Discovery of Atomic Structure

- Dalton's theory did little to elucidate their nature.

  How do atoms join together to form chemical compounds?

  What holds them together?

  Why do atoms combine with each other only in certain ratios and not in others?

- Answers to these and other such questions lie in understanding the internal structure of the atom.

- Investigations into the nature of atomic structure began almost immediately after Dalton published his theory and continued well into the 20th century.

The Idea of the Electron

1807 - Sir Humphrey Davy

Experiments in electrolysis show matter has an electrical character. Y Atoms must have an electrical character.

1834 - Michael Faraday

Quantitative experiments show relationship between amount of charge passed and amount of material produced in electrolysis (Faraday's Laws).

1874 - G. Johnstone Stoney

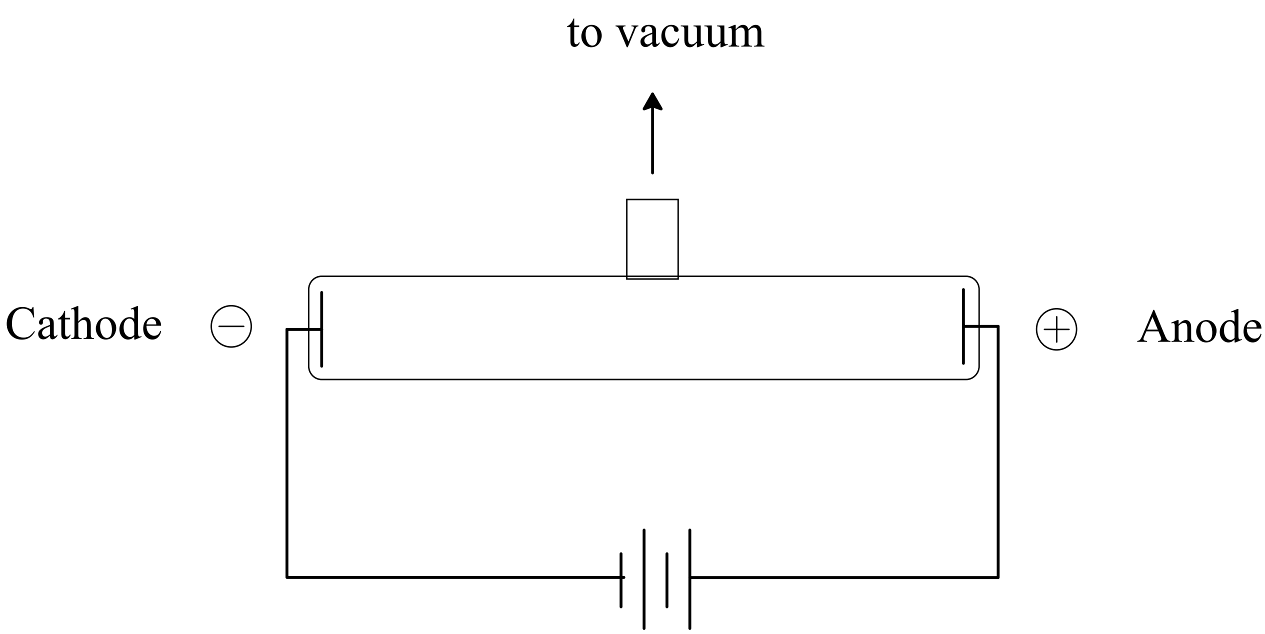
Review of Faraday's work suggests there must be fundamental units of charge associated with atoms.

1891 - G. Johnstone Stoney

Proposes calling the fundamental charges **electrons.**

Gas Discharge Tube - First Experiments

Faraday - 1838



Observations:

1. As gas is evacuated from the tube to lower the gas pressure in it, the remaining gas begins to glow.

2. With more complete evacuation, the glow inside the tube ceases, but the glass at the end of the tube with the positively charge plate (anode) begins to glow faintly.

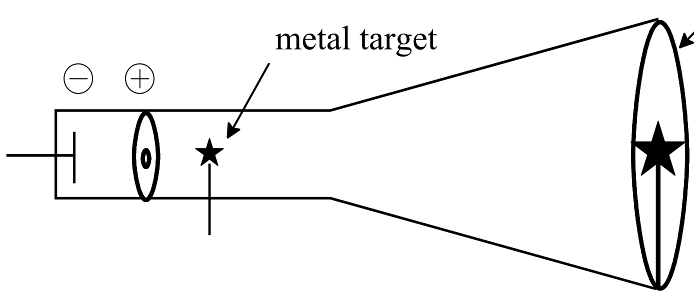
Cathode Ray Postulate

Sir William Crookes suggested that these observations were caused by a stream of negatively charged particles, which he called **cathode rays**, passing from the negative plate (cathode) to the positive plate (anode) in the tube.

The glow in either the gas or the glass itself is caused by the impact of these rays of particles with the atoms of the gas or glass.

Additional Observations
About Cathode Rays

1. An object placed in the path of the rays causes a sharp shadow on the anode end of the tube.



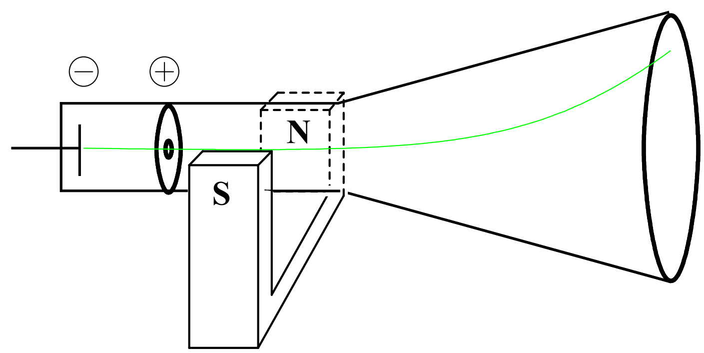
   Y The rays travel in straight lines from the cathode to the anode.

2. Cathode rays striking a small object (e.g., a pinwheel) cause its surface to heat and may make it move.
   Y The particles in the rays have mass.

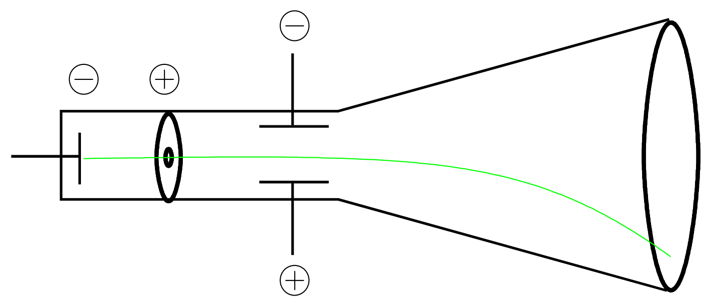
3. A magnetic or electric field perpendicular to the path of rays causes them to bend in the way a moving negative charge would bend.
   Y The cathode rays consist of negatively charged particles.

Effects of Magnetic and Electric Fields

Magnetic field effect:



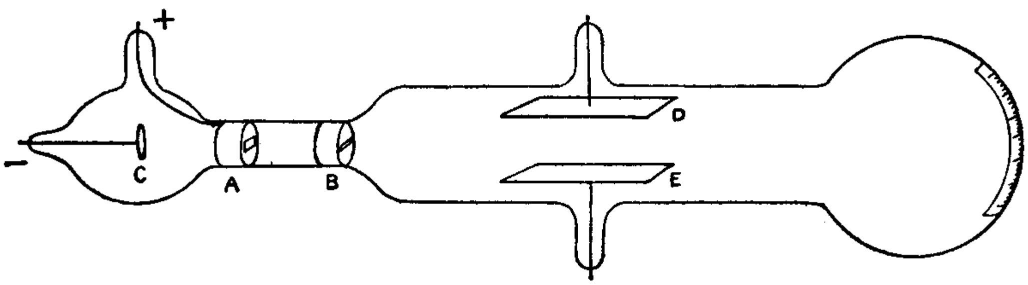
Electric field effect:



Cathode Rays are Electrons

- From these observations, J. J. Thomson concluded that the cathode rays are actually streams of the electrons that Stoney had postulated.

- Thomson did experiments with a special cathode ray tube, having both magnetic and electrical fields with opposite effects on the beam, to determine the ratio of the electron's charge (*e*) to its mass (*m*).

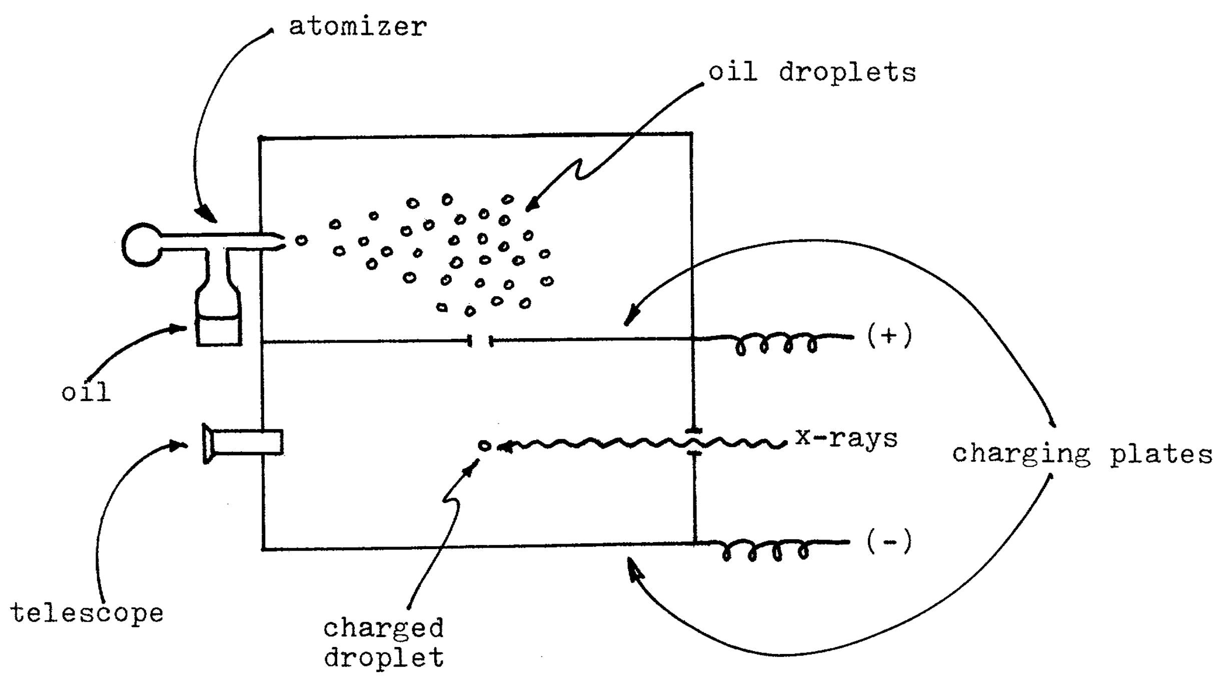


J. J. Thomson's drawing of his cathode ray tube from *Phil. Mag.* **1897**, *44 (5)*, 296.

- Thomson determined

$$e/m = -1.76 \times 10^{8} \text{ coulomb/g}$$

Milliken's Oil Drop Experiments



- Robert A. Milliken, in a series of experiments done in 1906-1914, determined the **unit negative charge**, the charge on the electron:

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

- From Thomson's *e/m* value, the mass of the electron could be calculated:

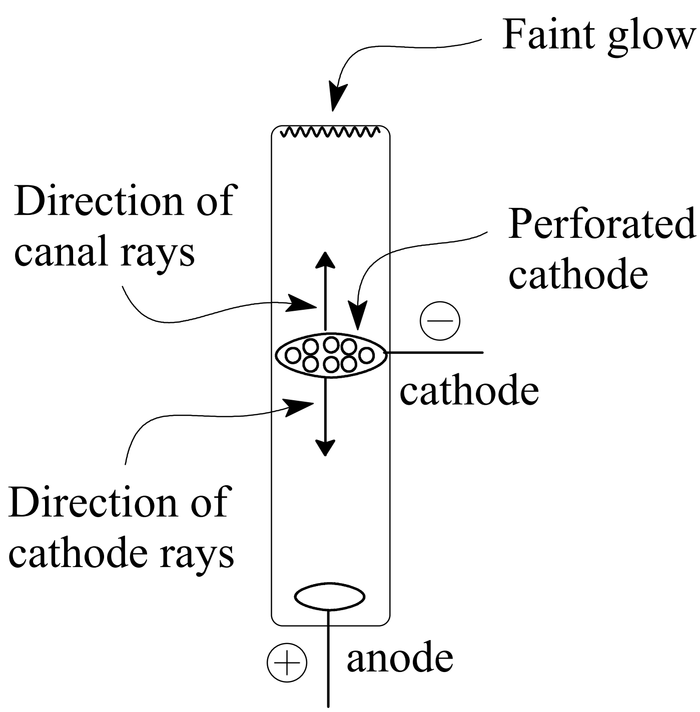
$$m_e = 9.1096 \times 10^{-28}\ \mathrm{g}$$

Canal Ray Tube

Eugene Goldstein, 1886

The canal ray tube, a special cathode ray tube, produces streams of positively charged atoms (ions) as a result of cathode rays hitting the gas atoms in the tube and knocking electrons off of them:

$$A(g)\ 6\ A^{+}(g) + e^{-}$$

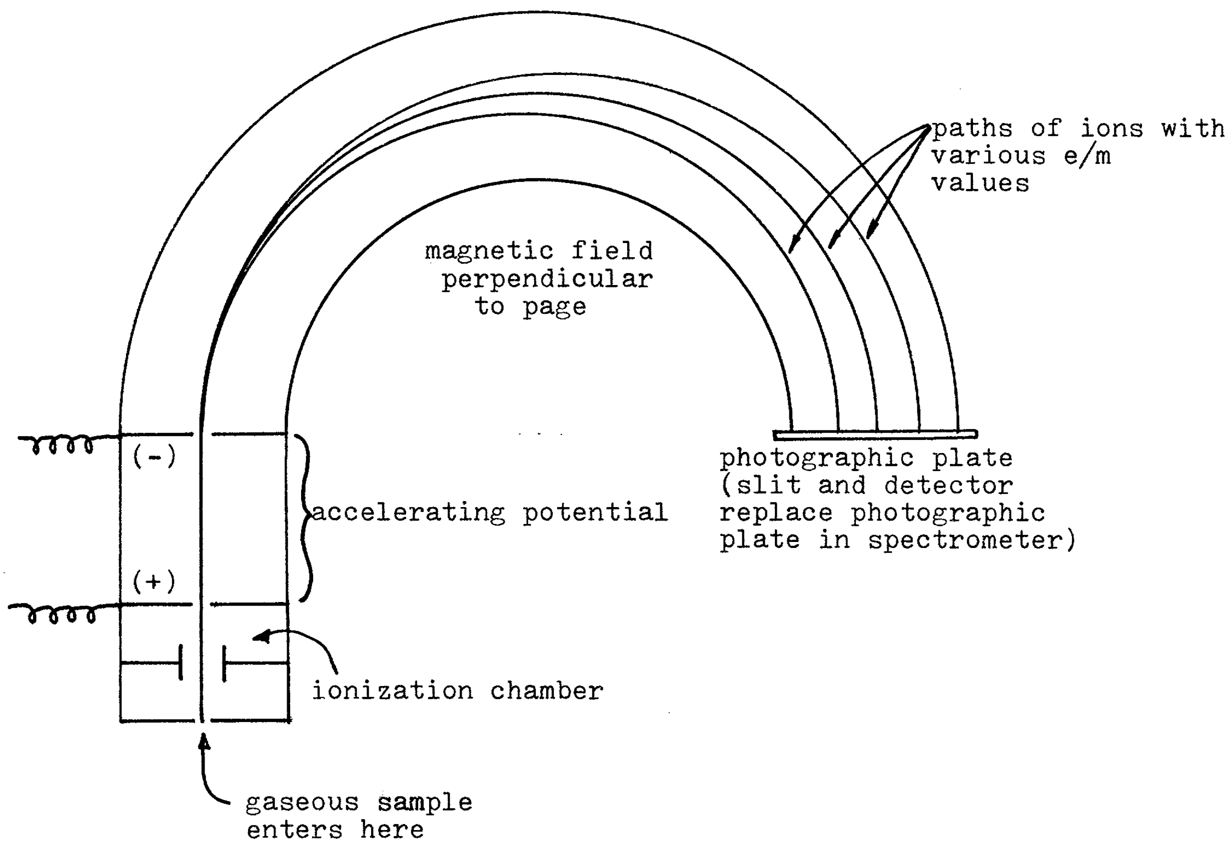


The Proton

- William Wein (1898) showed the maximum *e/m* occurred when hydrogen filled the tube:
$$e/m = +9.5791 \times 10^{4}\ \mathrm{C/g}$$
- The mass of H^+ had previously been determined, so it was taken as the mass of the proton:
$$m_p = 1.6726 \times 10^{-24}\ \mathrm{g}$$
- Using Wein's *e/m*, the **unit positive charge** on the proton was calculated to be
$$e = 1.6022 \times 10^{-19}\ \mathrm{C}$$

The Neutron

- In 1912 **J. J. Thomson** proposed the existence of **neutrons**, uncharged particles with about the same mass as the proton, to explain the existence of isotopes, which he had detected with his **mass spectrograph** experiments.



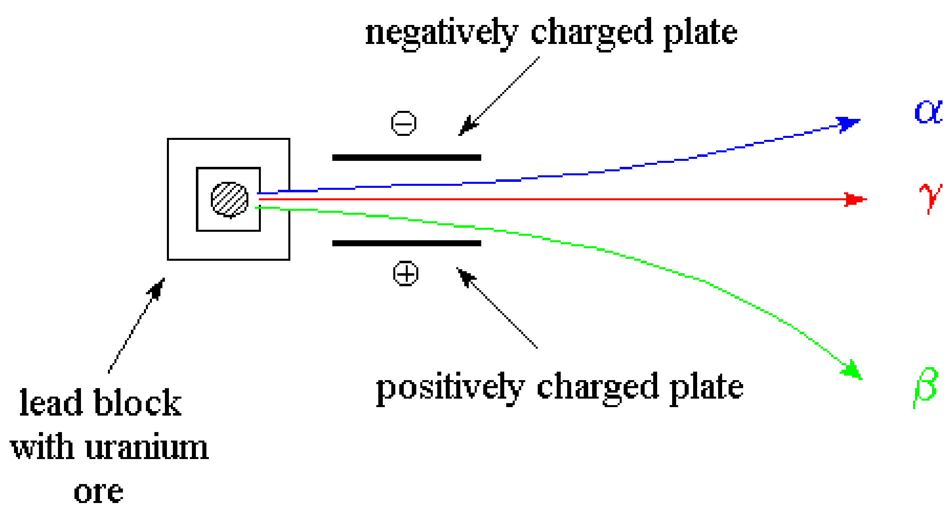
Verification of the Existence of Neutrons

- Verification of the existence of the neutron is credited to **James Chadwick**, who in 1932 used calculations concerning masses and energies of particles in nuclear reactions to characterize it.

$$m_n = 1.6749 \times 10^{-24}\ \text{g}$$
$$e_n = 0\ \text{C}$$

Radioactivity

- **Henri Becquerel** in 1896 discovered that the uranium ore pitchblende gave off high energy radiation, which was subsequently called **radioactivity**.



- **Ernest Rutherford** showed that the radiation consisted of three types, which differed in their behavior in an electric field:

  α Positively charged helium atoms, He^{2+}, composed of two protons and two neutrons.

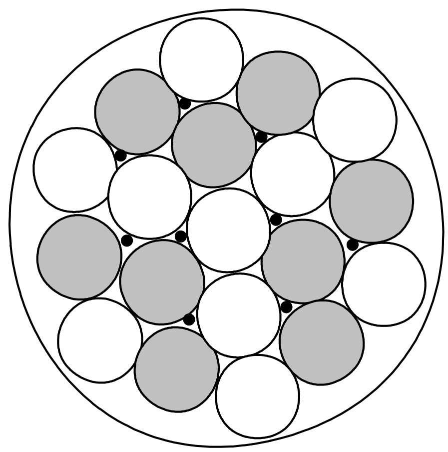
  β Negatively charged electrons.

  γ High energy radiation, unaffected by an electric field (no charge or mass).

Thomson's "Plum Pudding" Model

1898

- The atom is a ball of protons and neutrons with electrons in the interstices.



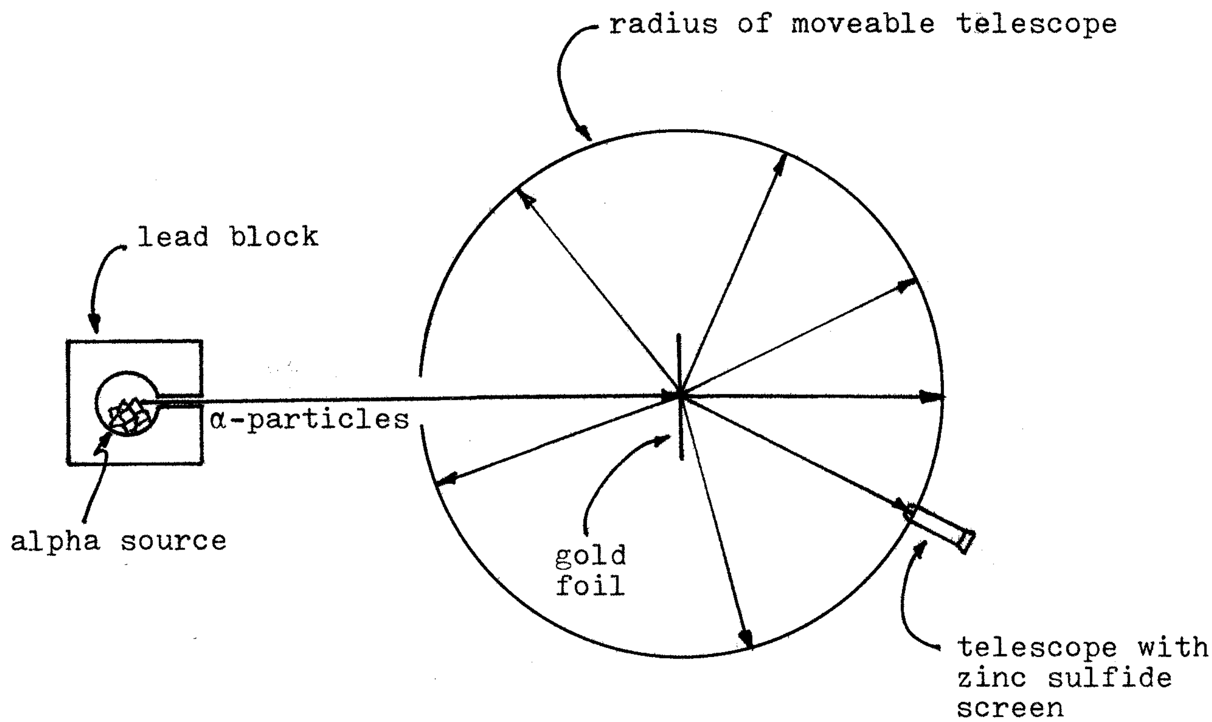
Hantaro Nagaoka's Saturnian Model

1904

- Electrons circulate in rings about a nucleus that contains the protons and neutrons.

Rutherford's
Gold Foil Experiments
1910

Rutherford used α particles to probe the internal structure of gold atoms.



"It was almost as if you fired a 15-inch shell into a piece of tissue paper and it came back and hit you."
– Ernest Rutherford

Conclusions from Rutherford's Experiments

1. "Plum Pudding" model is wrong.

2. Atoms are mostly empty space.

3. Most of the atom's mass and all of its positive charge are contained in a small nucleus (- 10^{-12} cm diameter).

4. Electrons are widely separated from the nucleus (- 10^{-8} cm away).