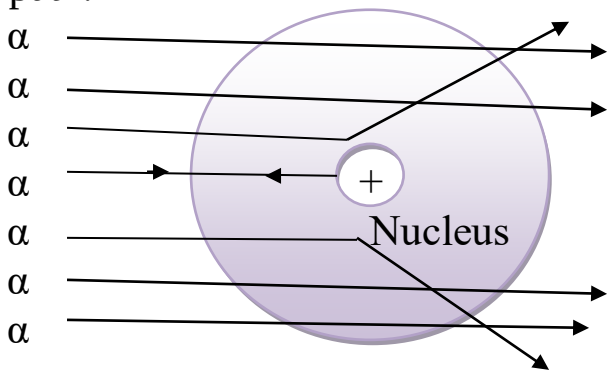


Fig.- α-particles scattering experiment

Based on these observations, Rutherford concluded that-

(1) Most of the part of atom is empty.

(2) There should be some positively charged object at the centre of atom.

(3) The positively charged object present at the centre of atom must be highly dense.

Thus, Rutherford's α-particles scattering experiment revealed that, there present highly dense positively charged object at the centre of atom, which was ultimately termed as nucleus.

Rutherford's Atomic Model

On the basis of conclusions drawn from α-particles scattering experiment, Rutherford proposed his atomic model, which is also called **Nuclear Model or Planetary Model** of atom. The main postulates of this model are as under-

(1) Most of the part of atom is empty.

(2) Almost entire mass and entire positive charge of atom remains concentrated in very small region at the centre of atom called nucleus. Hence, this model is also called nuclear model of atom.

(3) Electrons revolve around the nucleus just like planets revolve around the sun. Hence, this model is also called planetary model of atom.

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(4) The size of the atom is of the order of 10^{-10}m, while that of nucleus is of the order of 10^{-15}m. Thus, nucleus is about 10^5 times smaller as compared to the atom.

(5) Though there is nuclear attraction on electrons, they do not fall in the nucleus because they have sufficient energy to overcome this nuclear attraction.

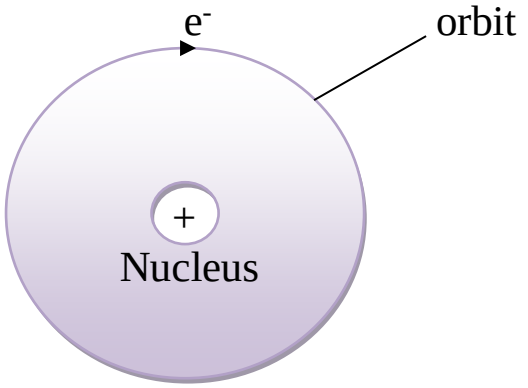


Fig-Rutherford's Atomic Model

Shortcomings of Rutherford's Atomic Model

(1) This model could not explain atomic stability. According to quantum mechanics electron revolving around nucleus, being charged particle would continuously emit energy so that nuclear attraction on electron would go on increasing. Thus, the radius of the circular path of electron would go on decreasing and electron would ultimately fall in the nucleus causing destruction of atoms. Thus, atoms must be unstable, but in practice, atoms of most of the elements are found to be stable.

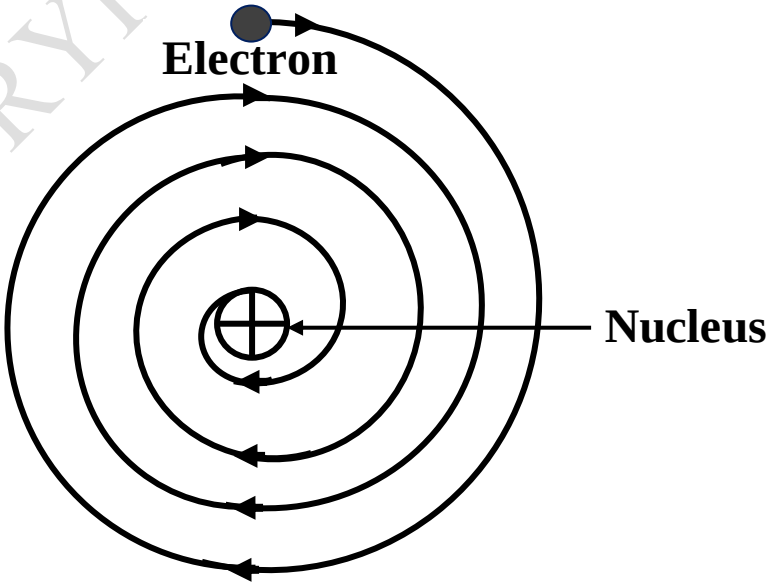


Fig.- Spiral path of electron around nucleus

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(2) This model could not explain discontinuous line spectra of atoms. According to quantum mechanics, since, the electron revolving around nucleus continuously emits energy, it must emit radiations of all the frequencies and wavelengths. Thus, atomic spectra should be continuous i.e. it must contain lines of all the frequencies and wavelengths. However, in practice, atomic spectra is found to be discontinuous and contains only few lines of definite frequencies and wavelengths, but not lines of all the frequencies and wavelengths.

Bohr's Atomic Model

This model has been proposed to overcome the shortcomings of Rutherford's atomic model. The main postulates of this model are as under –

(1) Atoms consist of centrally placed nucleus containing positively charged protons and neutral neutrons.

(2) Electrons revolve around the nucleus in some definite circular path called orbits.

(3) Numerous circular paths are possible around nucleus, but electrons do not revolve in all these paths but they revolve only in those circular path whose angular momentum is integral multiple of h/2π. Thus,

$$\text{Angular momentum of electron} = \frac{nh}{2\pi}$$

Here, corresponding to n = 1,2,3,4----- the orbits are designated as K, L, M, N-------orbits respectively.

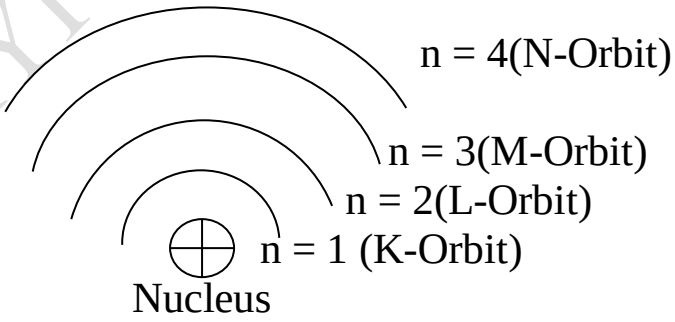


Fig - Different orbits of an atom

(4) When an electron revolves in a definite orbit, it neither emits nor absorbs energy. Thus, energy of an electron remains fixed in a definite orbit. Hence, these orbits are also called stationary orbits.

(5) When electron absorbs energy, it gets jumped to an orbit of higher energy. Here, it is unstable and therefore, returns back to its original state in one or more

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steps by releasing energy. This released energy is observed as a line of definite frequency in atomic spectra. The energy released in a definite electronic transition is equal to the difference of the energies of associated orbits.

If E_2 and E_1 are the energies of higher and lower energy levels respectively, then the frequency and wavelength of radiation released in electronic transition from higher to lower energy levels, is given by following formula-

$$\Delta E = E_2 - E_1$$

$$= h\nu \qquad (\because \nu = c/\lambda)$$

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

(6) The nuclear attraction acting on electrons revolving around nucleus, acts like centripetal force and is exactly balanced by centrifugal force acting outside the nucleus. It is the reason why though there is nuclear attraction on electrons revolving around nucleus, they do not fall in the nucleus.

Shortcomings of Bohr's Atomic Model

(1) Bohr's atomic model is applicable only on hydrogen atom and hydrogen like ions (He^+, Li^{2+}, Be^{3+} etc) containing only one electron. It could not explain the emission spectra of multi-electron atoms and ions.

(2) This model could not explain the splitting of spectral lines into finer lines in electric and magnetic fields (Zeeman and Stark effects). Thus , it could not explain the finer structure of spectral lines.

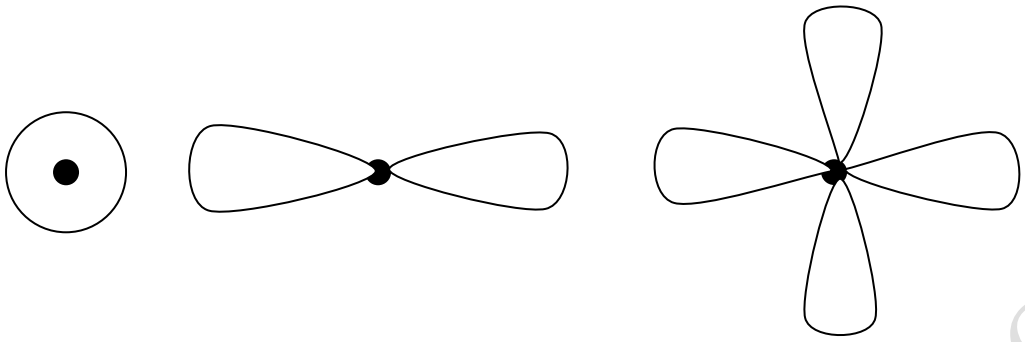
(3) This model is against Hiesenberg's uncertainty principle.

Orbitals

"The three dimensional space around nucleus where probability of finding electrons is maximum is called an orbital."

Orbitals may be spherical, dumb-bell shaped, double dumb-bell shaped or of any other complicated shape. On this basis they are designated as s, p, d and f-orbitals respectively.

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s- orbital (spherical) p - orbital (dumb-bell shaped) d- orbital (double dumb-bell shaped)

Fig- Different types of orbitals

Amongst all these orbitals, s-orbital is non-directional in nature, while all other orbitals are directional in nature i.e. remain directed in some specified directions in space around the nucleus.

Difference Between Orbit and Orbital

(1)It is circular path around nucleus on which electrons revolve.	(1)It is three dimensional space around nucleus where probability of finding electrons is maximum.
(2)It is two dimensional and planer.	(2)It is three dimensional and non-planer.
(3)It is always circular in shape.	(3)It may be spherical, dumb-bell shaped, double dumb-bell shaped or of any other complicated shape.
(4)It can accommodate a maximum of $2n^2$ electrons. Where n is orbit number.	(4)It can accommodate only a maximum of 2 electrons having opposite spin.
(5)In an orbit position of electron is fixed.	(5)In an orbital position of electron is not fixed but only probable.
(6)It is always non-directional.	(6)Except s-orbital , all the orbitals are directional in nature
(7)It is against Hiesenberg's uncertainty principle.	(7) It is accordance with Hiesenberg's uncertainty principle.

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Spectrum

When a beam of light is passed through a prism or a diffraction grating, it gets splitted into radiations of different wavelengths and frequencies. This phenomenon is called dispersion and the definite pattern of radiations observed after dispersion is called spectrum. Thus, the spectrum is a definite pattern of radiations taken on a screen.

Depending upon the source of radiations, spectra may be of following types-

(1) Emission spectra

Here, spectrum of radiations emitted from a self-luminous source is taken. It may be of following types-

(a) Continuous Spectra

Such spectra which contain lines of all the frequencies and wavelength of a definite range are called continuous spectra. For example, solar spectrum, spectrum of incandescent bulb, candle flame, carbon arc etc.

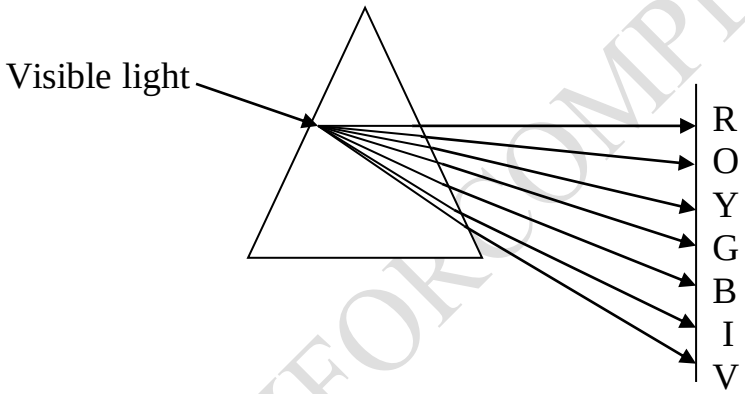


Fig.-Expression of continuous spectrum of visible light

(b) Discontinuous or Line Spectra

Such spectra which contain only few lines of some definite frequencies and wavelengths separated by dark spaces, but not the lines of all the frequencies and wavelengths are called discontinuous or line spectra. These are given by excited atoms of elements and therefore, they are also called atomic spectra. For example, spectra of atomic hydrogen, sodium vapours etc.

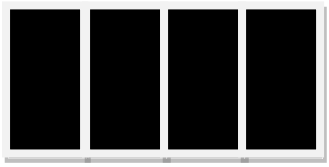


Fig.-Expression of line spectrum

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The pattern of lines in the atomic spectrum of an element is the characteristics of the element and is different from the other element. Thus, it acts like the finger print of the respective element. For example, Sodium vapour gives two lines in yellow region of visible spectrum corresponding to 5896 A^0 and 5890 A^0.

(c) Band Spectra

Such spectra which contain distinct bright bands of overlapped spectral lines separated by dark spaces are called band spectra. These are given by excited molecules and therefore, they are also called molecular spectra. For example, spectra of molecular hydrogen, CO, NH_3 etc.

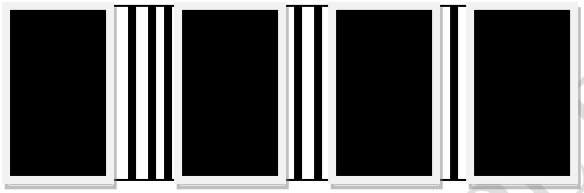


Fig- Expression of Band spectrum

(2) Absorption Spectra

Here, spectrum of light transmitted from a medium is taken. For example, when visible light is passed through a medium and the transmitted light is dispersed by the prism, few dark lines or bands are obtained in the otherwise continuous spectrum.

Here, the dark lines or bands depend upon the nature of absorbing medium and the spectrum is called absorption spectrum.

Like emission spectra, absorption spectra may also be continuous, line or band spectra.

Hydrogen Spectrum

When a sample of hydrogen is irradiated with a radiation of appropriate frequencies or wavelengths, the valence electron of different hydrogen atoms absorb different amount of energy and get excited to a higher energy level accordingly. In higher energy level, they are unstable and therefore, return back to their original state by releasing energy, either in one step or in several steps. This released energy is observed as a line of definite frequency and wavelength in atomic spectra. Here, the energy released in a definite electronic transition is equal to the difference of the energies of associated energy levels.

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In hydrogen spectrum all the electronic transitions from any higher energy level to a definite lower energy level in any atom give rise a definite series. In all six such series have been observed in hydrogen spectra –

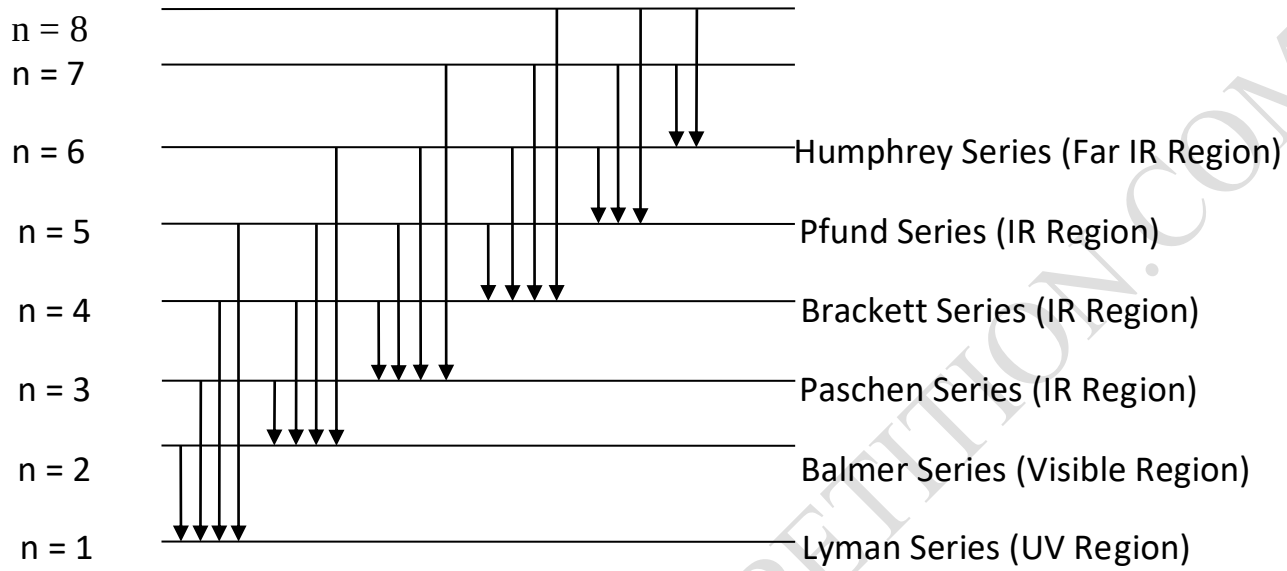


Fig.- Different series of hydrogen spectrum

(1)Lyman Series- This series arises due to transition of electrons directly from any higher energy level to 1st energy level. The spectral lines of this series lie in UV region of electromagnetic spectrum and their wave numbers are obtained using following formula-

$$\bar{\upsilon} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$ Where, R = Rydberg's constant = 109678 cm^{-1}

$n_1 = 1$ & $n_2 = 2, 3, 4,$-----

Thus, wave number of first spectral line of Lyman series-

$$\bar{\upsilon}_1 = R\left[1 - \frac{1}{2^2}\right] cm^{-1}$$

$$= \frac{3}{4} R\ cm^{-1}$$

Similarly, wave number of second spectral line of Lyman series-

$$\bar{\upsilon}_2 = R\left[1 - \frac{1}{3^2}\right] cm^{-1}$$

$$= \frac{8}{9} R\ cm^{-1}$$

Similarly, wave number of other spectral lines can be calculated.

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(2)Balmer Series-This series arises due to the transition of electrons directly from any higher energy level to 2^{nd} energy level. The spectral lines of this series lie in visible region of electromagnetic spectrum and their wave numbers are obtained using following formula-

$$\bar{\upsilon} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad \text{Where, } n_1 = 2 \quad \& \quad n_2 = 3, 4, 5,\text{----}$$

Thus, wave number of first spectral line of Balmer series-

$$\bar{\upsilon}_1 = R\left[\frac{1}{2^2} - \frac{1}{3^2}\right] \text{ cm}^{-1}$$

$$= \frac{5}{36} R \text{ cm}^{-1}$$

Similarly, wave number of second spectral line of Balmer series-

$$\bar{\upsilon}_2 = R\left[\frac{1}{2^2} - \frac{1}{4^2}\right] \text{ cm}^{-1}$$

$$= \frac{3}{16} R \text{ cm}^{-1}$$

Similarly, wave number of other spectral lines can be calculated.

(3)Paschen Series- This series arises due to transition of electron directly from any higher energy level to 3^{rd} energy level. The spectral lines of this series lie in IR region of electromagnetic spectrum and their wave numbers are obtained using following formula-

$$\bar{\upsilon} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{ cm}^{-1} \quad \text{Where, } n_1 = 3 \quad \& \quad n_2 = 4, 5, 6,\text{-----}$$

(4)Brackett Series- This series arises due to transition of electron directly from any higher energy level to 4^{th} energy level. The spectral lines of this series lie in IR region of electromagnetic spectrum and their wave numbers are obtained using following formula-

$$\bar{\upsilon} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{ cm}^{-1} \quad \text{Where, } n_1 = 4 \quad \& \quad n_2 = 5, 6, 7,\text{-----}$$

(5)Pfund Series- This series arises due to transition of electrons directly from any higher energy level to 5^{th} energy level. The spectral lines of this series also lie in IR region of electromagnetic spectrum and their wave numbers are obtained using following formula-

$$\bar{\upsilon} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{ cm}^{-1} \quad \text{Where, } n_1 = 5 \quad \& \quad n_2 = 6, 7, 8,\text{-----}$$

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(6)Humphrey Series- This is newly discovered series of hydrogen spectrum and arises due to transition of electrons directly from any higher energy level to 6^{th} energy level. The spectral lines of this series lie in far IR region of electromagnetic spectrum and their wave numbers are obtained using following formula-

$$\bar{\upsilon} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{ cm}^{-1} \quad \text{Where, } n_1 = 6 \quad \& \quad n_2 = 7, 8, 9, \text{-----}$$

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