

CHEMISTRY

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INORGANIC CHEMISTRY

ATOMIC STRUCTURE AND PERIODIC CLASSIFICATION

ATOMIC STRUCTURE AND PERIODIC TRENDS

SUB-ATOMIC PARTICLES

Discovery of Electron

Electron was discovered by J. J. Thomson by Cathode ray discharge tube experiment. A cathode ray tube is made of glass containing two thin pieces of metal (called electrodes) sealed in it. The electrical discharge through the gases could be observed only at very low pressures and at very high voltages.

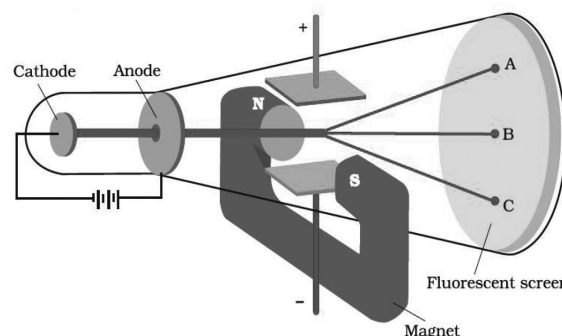
When a very high voltage (about 10,000 volts) is applied between the two electrodes, no electric discharge occurs at normal pressure. When the pressure of the gas inside the tube is less than 1 mm of mercury, a dark space appears near the cathode. When the pressure is reduced to 0.01 mm Hg, it fills the whole tube. When the pressure is further reduced (10^{-4} mm Hg), the electric discharge passes between the electrodes and the tube begins to glow. This is due to the striking of some invisible rays from the cathode. These rays which start from the cathode and move away from it, in straight lines are called cathode rays or cathode ray particles. These rays can be further checked by making a hole in the anode and coating the tube behind anode with phosphorescent material like zinc sulphide. When these rays strike the zinc sulphide coating, a bright spot on the coating is developed.

Properties of Cathode Rays

- ✦ The cathode rays start from cathode and move towards the anode.
- ✦ They are invisible, but their behaviour can be observed with the help of fluorescent or phosphorescent materials.
- ✦ In the absence of electrical or magnetic field, these rays travel in straight lines.
- ✦ In the presence of electric or magnetic field, the cathode rays behave similar to that of negatively charged particles. From this it is clear that the cathode rays consist of negatively charged particles called electrons.
- ✦ The characteristics of cathode rays (electrons) do not depend upon the material of electrodes and the nature of the gas present in the cathode ray tube.
- ✦ These rays possess kinetic energy and hence can do mechanical work.
- ✦ They can produce x-rays when incident on metals with high atomic mass.

Charge to Mass Ratio of Electron

J.J. Thomson measured the ratio of electrical charge (e) to the mass of electron (m_e) by using cathode ray tube and applying electrical and magnetic field perpendicular to each other as well as to the path of electrons.



In the absence of electric or magnetic field, the cathode rays hit the screen at point B. When only electric field is applied, the electrons deviate from their path and hit the cathode ray tube at point A. Similarly, when only magnetic field is applied, electron strikes the cathode ray tube at point C. By carefully balancing the electrical and magnetic field strength, it is possible to bring back the electron beam to the point B. From the strength of electric and magnetic field, Thomson was able to calculate the value of e/m_e as:

$$e/m_e = 1.758 \times 10^{11} \text{ C kg}^{-1}$$

Where m_e is the mass of the electron in kg and e is the magnitude of the charge on the electron in coulomb (C). Charge on the Electron (e)

R.A. Millikan determined the charge on the electrons by a method known as 'oil drop experiment'. He found that the charge on the electron to be $1.6022 \times 10^{-19} \text{ C}$.

Mass of electron (m_e). The mass of the electron (m_e) was determined as follows:

$$e/m_e = 1.758 \times 10^{11} \text{ C kg}^{-1}$$

$$e = 1.6022 \times 10^{-19} \text{ C}$$

$$\text{Mass of electron } (m_e) = 1.6022 \times 10^{-19} / 1.758 \times 10^{11} \\ = 9.1 \times 10^{-31} \text{ kg}$$

Discovery of Protons

E. Goldstein modified the discharge tube experiment by perforated (with small holes) cathode. After evacuating the tube and on applying high voltage, he found that some rays were emitting behind the cathode and moving in the opposite direction of cathode rays. These rays deflect to the negative plate of electric field. So they carry positive charge and were called anode rays or canal rays. Properties of Canal rays.

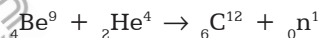
The characteristics of canal rays are:

- ★ They depend on the nature of gas present in the cathode ray tube. These are positively charged gaseous ions.
- ★ The charge to mass ratio of these particles depends on the nature of the gas.
- ★ Some of the positively charged particles carry a multiple of the fundamental unit of electric charge.
- ★ The behaviour of these particles in the magnetic or electrical field is opposite to that observed for cathode rays.
- ★ They can produce heating effect and can do mechanical work.

- ★ They are invisible and can be observed with the help of fluorescent or phosphorescent materials.
- ★ They also travel in straight lines.
- ★ The smallest and lightest positive ion was obtained from hydrogen and was called proton.

Discovery of Neutrons

Neutrons were discovered by Chadwick by bombarding a thin sheet of beryllium by α -particles.



They are electrically neutral particles having mass slightly greater than that of the protons.

Characteristics of sub-atomic particles

Sub atomic particle	Symbol	Discoverer	Absolute Charge (in Coulomb)	Relative charge	Mass/kg
Electron	e	J J Thomson	-1.6022×10^{-19}	-1	9.01×10^{-31}
Proton	p	E. Goldstein	$+1.6022 \times 10^{-19}$	+1	1.6726×10^{-27}
Neutron	n	James Chadwick	0	0	1.675×10^{-27}

Some important terms relating to Atomic structure

Atomic Number: It is the number of protons present in the nucleus or number of electrons present outside the nucleus. It is denoted by the symbol 'Z'.

Atomic number (Z) = nuclear charge or number of protons (p) = number of electrons (e) **Mass Number:** It is the total number of protons and neutrons in atom. Or, it is the total number of nucleons in an atom.

It is denoted by 'A'. i.e. Mass number (A) = no. of protons (p) + no. of neutrons (n) or, $A = p + n$

By knowing the atomic number and mass number,

we can calculate the number of neutrons as: $n = A - Z$

If an element X has the atomic number Z and the mass number A, it is denoted as: or ${}_Z\text{X}^A$

ISOTOPES, ISOBARS AND ISOTONES

Isotopes are atoms with same atomic number but different mass number. That is, they contain same number of protons but different number of neutrons. Almost all the elements have isotopes. All the isotopes of a given element have same chemical properties, but they differ in their physical properties. Hydrogen has three isotopes: Protium (${}_1\text{H}^1$), Deuterium (${}_1\text{H}^2$ or ${}_1\text{D}^2$) and Tritium (${}_1\text{H}^3$ or ${}_1\text{T}^3$). Among these, Protium is the ordinary hydrogen and Tritium is the radioactive isotope of Hydrogen.

Isobars are atoms of different elements having same mass number (same number of neutrons) but different atomic number. i.e. they have different number of protons but have equal sum of the protons and neutrons.

e.g. ${}_6\text{C}^{14}$ and ${}_7\text{N}^{14}$

${}_{18}\text{Ar}^{40}$ and ${}_{20}\text{Ca}^{40}$

Isotope				Isotones			
Isotope	p	e	n	Isotones	p	e	n
Protium	1	1	0	${}_6\text{C}^{14}$	6	6	8
Deuterium	1	1	1	${}_7\text{N}^{14}$	7	7	8
Tritium	1	1	2	${}_8\text{O}^{16}$	8	8	8

ATOM MODELS

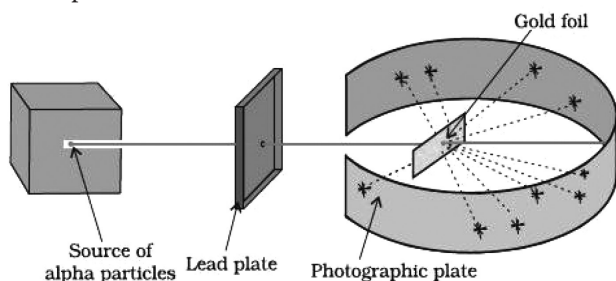
Thomson's Model of Atom

J. J. Thomson proposed the first atom model, which is known as the plum pudding or raisin pudding or watermelon model. According to this model, an atom has a spherical shape in which the positive charge is uniformly distributed. The electrons are distributed in it, just like the seeds are distributed in a water melon or

plums are distributed in a pudding. An important feature of this model is that the mass of the atom is assumed to be uniformly distributed over the atom. Also the total positive charge in an atom is equal to the total negative charge and hence the atom is electrically neutral.

Rutherford's Nuclear Model of Atom

Rutherford proposed an atom model based on his α -particle scattering experiment. He bombarded a very thin gold foil (approximately 10^{-7} m thickness) with α -particles. The Experiment: A stream of high energy α -particles from a radioactive source was directed at a thin gold foil. The thin gold foil had a circular fluorescent zinc sulphide screen around it. Whenever α -particles struck the screen, a tiny flash of light was produced at that point.



Observations:

The important observations made by Rutherford are:

- ✦ Most of the α -particles passed through the gold foil without any deviation.
- ✦ A small fraction of the α -particles was deflected by small angles.
- ✦ A very few α -particles (~ 1 in 20,000) bounced back, that is, were deflected by nearly 180° .

Conclusions:

From the above observations, Rutherford made the following conclusions:

- ✦ Since most of the α -particles passed through the foil without any deviation, most space in the atom is empty.
- ✦ A few positively charged α -particles were deflected. This is because the positive charge of the atom is concentrated in a very small volume at the centre called nucleus.
- ✦ The volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The radius of the atom is about 10^{-10} m, while that of nucleus is 10^{-15} m.

On the basis of above observations and conclusions, Rutherford proposed the nuclear model (Planetary model) of atom. According to this model:

- ✦ All the positive charge and most of the mass of the atom are concentrated in an extremely small region called nucleus.
- ✦ Electrons are revolving round the nucleus with a very high speed in circular paths called orbits.

- ✦ Electrons and the nucleus are held together by electrostatic forces of attraction.

Drawbacks or Limitations of Rutherford's atom model

- ✦ Rutherford's model cannot explain the stability of the atom.
- ✦ He cannot explain the electronic structure of atom.

Moseley's Experiment

Henry Moseley's work reinforced the one-to-one identification of an atomic number Z with each element shortly after Rutherford's scattering hypothesis was validated by experiment (about 1913). (1887- 1915). He calculated the energy released when low-level electrons change orbitals using Bohr's atomic structure model. Because this energy has a strong relationship with an atomic number, the atomic number Z of an element may be established unambiguously by measuring the energy of its characteristic x-rays.

Moseley's law is an empirical law that applies to the distinctive x-rays that atoms release. Henry Moseley, an English physicist, discovered and published the law in 1913 by the assumption that when the nucleus is screened by an unpaired electron that remains in the K-shell, the effective charge of the nucleus reduce by one is a common simplification.

Apparatus:

- ✦ The setup is quite simple. First, a ^{57}Co γ -ray source decays in such a way as to produce (among other things) several photons mainly consisting of 136 keV, 122 keV, and 14 keV γ -rays. ^{57}Co undergoes electron capture, the product of which is a ^{57}Fe nucleus in an excited state. Upon relaxation the ^{57}Fe nucleus emits the γ -rays. The γ -rays strike the shielded target and knock electrons out from the target atoms. Other electrons drop to fill the hole created by the ejected electron and in the process emit characteristic x-rays.
- ✦ A proportional tube is used to detect the x-rays. It consists of a chamber filled with a noble gas (typically xenon). A thin positively charged wire runs along the axis. When an x-ray interacts inside the tube, it ejects electrons from the gas atoms. These are attracted to the wire, speed up enough to eject other electrons, and eventually cause a cascade of electrons to accelerate toward the wire. This charge pulse is amplified and recorded. The strength of the signal is proportional to the x-ray energy deposited in the tube; hence the name "proportional tube."
- ✦ The multi-channel analyzer is used to determine x-ray energies. The multi-channel analyzer is mounted on a card inside the PC. A multi-channel analyzer measures all the voltage pulses from the proportional tube and sorts them into bins according to their strength. Each bin records pulses that fall within a set energy range and the bins form a sequential array so that the bin number N is proportional to the strength of the voltage pulse.

Experiment:

- ✦ The detector will pick up on more than simply the x -rays. In addition, the detector will be hit by γ -rays directly from the Co source. More crucially, in the shielding, the sources will interact, resulting in a lead x -ray spectrum. Because the lead shielding is so much greater than the sample size, the signal may be masked. The data is gathered in two steps to remove the background. First, data is accumulated for predetermined amounts of time with the multi-channel analyzer on add. The sample is then withdrawn from the analyser, which is then set to subtract. For the same period of time, data is accumulated. This removes background counts at the same pace as they were accumulated; resulting in data that only represents the sample's contribution.
- ✦ To begin, compare the x -ray spectra of six well-known materials: Al, Ti, Cu, Zr, Ag, and Te. Save the information in a file that which can access later.

Analysis:

First, use six known samples to confirm Moseley's law. Because the energy of the characteristic x -ray should be proportional to $(Z-\delta)^2$ and channel number N is proportional to E , N is proportional to $(Z-\delta)^2$. As a result, $N \text{ kZ} = b\delta$. Plot N vs. Z for each of the six known samples. From this graph, find the optimal value for k and δ . Examine the spectra carefully and consider the sources of uncertainty in the data. Determine the uncertainties in δ and k using an acceptable technique. Compare the peak positions of the unknowns to your results from the six known samples to determine Z .

WAVE NATURE OF ELECTROMAGNETIC RADIATION

James Maxwell suggested that when electrically charged particle moves under acceleration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the forms of waves called electromagnetic waves or electromagnetic radiation (emr). These are the radiations associated with electric and magnetic fields. E.g. light.

The important characteristics of these radiations are:

- ✦ The oscillating electric and magnetic fields are perpendicular to each other and both are perpendicular to the direction of propagation of the wave.
- ✦ The electromagnetic waves do not require a medium for propagation and can move in vacuum.
- ✦ There are many types of electromagnetic radiations, which differ from one another in wavelength (or frequency). These constitute electromagnetic spectrum. The important electromagnetic radiations in the increasing order of wavelength are: Cosmic rays, Gamma rays, X-rays, Ultra-violet rays, Visible light, Infra red rays, Microwaves, Radio waves.
- ✦ All electromagnetic radiation travel through vacuum with a constant speed of 3×10^8 m/s.

Some important terms relating to electromagnetic radiations

- ✦ Frequency (ν): It is defined as the number of waves that pass through a given point in one second. The SI unit for frequency is hertz (Hz, s^{-1}).
- ✦ Wavelength (λ): It is the distance between two adjacent crests or two adjacent troughs. Its unit is m or cm.
- ✦ Wave number ($\bar{\nu}$): It is defined as the number of wavelengths per unit length. It is the reciprocal of wavelength. Its unit is m^{-1} or cm^{-1} .

The frequency (ν), speed of light (c) and the wavelength (λ) are related to each other as: $c = \nu \lambda$

PARTICLE NATURE OF ELECTROMAGNETIC RADIATION: PLANCK'S QUANTUM THEORY

Some of the experimental phenomenon like diffraction and interference can be explained by the wave nature of the electromagnetic radiation. But some phenomena like black body radiation, photoelectric effect, variation of heat capacity of solids with temperature, line spectra of atoms etc. could not be explained by wave nature of emr.

BLACK BODY RADIATION

An ideal body which emits and absorbs all frequencies of radiations is called a black body and the radiation emitted by such a body is called black body radiation. The frequency distribution of radiation emitted from a black body depends only on its temperature. At a given temperature, intensity of radiation emitted increases with decrease of wavelength, reaches a maximum value at a given wavelength and then starts decreasing. The phenomenon of black body radiation was first explained by Max Planck by his Quantum theory. According to this theory:

- ✦ Atoms and molecules could emit (or absorb) energy not in a continuous manner, but discontinuously in small packets of energy called quanta or photons.
- ✦ The energy (E) of a quantum of radiation is proportional to its frequency (ν) It is expressed by the equation, $E = h\nu$ Where ' h ' is known as Planck's constant and its value is 6.626×10^{-34} J s.

PHOTOELECTRIC EFFECT

It is the phenomenon of ejection of electrons by certain metals (like potassium, rubidium, caesium etc.) when light of suitable frequency incident on them. The electrons ejected are called photoelectrons. This phenomenon was first observed by H.Hertz. The important characteristics of photoelectric effect are:

- ✦ The electrons are ejected from the metal surface as soon as the beam of light strikes the surface. i.e., there is no time lag between the striking of light beam and the ejection of electrons from the metal surface.
- ✦ The number of electrons ejected is proportional to the intensity or brightness of light.

- ✦ For each metal, there is a minimum frequency (known as threshold frequency ν_0) below which photoelectric effect is not observed.
- ✦ The kinetic energy of the ejected electrons is directly proportional to the frequency of the incident light.

Explanation of photoelectric effect

A satisfactory explanation to photoelectric effect was first given by Albert Einstein using Planck's Quantum theory. According to him, when a photon of sufficient energy strikes the metal surface, it transfers its energy to the electron of the atom of the metal instantaneously and the electron is ejected without any time lag. A part of the energy is used to eject the electron from the metal surface (i.e. to overcome the attractive force of the nucleus ϕ_0 work function, $h\nu_0$) and the other part is given to the ejected electron in the form of kinetic energy. Greater the energy possessed by the photon, greater will be transfer of energy to the electron and greater the kinetic energy of the ejected electron.

Since the striking photon has energy equal to $h\nu$ and the minimum energy required to eject the electron is $h\nu_0$ (also called work function, W_0) then the difference in energy ($h\nu - h\nu_0$) is transferred as the kinetic energy of the photoelectron.

Following the law of conservation of energy principle, the kinetic energy of the ejected electron is given by

$$K.E = h\nu - h\nu_0 \text{ (or), } h\nu = h\nu_0 + \frac{1}{2} m_e v^2$$

Where m_e is the mass of the electron and v is the velocity of the ejected electron.

A more intense beam of light contains larger number of photons, so the number of electrons ejected is also larger.

DUAL BEHAVIOUR OF ELECTROMAGNETIC RADIATION

Electromagnetic radiations possess both particle and wave nature. This is known as dual nature of Electromagnetic Radiation.

Atomic spectrum

When a ray of white light is passed through a prism, we get a series of coloured bands called spectrum. This spectrum is called continuous spectrum, because here violet merges into blue, blue into green and so on.

Similarly, when electromagnetic radiation interacts with matter, atoms and molecules may absorb energy and reach to a higher energy unstable state. To attain stability, they emit radiations in the form of spectrum. Such a spectrum is called atomic spectrum.

Emission and Absorption Spectra

The spectrum of radiation emitted by a substance that has absorbed energy is called an emission spectrum. Atoms, molecules or ions that have absorbed radiation are said to be "excited". To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it and the wavelength (or frequency) of the radiation emitted is recorded.

An absorption spectrum is like the photographic negative of an emission spectrum. Here a continuum of radiation (like white light) is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelengths leave dark spaces in the bright continuous spectrum. The study of emission or absorption spectra is referred to as spectroscopy.

The emission spectra of atoms in the gas phase do not form a continuous spectrum. The excited atoms emit light only at specific wavelengths with dark spaces between them. Such spectra are called line spectra or atomic spectra.

Line emission spectra are very useful in the study of electronic structure of atoms. Each element has a unique line emission spectrum. The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms in the same way as finger prints are used to identify people. So line emission spectra are also called finger print of atoms.

Line Spectrum of Hydrogen

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 hydrogen spectrum consists of several series of lines named after their discoverers. The first five series of lines are Lyman, Balmer, Paschen, Brackett and Pfund series. Among these lines, the Balmer series is the only series that we can be visible (since it lies in the visible region of emr). Johannes Rydberg proposed an equation for finding the wave number of the different lines in Hydrogen spectrum.

The expression is:

$$\bar{\nu} = 1/\lambda = 109677 (1/n_1^2 - 1/n_2^2) \text{ cm}^{-1}$$

Where $n_1 = 1, 2, 3, \dots$ and $n_2 = n_1 + 1, n_1 + 2, \dots$

The different spectral lines, their n_1 and n_2 values and their spectral region are:

Series	Spectral region	n_1	n_2
Lyman	Ultra violet	1	2,3,4....
Balmer	Visible	2	3,4,5....
Paschen	Infra red	3	4,5,6.....
Brackett	Infra red	4	5,6,7....
Pfund	Infra red	5	6,7,8.....

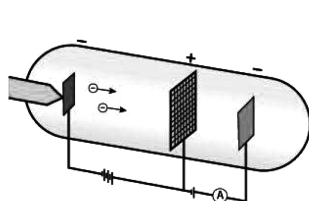
FRANCK-HERTZ EXPERIMENT

The Franck Hertz experiment was first studied in 1914 by James Franck and Gustav Hertz and presented to the German Physical Society. It was the first electrical measurement to show the quantum nature of atoms. The Franck Hertz experiment consisted of a vacuum tube designed to study the energetic electrons that flew through a thin vapour of mercury atoms. It was discovered that only a specific amount of an atom's kinetic energy would lose as the electrons collide with the mercury atom.

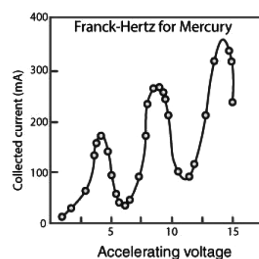
The main aim of this experiment is to demonstrate the concept of quantisation of the energy levels according to the Bohr's model of an atom.

Theory:

The original experiment used a heated vacuum tube of temperature 115°C with a drop of mercury of vapour pressure 100 Pa. Three electrodes, an electron-emitting hot cathode, a metal mesh grid, and an anode are attached to the tube. To draw the emitted electrons, the grid's voltage is made positive with respect to the cathode. The electric current measured in the experiment results from the movement of electrons from the grid to the anode. The electric potential at the anode is slightly more negative than the grid so the electrons have the kinetic energy the same as in the grid. The Franck Hertz experiment was explained in terms of elastic and inelastic collisions between the electrons and the mercury atoms.



Accelerating apparatus



The graphs show the dependence of the electric current flowing out of the anode and the electric potential between the grid and the cathode. Following are the observations from the graph:

- ✦ With the steady increase in the potential difference, the current increases steadily through the tube.
- ✦ The current drops almost to zero at 4.9 volts.
- ✦ Again there is an increase in the current as the voltage increases to 9.8 volts.
- ✦ Again a similar drop is observed at 9.8 volts.

Energy absorption from electron collisions in the case of neon gas is seen. When the accelerated electrons excite the electrons in neon to upper states, they de-excite in such a way as to produce a visible glow in the gas region in which the excitation is taking place. There are about ten peak electron levels in the range of 18.3 to 19.5 eV. They de-excite by dropping to lower states at 16.57 and 16.79 eV. This energy difference gives the light in the visible range.

Elastic Collision

An elastic collision is defined as an encounter between two bodies such that the total kinetic energy of the two bodies remains the same. During the collision, kinetic energy is first converted to potential energy related to repulsive force between the particles and converted back to kinetic energy. Rutherford back-scattering is an example of an elastic collision.

One-dimensional form of the elastic collision of particles 1 and 2:

$$\frac{1}{2}m_1u_1^2 + \frac{1}{2}m_2u_2^2 = \frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2$$

Where,

m_1, m_2 are the masses of particles 1 and 2

u_1, u_2 are the velocities of particles before the collision

v_1, v_2 are the velocities of particles after the collision

The magnitude of the velocities of the particles after the collision is given with two-dimensional form:

$$v_1' = v_1 \frac{\sqrt{m_1^2 + m_2^2 + 2m_1m_2 \cos \theta}}{m_1m_2}$$

$$v_2' = v_1 \frac{2m_1}{m_1 + m_2} \sin \frac{\theta}{2}$$

Inelastic Collision

An inelastic collision is defined for the two bodies whose kinetic energies are not conserved due to internal friction. Macroscopic collisions result in effects, vibrations of the atoms and the deformation of the bodies. The formula of one-dimensional collision for particles a and b:

$$v_a = \frac{C_R m_b (u_b - u_a) + m_a u_a + m_b u_b}{m_a + m_b}$$

$$v_b = \frac{C_R m_a (u_a - u_b) + m_a u_a + m_b u_b}{m_a + m_b}$$

Where,

v_a is the final velocity of the first object after impact

v_b is the final velocity of the second object after impact

u_a is the initial velocity of the first object before impact

u_b is the initial velocity of the second object before impact

m_a is the mass of the first object

m_b is the mass of the second object

C_R is the coefficient of restitution (ratio of final and initial relative velocities)

BOHR'S MODEL FOR HYDROGEN ATOM

The general features of the structure of hydrogen atom and its spectrum was first explained by Niels Bohr. The important postulates of his theory are:

- ✦ The electron in the hydrogen atom can move around the nucleus in circular paths of fixed radius and energy. These paths are called orbits or stationary states or allowed energy states. These energy levels are numbered as 1,2,3 etc or as K, L, M, N, etc. These numbers are known as Principal quantum numbers.
- ✦ The energy of an electron in an orbit does not change with time. However, when an electron absorbs energy, it will move away from the nucleus (i.e. to a higher energy level) and when it loses

energy, it will move towards the nucleus (i.e. to a lower energy level).

- ✦ The radius of orbits can be given by the equation: $r_n = a_0 n^2$ where $a_0 = 52.9$ pm. Thus the radius of the first stationary state is 52.9 pm (called the Bohr radius). As n increases, the value of r will increase.
- ✦ The energy of electron in an orbit is given by the expression: $E_n = -RH (1/n^2)$, where $n = 1, 2, 3, \dots$ and RH is a constant called Rydberg constant. Its value is 2.18×10^{-18} J. The energy of the lowest state (the ground state) is given by $E_1 = -2.18 \times 10^{-18}$ J. As the value of n increases, the energy of the electron also increases.
- ✦ The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE , is given by:

$$\nu = \Delta E/h = (E_2 - E_1)/h$$
 Where E_1 and E_2 are the energies of lower and higher energy levels respectively. This expression is commonly known as Bohr's frequency rule.
- ✦ The angular momentum of an electron is an integral multiple of $h/2\pi$. i.e. $m_e v r = nh/2\pi$

Where m_e is the mass of electron, v is the velocity of electron and r is the radius of Bohr orbit. $n = 1, 2, 3, \dots$. Thus an electron can move only in those orbits whose angular momentum is an integral multiple of $h/2\pi$. So only certain fixed orbits are allowed.

Significance of negative energy of electron

When the electron is free from the influence of nucleus, its energy is taken as zero. In this situation, the electron is at the orbit with $n = \infty$. When the electron is attracted by the nucleus and is present in orbit n , the energy is emitted and its energy is lowered. That is the reason for the presence of negative sign in equation.

Explanation of Line Spectrum of Hydrogen

According to Bohr atom model, radiation is absorbed if the electron moves from lower energy to higher energy level and radiation is emitted if the electron moves from higher orbit to lower orbit. The energy gap between the two orbits is given by equation:

$$\Delta E = E_2 - E_1$$

$$\text{But } E_1 = -R_H/n_1^2 \text{ and } E_2 = -R_H/n_2^2$$

$$\begin{aligned} \text{Therefore, } \Delta E &= R_H [1/n_1^2 - 1/n_2^2] \\ &= 2.18 \times 10^{-18} [1/n_1^2 - 1/n_2^2] \end{aligned}$$

The frequency associated with the absorption and emission of the photon can be given as

$$\begin{aligned} \nu &= \Delta E/h = RH/h [1/n_1^2 - 1/n_2^2] \\ &= [2.18 \times 10^{-18} / 6.626 \times 10^{-34}] [1/n_1^2 - 1/n_2^2] \\ &= 3.29 \times 10^{15} [1/n_1^2 - 1/n_2^2] \end{aligned}$$

$$\text{The wave number } (\bar{\nu}) = 1/\lambda = \nu/c$$

$$\begin{aligned} &= \{R_H/c\} [1/n_1^2 - 1/n_2^2] \\ &= \{3.29 \times 10^{15} / 3 \times 10^8\} [1/n_1^2 - 1/n_2^2] \\ &= 1.09677 \times 10^7 [1/n_1^2 - 1/n_2^2] \text{ m}^{-1} \\ &= 109677 [1/n_1^2 - 1/n_2^2] \text{ cm}^{-1} \end{aligned}$$

In case of absorption spectrum, $n_2 > n_1$ and the term in the bracket is positive and energy is absorbed. On the other hand, in case of emission spectrum $n_2 > n_1$, ΔE is negative and energy is released.

Limitations of Bohr Atom Model:

Bohr atom model could explain the stability and line spectra of hydrogen atom and hydrogen like ions (e.g. He^+ , Li^{2+} , Be^{3+} etc). But it has the following limitations:

- ✦ It could not explain the fine spectrum of hydrogen atom.
- ✦ It could not explain the spectrum of atoms other than hydrogen.
- ✦ It was unable to explain the splitting of spectral lines in the presence of electric field (Stark effect) and in magnetic field (Zeeman effect).
- ✦ It could not explain the ability of atoms to form molecules by chemical bonds.
- ✦ It did not consider the wave character of matter and Heisenberg's uncertainty principle.

DUAL BEHAVIOUR OF MATTER – DE BROGLIE'S EQUATION

- ✦ de Broglie proposed that like radiation, matter also exhibit dual behaviour i.e., both particle and wave like properties. This means that electrons should also have momentum as well as wavelength. He gave the following relation between wavelength (λ) and momentum (p) of a material particle.

$$\lambda = h/mv = h/p$$

- ✦ Where m is the mass of the particle, v is the velocity and p is the momentum. The above equation is known as de Broglie's equation.
- ✦ Just like electromagnetic radiations, an electron beam also undergoes diffraction. This is an evidence for the wave nature of electrons. An electron microscope works on the principle of wave nature of electron.
- ✦ According to de Broglie, every moving object has a wave character. The wavelengths associated with ordinary objects are so short (because of their large masses) that their wave properties cannot be detected. The wavelengths associated with electrons and other subatomic particles (with very small mass) can be detected experimentally.

DAVISSON GERMER EXPERIMENT

- ✦ In 1923 Louise de Broglie suggested that like radiation matter also possess dual nature that are particle and wave. According to him a particle of mass m moving with velocity v always associated with a wave with wavelength $\lambda = h/p$ here h is Planck's constant and p is momentum of the particle.
- ✦ In 1926 Walter Maurice Elsasser suggested that wave like nature of matter might be investigated by electrons scattering experiment in crystalline solids.
- ✦ In 1927 Davisson and Germer proved that fast moving electrons show diffraction effect (property of

waves) and calculated the wave length of electrons wave.

- ✦ In the same time G P Thomson also proved experimentally the wave nature of electrons.

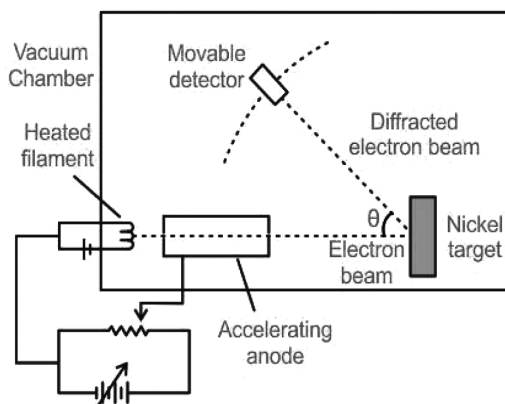
Davisson and Germer Experiment:

- ✦ The Davisson and Germer experiment confirmed the earlier hypothesis of de Broglie which demonstrated the wave nature of the electrons, this experiment confirms that electrons exhibit diffraction pattern when they are scattered from a crystal plane.

Davisson and Germer Apparatus:

Davisson Germer Experiment is carried out inside a vacuum Chamber. The key components are-

- ✦ Electron Gun – It contains a tungsten filament, which emits or produces electrons through a process called Thermionic Emission when heated to a specific temperature. The tungsten filament is coated with barium oxide.
- ✦ ElectroStatic Particle Accelerator – two oppositely charged plates are provided with high voltage and are used to accelerate the electrons.
- ✦ Collimator- this is a cylindrical shaped, perforated element, through which the emitted electrons are aimed towards the target- Nickel Crystal
- ✦ Target- A nickel crystal is placed as a target, upon which the electrons are accelerated and then get deflected after striking the nickel crystal
- ✦ Secondary Electron Detector (SED) – a movable detector is placed at a certain angle (θ) from the nickel crystal. This detector collects the electrons deflected at different angles (θ) and cross-referenced with the intensity of the current produced in a sensitive galvanometer.



Davisson Germer Experiment

Working of Davisson Germer Experiment

- ✦ First, the electrons are produced by heating the tungsten filament, coated with barium oxide, using a low-voltage power source. The process is called Thermionic Emission.
- ✦ Then, these emitted electrons are then accelerated and directed towards a nickel crystal by applying

high voltage across the cylindrical accelerating anode and cathode with perforations. This, in turn, outputs a finely collimated beam of electrons.

- ✦ Once the electron hits the nickel crystal surface, they get deflected in different directions. The intensity of the deflected electrons in various directions depends mainly on the angle of the nickel crystal.
- ✦ A moving Secondary Electron Detector (SED) detects these deflected electrons. SED records the intensity of the deflected electrons in different directions.

Davisson and Germer Experiment Observations

- ✦ SED is connected to a sensitive galvanometer. This converts the detected electrons into the current, and the intensity of the current is reflected in the gauge. The electron intensities are seen in multiple directions by moving the SED, and the direction or the angle (θ) with maximum and minimum intensities are recorded.

Outcomes of Davisson Germer Experiment

- ✦ Intensities of the deflected electrons are obtained by changing the angle (θ) of deflection
- ✦ The detector detects the particle nature of the electron. As a result, only the current will be detected by the detector.
- ✦ By changing the voltage across the accelerator plates, the acceleration of the electrons can be varied.
- ✦ The intensity of the dispersed electrons is not constant and provides a maximum and minimum value corresponding to the diffraction pattern.
- ✦ It is found that by changing the angle of scattering (θ), the intensity of the deflected electrons can be varied.
- ✦ In the experiment, it was followed that when the potential across the accelerating plates was adjusted between 44V to 68V and when the angle of deflection (θ) was at 50° , the maximum intensity (I) of the scattered electrons was observed at 54V.
- ✦ Due to the constructive interference of the deflected electrons, the maximum intensity (I) was observed from different layers of the nickel crystals with evenly spaced atoms.
- ✦ The wavelength of the deflected electrons was found using the electron diffraction method, and it was determined that the wavelength was 0.165 nm.

Co-relating Davisson Germer Experiment and de Broglie Relation

According to de Broglie,

$$\lambda = h/p$$

$$\lambda = h/\sqrt{2mE}$$

$$\lambda = h/\sqrt{2meV} \dots\dots(1)$$

where, m = mass of an electron; e = charge on an electron and h = Plank's constant Therefore for a given V , an electron will have a wavelength given by equation (1).

The following equation gives Bragg's Law:

$$n\lambda = 2d\sin(90^\circ - \theta/2) \dots\dots(2)$$

For $V = 54$ V, we have

$$\lambda = 1.227/\sqrt{54} = 0.167\text{nm}$$

Proof of Davisson Germer Experiment

- ✦ In the Davisson Germer experiment, an assumption was made that deflected waves from two distinct atomic levels of the nickel crystal will have a constant phase difference.
- ✦ After deflection, the waves will either form constructive or destructive interference. Hence a diffraction pattern was formed, and the dual nature of the element was confirmed.

HEISENBERG'S UNCERTAINTY PRINCIPLE

- ✦ Werner Heisenberg proposed the uncertainty principle which is the consequence of dual behaviour of matter and radiation. It states that "it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of a moving microscopic particle like electron". Mathematically, it can be given as in equation:

$$\Delta x \cdot \Delta p \geq h/4\pi$$

$$\text{or, } \Delta x \cdot m\Delta v \geq h/4\pi$$

$$\text{or, } \Delta x \cdot \Delta v \geq h/4\pi m$$

- ✦ Where Δx is the uncertainty in position and Δp (or, Δv) is the uncertainty in momentum (or velocity) of the particle.
- ✦ If the position of the electron is known with high degree of accuracy (Δx is small), then the velocity of the electron will be uncertain [Δv is large] and vice versa.

Significance of Uncertainty Principle

- ✦ Heisenberg Uncertainty Principle is significant only for motion of microscopic objects and is not applicable to macroscopic objects. According to this Principle, we cannot determine the exact position and momentum of an electron. Thus it rules out the existence of definite paths or orbits of electrons. We can only say the probability of finding an electron at a given point.

Reasons for the Failure of the Bohr Model

- ✦ In Bohr model, electrons are moving in well defined circular orbits about the nucleus. The wave character of the electron is not considered in Bohr model. Further, an orbit is a clearly defined path and this path can completely be defined only if both the position and the velocity of the electron are known exactly at the same time. This is not possible according to the Heisenberg uncertainty principle. Therefore, Bohr model of the hydrogen atom not only ignores dual behaviour of matter but also contradicts Heisenberg uncertainty principle.

RULES FOR FILLING OF ELECTRONS IN VARIOUS

Rules for Filling of electrons in various orbitals The filling of electrons into the orbitals of different atoms takes place according to the 3 rules - aufbau principle, Pauli's exclusion principle and the Hund's rule of maximum multiplicity.

Aufbau principle:

The German word aufbau means 'build up'. The building up of orbitals means the filling up of orbitals with electrons. It states that the orbitals are filled in order of their increasing energies. In other words, electrons first occupy the lowest energy orbital and then to higher energy orbitals. This rule has two sub rules:

- ✦ The various orbitals are filled in the increasing order of their $(n + l)$ value.
- ✦ If two orbitals have the same $(n + l)$ values, the orbital with the lower n value is filled first.

The increasing order of orbitals is as follows: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s...

Pauli's Exclusion Principle

It states that no two electrons in an atom can have the same set of four quantum numbers. i.e. an orbital can accommodate a maximum of only 2 electrons with opposite spin. If 2 electrons have same values for n , l and m , they should have different values for s . i.e. if $s = +\frac{1}{2}$ for the first electron, it should be $-\frac{1}{2}$ for the second electron.

Hund's rule of maximum multiplicity

It states that electron pairing takes place only after partially filling all the degenerate orbitals. Orbitals having same energies are called degenerate orbitals. For example the electronic configuration of N is $1s^2 2s^2 2p_x^1 p_y^1 p_z^1$ and not $1s^2 2s^2 2p_x^2 p_y^1$.

Electronic Configuration of Atoms

The distribution of electrons into various orbitals of an atom is called its electronic configuration. The electronic configuration of different atoms can be represented in two ways.

- $s^a p^b d^c \dots$ notation
- Orbital diagram

The electrons in the completely filled shells are known as core electrons and the electrons in the outer most shell are called valence electrons.

Stability of Completely Filled and Half Filled Subshells

- ✦ For atoms having half filled or completely filled electronic configurations have extra stability compared to other atoms. This is due to their symmetrical distribution of electrons and greater exchange energy. For example, the electronic configuration of Cr is $[\text{Ar}] 3d^5 4s^1$ and not $3d^4 4s^2$. This is because d^5 represents a half filled configuration and has extra stability. Similarly for Cu the electronic configuration is $[\text{Ar}] 3d^{10} 4s^1$ and not $3d^9 4s^2$.