Chapter 2

Structure of Atom

ATOMIC STRUCTURE

Introduction

The term "atom" originates from the Greek word meaning indivisible, signifying the concept of an ultimate particle that cannot undergo further subdivision. The notion that all matter fundamentally comprises exceedingly small particles was initially postulated by ancient Indian and Greek philosophers. John Dalton solidified this ancient concept through the development of atomic theory between 1803 and 1808, marking a pivotal moment in the history of chemistry. According to Dalton's theory, an atom is the smallest, indivisible component of matter that actively participates in chemical reactions. Furthermore, atoms are immutable; they neither come into existence nor cease to exist. Atoms of the same element share similarities in size, mass, and characteristics. However, atoms belonging to distinct elements exhibit variations in size, mass, and characteristics.

In 1833, Michael Faraday established a connection between matter and electricity, representing a groundbreaking discovery. This revelation was the initial significant stride indicating that an atom was not a simple, indivisible particle constituting all matter but rather composed of smaller particles.

Discovery of electrons, protons and neutrons discarded the indivisible nature of the atom proposed by John Dalton.

The complexity of the atom was further revealed when the following discoveries were made in subsequent years:

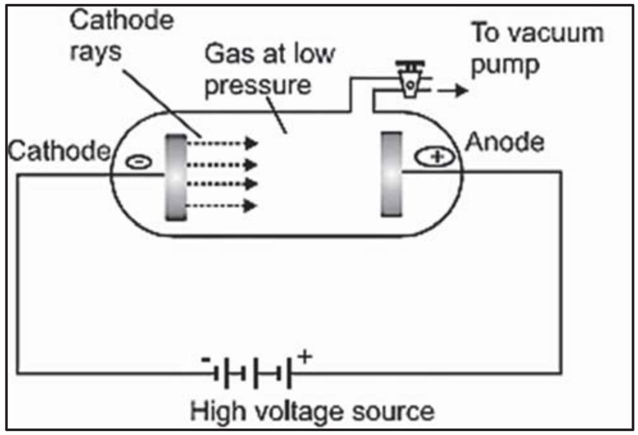
(i) Discovery of cathode rays.
(ii) Discovery of positive rays.
(iii) Discovery of X-rays.
(iv) Discovery of radioactivity.
Discovery of isotopes and isobars.
(vi) Discovery of quarks and the new atomic model.

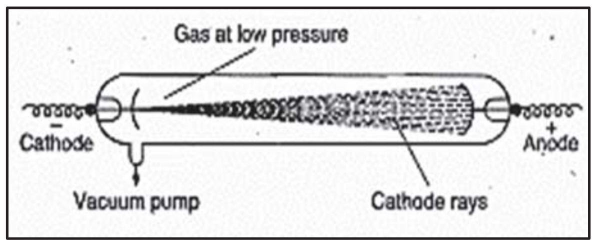
Over the last century, scientists have made significant contributions that have played a crucial role in shaping the modern theory of atomic structure.

The research of J.J. Thomson and Ernest Rutherford, in particular, served as the cornerstone for the contemporary understanding of the atom. Presently, it is accepted that the atom is composed of various subatomic particles, including electrons, protons, neutrons, positrons, neutrinos, mesons, and more.

Among these particles, the electron, proton, and neutron are referred to as fundamental particles, serving as the foundational components of atoms.

Cathode Rays- Discovery of Electron





In 1859, Julius Plücker initiated the exploration of electrical conduction through gases at low pressure in a discharge tube. When a high voltage, typically around 10,000 volts or more, was applied across the electrodes, imperceptible rays moved from the negative (-ve) electrode to the positive (+ve) electrode. As the negative electrode is termed the cathode, these rays were named cathode rays.

Subsequent investigations were conducted by W. Crookes, J. Perrin, J.J. Thomson, and others. Cathode rays exhibit the following characteristics:

(i.) They travel in straight lines away from the cathode at a very high velocity, approximately one-tenth of the speed of light.

(ii.) A shadow of a metallic object placed in their path is cast on the wall opposite to the cathode.

(iii.) When striking the glass wall, they produce a green glow, and light is emitted when they strike a zinc-sulphide screen.

(iv.) When a small pinwheel is placed in their path, the blades of the wheel are set in motion, indicating that cathode rays consist of material particles with mass and velocity.

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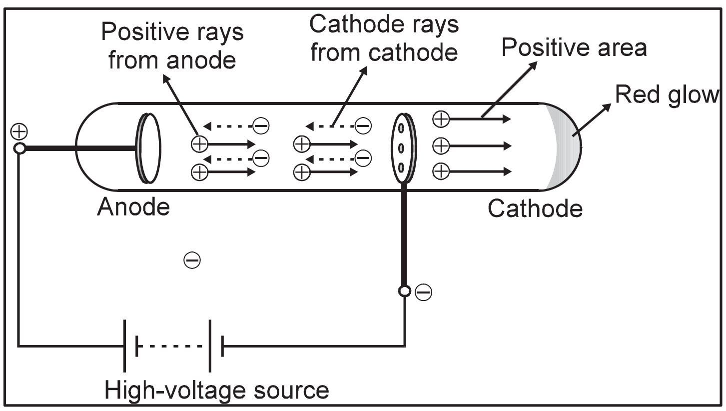
(vii.) They are deflected by electric and magnetic fields. When passed between two electrically charged plates, they are deflected towards the positively charged plate, indicating a negative charge. J.J. Thomson named these negatively charged particles "negatrons," which later became known as "electrons" by Stoney.
(viii.) They generate heat energy upon collision with matter, demonstrating that cathode rays possess kinetic energy, which is converted into heat energy upon stopping.
(ix.) These rays affect photographic plates.
(x.) Cathode rays can penetrate thin foils of solid materials.
(xi.) Cathode rays can ionize the gases through which they pass.
(xii.) The nature of cathode rays is independent of:
(a) the nature of the cathode
(b) the gas in the discharge tube.

Anode Rays or Positive Rays: (Discovery of Proton)

- Goldstein conducted the initial experiment that led to the identification of the positive particle.
- In his investigation, he employed a perforated cathode within a modified cathode ray tube.



- It was noted that applying a high potential difference between the electrodes resulted not only in the production of cathode rays but also in the simultaneous generation of a new set of rays moving from the anode towards the cathode, passing through the holes or canals of the cathode. These rays were labeled as canal rays due to their passage through the canals of the cathode, and alternatively, they were referred to as anode rays since they originated from the anode.
- Upon studying the properties of these rays, Thomson observed that they comprised positively charged particles, and he designated them as positive rays.
- The positive rays exhibit the following characteristics:
  (i) They travel in straight lines, casting a shadow of objects placed in their path.
  (ii) Similar to cathode rays, these rays can rotate a wheel in their path and have a heating effect, indicating the presence of kinetic energy and mass particles.
  (iii) The rays are subject to deflection by electric and magnetic fields toward the negatively charged plate, indicating their positive charge.
  (iv) Positive rays produce flashes of light on a ZnS screen.
  (v) They can pass through thin metal foil.
  (vi) These rays are capable of inducing ionization in gases.

(vii) The positive particles within these rays have an $\frac{e}{m}$ value much smaller than that of electrons. A smaller $\frac{e}{m}$ value suggests that positive particles possess higher mass.

(viii) The $\frac{e}{m}$ value is contingent on the nature of the gas present in the discharge tube, implying that positive particles vary in different gases.

- In 1906, J.J. Thomson conducted precise measurements of the charge and mass of particles within a discharge tube containing hydrogen, the lightest among all gases. The $\frac{e}{m}$ value for these particles was determined to be $+9.579 \times 10^4 \frac{\text{coulomb}}{\text{gram}}$, representing the highest observed $\frac{e}{m}$ value for any positive particle.
- As a result, it was inferred that the positive particle associated with hydrogen constitutes a fundamental particle with a positive charge. This particle was officially named the proton by Rutherford in 1911. Its charge was identified to be equal in magnitude but opposite in sign to that of the electron.

  Thus, charge on proton = $+ 1.602 \times 10^{-19}$ columbo i.e. one unit +ve charge
- The mass of the proton, thus can be calculated.

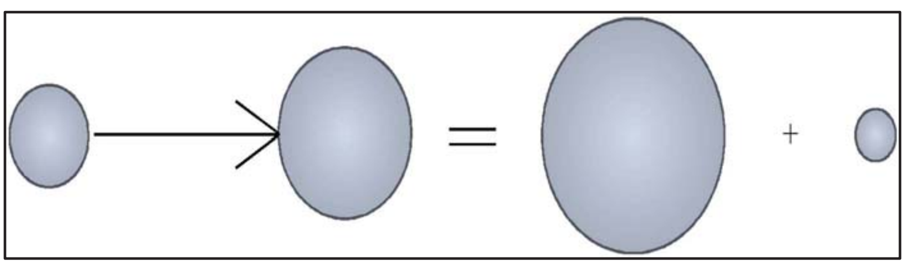
  Mass of the proton = $\frac{e}{e/m} = \frac{1.602\times10^{-19}}{9.579\times10^{4}} = 1.672 \times10^{-24}$ g = 1.672×10^{-27} kg

  Mass of proton in amu = $\frac{1.672\times10^{-24}}{1.66\times10^{-24}} = 1.00757$ amu.

Discovery of Neutron

In 1920, Rutherford proposed the existence of a third type of fundamental particle within an atom, one that should be electrically neutral and possess mass nearly equal to that of a proton. He coined the term "neutron" for such fundamental particles.

In 1932, Chadwick conducted an experiment by bombarding beryllium with a stream of α-particles. He observed the production of penetrating radiations that remained unaffected by electric and magnetic fields. These neutral particles were identified as neutrons. The nuclear reaction can be represented as follows:



α-particle	Be-atom	Carbon	Neutron
Charge = +2	Atom Atomic No. = 4	Atomic No. = 6	Charge = 0
Mass = 4 amu	Mass = 9 amu	Mass = 12 amu	Mass = 1 amu
[$^{4}_{2}He$	$+ ^{9}_{4}Be \longrightarrow$	$^{12}_{6}C$	$+ ^{1}_{0}n$]

Therefore, a neutron is a subatomic particle with a mass of approximately 1.675×10^{-24} g, roughly equivalent to 1 atomic mass unit (amu) and nearly identical to the mass of a proton or a hydrogen atom. Notably, neutrons carry no electrical charge.

- The $\frac{e}{m}$ value of a neutron is zero.

Atomic Structure

Atom is actually made of 3 fundamental particles

1. Electron 2. Proton 3. Neutron

Fundamental Particle	Discovered By	Charge	Mass	$\frac{\text{Charge}}{\text{mass}}$ (Specific Charge)
Electron (e^- or β)	J.J. Thomson	-1.6×10^{-19} coloumb -4.8×10^{-10} esu -1 Unit	9.1×10^{-31}kg 9.1×10^{-28} g 0.000548amu	1.76×10^{8}C/g
Proton (P) (Ionized H atom, H^+)	Goldstein	$+1.6 \times 10^{-19}$ coloumb $+4.8 \times 10^{-10}$ esu +1 Unit	1.672×10^{-27}kg 1.672×10^{-24} g 1.00757amu	9.58×10^{4}C/g
Neutron	James Chadwick	0	1.675×10^{-27}kg 1.675×10^{-24} g 1.00893 amu	0

Order of Specific Charge

$$\left(\frac{e}{m}\right)_n < \left(\frac{e}{m}\right)_p < \left(\frac{e}{m}\right)_{e^-}$$

$$\left(\frac{\text{mass of proton}}{\text{mass of electron}}\right) \frac{m_p}{m_{e^-}} = 1837$$

Measurement Of E / M For Electron

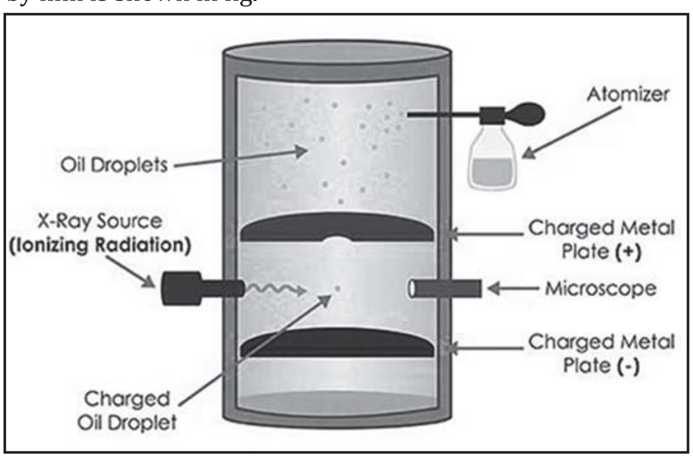
In 1897, J.J. Thomson calculated the electron's $\frac{e}{m}$ value ($\frac{\text{charge}}{\text{mass}}$) through an examination of the deflection of cathode rays in electric and magnetic fields. The determined value of $\frac{e}{m}$ is -1.7588×10^{8} $\frac{\text{coulomb}}{\text{gram}}$.

- Through a series of experiments, Thomson demonstrated that irrespective of the gas present in the discharge tube and the material of the electrodes used, the value of $\frac{e}{m}$ remains constant. Consequently,
- Electrons are identified as universal constituents common to all atoms.

Determination Of the Charge on An Electron

R.A. Millikan conducted the oil drop experiment in 1909, measuring the absolute value of the charge on an electron.

- The apparatus used by him is shown in fig.



- An oil droplet descends through a hole in the upper plate, and the air between the plates is exposed to X-rays, causing the ejection of electrons from air molecules. Some of these electrons are captured by the oil droplet, imparting a negative charge to it.
  The metal plates are then charged electrically, and by increasing the electric field between the plates, certain droplets can be made to ascend at the same rate they were initially falling. Milikan determined the magnitude of the charge on the oil droplets by measuring their speed, considering factors such as the field strength, oil density, and the radius of the oil drops. The smallest charge identified on the drops was approximately 1.59×10^{-19} C, acknowledged as the charge on an electron. The modern value stands at 1.602×10^{-19} C.

Mass Of the Electron

Mass of the e^- can be calculate from the value of e/m and the value of e

$$m = \frac{e}{e/m} = \frac{-1.602\times10^{-19}}{-1758 \ \times10^{8}}$$

$$= 9.1096 \times10^{-28} \text{ g} \quad \text{or}$$

$$= 9.1096 \times 10^{-31} \text{ kg}$$

This is referred to as the rest mass of the electron, indicating the mass of the electron when it is moving at low speed. The mass of a moving electron can be calculated using the following formula.

$$\text{Mass of moving } e^- = \frac{\text{rest mass of } e^-}{\sqrt{1-(v/c)^2}}$$

Where v is the velocity of the electron and c is the speed of light.

When, $v = c$

$\Rightarrow$ mass of $e^- = \infty$

When, $v > c$

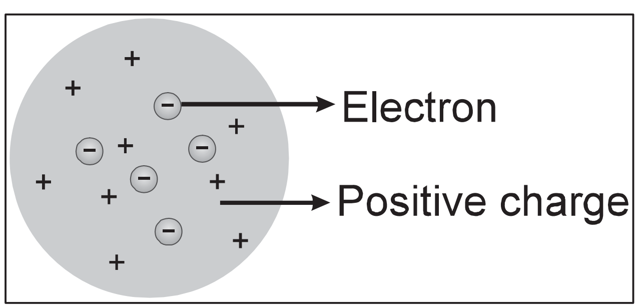
$\Rightarrow$ mass of e^- = imaginary

Discovery of Sub-Atomic Particles

Atomic Models

Thomson's Model of Atom [1904]

Thomson was the initial proponent of a comprehensive atomic model, suggesting that an atom is composed of a uniformly charged sphere with positive charge, wherein electrons are distributed at specific locations. This atomic model is commonly referred to as the "Plum-Pudding model."

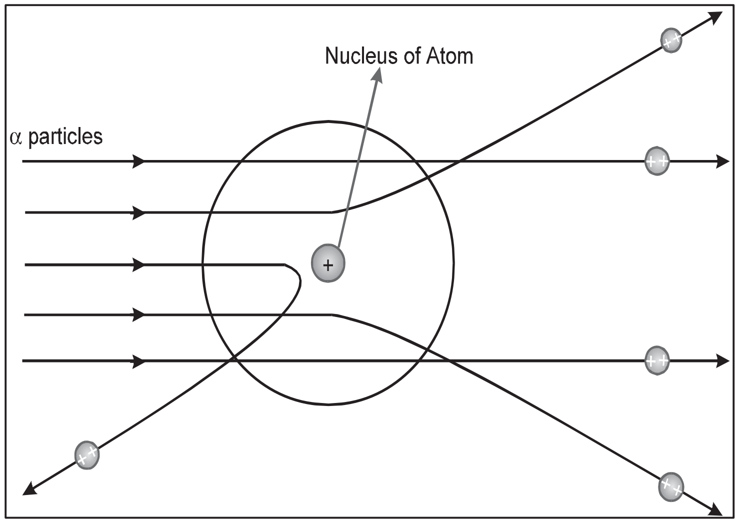


Drawbacks

- One significant limitation of this model is the assumption that the mass of atoms is uniformly distributed throughout the atom.
- This model is static and does not account for the movement of electrons.

Rutherford's α- Scattering Experiment

α-Scattering Experiment

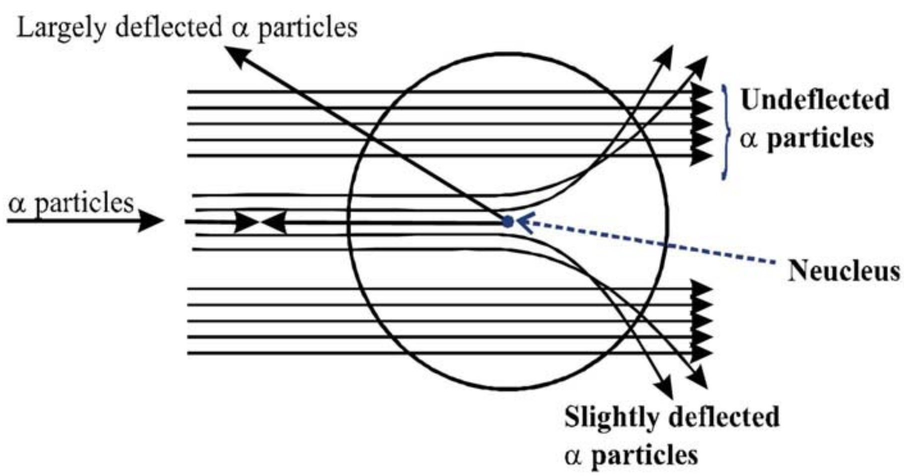


Rutherford Observed That

(i) The majority of α-particles, almost 99.9%, proceeded in a straight path without experiencing any deflection.

(ii) A small number of α-particles were deflected at minor angles.

(iii) Only a very small fraction of α-particles, approximately one in 20,000,



did not pass through the foil at all but suffered large deflections (more than 90°) or even come back in the direction from which they have come i.e. a deflection of 180°.

Following Conclusions were Drawn from the Above Observations

(1) Considering that the majority of α-particles passed through the metal foil without any deviation, it implies the existence of a significant empty space within the atom.

(2) As a few α-particles were deflected at moderate angles, it was inferred that the entire positive charge is concentrated in a small space within the atom. Whenever α-particles approached this point, they experienced a repulsive force, causing them to deviate from their original paths. This positively

charged heavy mass, occupying only a small volume within the atom, is referred to as the nucleus, presumed to be situated at the center of the atom.

(3) A very limited number of α-particles underwent substantial deflections or even reversed their paths, suggesting the rigid nature of the nucleus. This phenomenon indicates that α-particles recoil due to direct collisions with the densely charged, heavy mass at the center of the atom.

(4) The relation between number of deflected particles and deflection angle θ is

$$\mu = \frac{1}{sin^4\frac{\theta}{2}} \text{ [θ increases μ decreases]}$$

where μ = deflected particles

θ = deflection angle

As the atomic number rises, there is an increase in the number of protons, leading to heightened repulsion and consequently an increase in the deflection angle θ.

Applications Of Rutherford Model

Based on scattering experiments, Rutherford introduced the nuclear atomic model, which posits the following:

(i) An atom is comprised of a dense, positively charged nucleus housing all the protons.

(ii) The nucleus occupies a very small volume, representing only a tiny fraction of the total atom volume. The nucleus has a radius on the order of 10^{-13} cm, while the atom itself has a radius on the order of 10^{-8} cm.

$$\frac{r_A}{r_N} = \frac{\text{radius of the atom}}{\text{radius of the nucleus}} = \frac{10^{-8}}{10^{-13}} = 10^5, \quad r_A = 10^5\, r_N$$

Thus radius (size) of the atom is 10^5 times the radius of the nucleus.

- The radius of a nucleus is proportional to the cube root of the mass no. of the nucleus.

$$R \propto A^{1/3} \Rightarrow R = R_0 A^{1/3} \text{ cm}$$

Where $R_0 = 1.33 \times 10^{-13}$(a constant) and, A = mass number (p + n)

R = radius of the nucleus.

$$R = 1.33 \times 10^{-13}\, A^{1/3} \text{ cm}$$

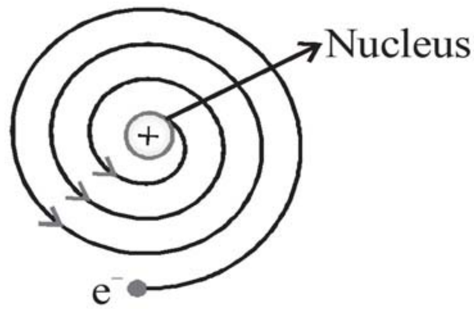
(iii) Surrounding the nucleus is a region referred to as the extranuclear section, where electrons are located. The number of electrons in an atom always corresponds to the number of protons within the nucleus. While the nuclear component is accountable for the atom's mass, the extranuclear part contributes to its volume. The volume of the atom is approximately 10^{15} times greater than the volume of the nucleus.

$$\frac{\text{Volume of the atom}}{\text{Volume of the nucleus}} = \frac{(10^{-8})^3}{(10^{-13})^3} = \frac{10^{-24}}{10^{-39}} = 10^{15}$$

(iv) Electrons orbit the nucleus in closed paths at high velocities. This model bears a resemblance to the solar system, with the nucleus playing the role of the sun and the orbiting electrons akin to planets.

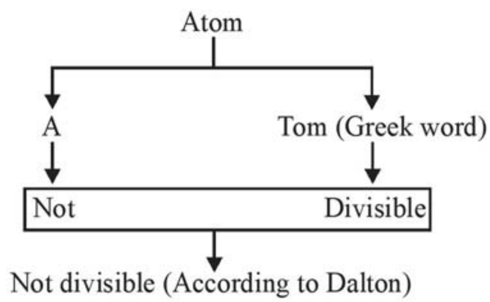
Drawbacks of Rutherford Model

(1) This theory failed to account for the stability of an atom. Maxwell proposed that electrons continuously lose energy in the form of electromagnetic radiation. Consequently, electrons should lose energy with each revolution, spiraling inward toward the nucleus. Ultimately, this would lead to the electron falling into the nucleus, rendering the atom unstable.



(2) If electrons were to lose energy continuously, the expected spectrum would be continuous; however, the observed spectrum comprises distinct lines with specific frequencies, indicating discontinuity. Therefore, the energy loss by electrons within an atom is not continuous.

Atom



Atom is a Greek Word

It signifies being indivisible, implying an ultimate particle that cannot be further subdivided. John Dalton (1803 - 1808) proposed that all matter is composed of small particles known as atoms.

According To Dalton's Theory

(1) Atom is the smallest indivisible part of matter which takes part in chemical reaction.

(2) Atom is neither created nor destroyed.

(3) Representation of atom: $_{Z}X^{A}$.

Where: A $\rightarrow$ Mass number, Z $\rightarrow$ Atomic number, X $\rightarrow$ Symbol of atom.

Atomic Number and Mass Number

Mass Number

Denoted by the capital A, the mass number of an element is the sum of the neutrons and protons within its nucleus. This quantity is also referred to as the number of nucleons, as both neutrons and protons reside in the nucleus.

$$A = \text{number of protons} + \text{number of neutrons}$$

Note: It is always a whole number.

Atomic Number

Designated as Z, the atomic number of an element is the count of protons within its nucleus. This characteristic is also referred to as the nuclear charge.

For Neutral Atom: Number of protons = Number of electrons

For Charged Atom: Number of e^- = Z – (charge on atom)

Z= number of protons only

Ex. $_{17}Cl^{35}$

n = 18

p = 17

e = 17

Two different elements cannot have the same Atomic Number

Number of Neutrons = Mass number – Atomic number

= A – Z

= (p + n) – p

= n

Method for Analysis of Atomic Weight

Ex. $_6C^{12}$

$P^+ \rightarrow 6$	Weight of Proton = 6 × 1.00750
$n^0 \rightarrow 6$	Weight of Neutron = 6 × 1.00850
$e^- \rightarrow 6$	Weight of Electron = 6 × 0.000549
	Weight of C atom = 12.011 a.m.u.

Mass no. of C atom = 12 [P and n]

Note: Mass no. of atom is always a whole no. but atomic weight may be in decimal.

Ex. If no. of protons in X^{-2} is 16. then no. of e^- in X^{+2} will be–

(1) 14 (2) 16 (3) 18 (4) None

Sol. ∵ No. of proton in X^{-2} is = 16

∴ No. of electron in X^{+2} is = 14

Ex. In C^{12} atom if mass of e^- is doubled and mass of proton is halved, then calculate the percentage change in mass no. of C^{12}.

Sol. $_6C^{12}$

$P^+ \rightarrow 3$

$e^- \rightarrow 12$

e^-	P^+	n°	
6	6	6	$A \rightarrow 12$
12	3	6	$A \rightarrow 9$

Percentage % change = × 100 = 25%

Ex. Assuming that atomic weight of C^{12} is 150 unit from atomic table, then according to this assumption, the weight of O^{16} will be:

Sol. ∵ 12 amu = 150

∴ 1 amu =

∴ 16 amu = × 16 = 200 Unit

Characteristics of Cathode Rays:

(i) Cathode rays possess mechanical energy and exhibit a straight-line trajectory.

(ii) These rays exhibit deflection towards the positive plate of an electric field, implying that they are composed of negatively charged particles known as electrons. The term "electron" was introduced by Stoney.

(iii) The observed characteristics are found to be independent of the nature of the gas.

(iv) Mulliken was instrumental in determining the charge on an electron, establishing it at 1.602×10^{-19} Coulombs.

(v) J.J. Thomson was responsible for calculating the specific charge on an electron.

Charge to Mass Ratio

The origins of quantum mechanics and the understanding of atomic structure can be traced back to the era of Democritus, the first proponent of the theory that matter is composed of atoms. However, despite Democritus's early insights, these theories lacked prominence due to the absence of requisite technology. Experiments conducted in the nineteenth and early twentieth centuries revealed that an isolated atom was not the ultimate building block of matter. It was through the persistent efforts of various scientists that the existence of subatomic particles, including protons, neutrons, and electrons, was eventually uncovered.

J.J. Thomson, in the nineteenth century, introduced the Thomson Atomic Model, a groundbreaking development that identified the electron and marked the initiation of subatomic particle exploration. Following the electron's discovery, Thomson continued his research to determine both the mass and charge of this particle. Utilizing these findings, he derived a formula for calculating the charge-to-mass ratio of electrons. This article delves into the examination of the mass-to-charge ratio and the methodologies involved in calculating the charge-to-mass ratio.

The ratio of the charge to the mass of an electron is expressed as:

$$\frac{e}{m} = 1.758820 \times 10^{11}\ \text{C/kg}$$

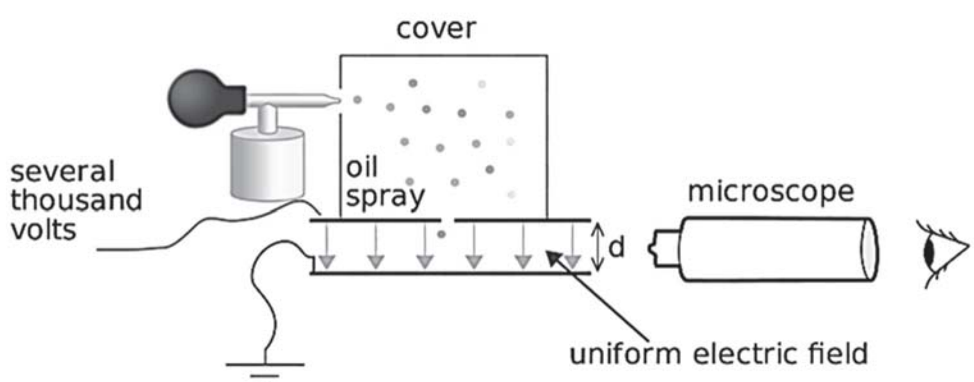
Here, the variables are defined as follows:

m (mass of an electron) = $9.10938356 \times 10^{-31}$ kilograms

e (magnitude of the charge of an electron) = 1.602×10^{-19} coulombs

Millikan's Oil Drop Experiment

During the experimental procedure, Millikan permitted minute charged oil droplets to traverse a hole and enter an electric field. Through the manipulation of the electric field strength, the charge carried by an oil droplet was determined, consistently yielding values that were integral multiples of 'e.'



Milliken's Oil Drop Experiment Procedure

- Atomized oil is introduced into the apparatus through an atomizer, emerging as minuscule droplets that traverse through perforations in the upper plate.
- Microscopic observation tracks the downward movements of these droplets, and their mass is subsequently measured at terminal velocity.
- Within the chamber, air undergoes ionization induced by X-ray exposure, endowing the oil droplets with electrical charge through collisions with gaseous ions generated during air ionization.
- A distinct electric field is established between two plates, influencing the motion of charged oil droplets within it.
- The gravitational force acts downward on the oil, while the electric field exerts an upward force on the charged droplets. The strength of the electric field is carefully adjusted to achieve equilibrium, where the oil droplet reaches a stable position against gravitational forces.
- The determination of charge on the droplet at this equilibrium point hinges on factors such as the electric field's intensity and the droplet's mass.

Example: In Millikan's oil drop experiment, the charges of three oil drops labeled X, Y, and Z are determined to be 2, 0.04, and 0.8, respectively. The objective is to ascertain the probable charge of an electron and the number of electrons associated with each oil drop.

Solution: The approach involves identifying the smallest charge, with the expectation that all other charges are integral multiples of this minimal value. In this dataset, the smallest charge is 0.04, and all other charges are integral multiples of it. Hence, the charge on an electron (e) is calculated as 0.04 C. Given the relation $q = ne$ (where $n = 1, 2, 3...$) and $e = 0.04$, the calculation for the number of electrons (n) is as follows:

For $q = 2$, n is determined to be 50.
For $q = 0.04$, n is equal to 1.
For $q = 0.8$, n is found to be 20.

Discovery of Anode Rays

Goldstein conducted an experiment utilizing a discharge tube equipped with a perforated cathode. Applying a potential difference of 10,000 volts at a pressure of 10^{-2} mm of Hg, he made a noteworthy observation of a luminous phenomenon occurring behind the cathode. This illumination was attributed to the impact of imperceptible rays generated between the anode and cathode.

Termed as canal rays or anode rays, these invisible rays exhibit distinct properties:

- **Deflection Towards Negative Plate:** These rays demonstrate deflection towards the negative plate in an applied electric field, implying their composition of positively charged particles.
- **Dependence on Gas Nature:** The properties of anode rays are contingent upon the nature of the gas involved in the experiment.
- **Straight-Line Travel and Mechanical Energy:** Anode rays possess the characteristics of traveling in a straight line and possessing mechanical energy.