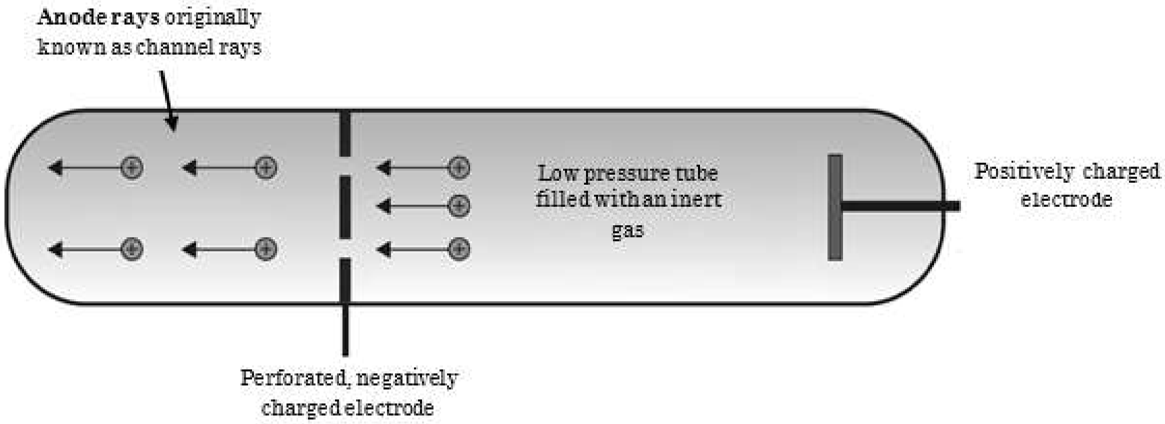
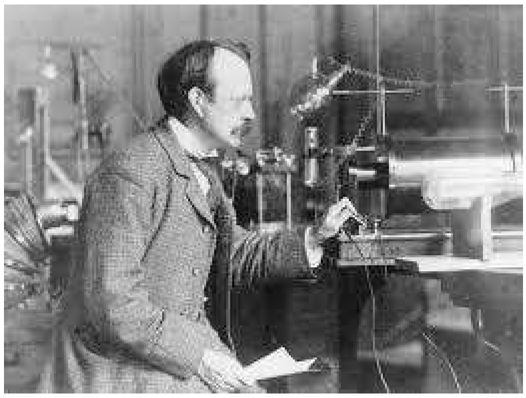
The Discovery of Anode Rays and Cathode Rays

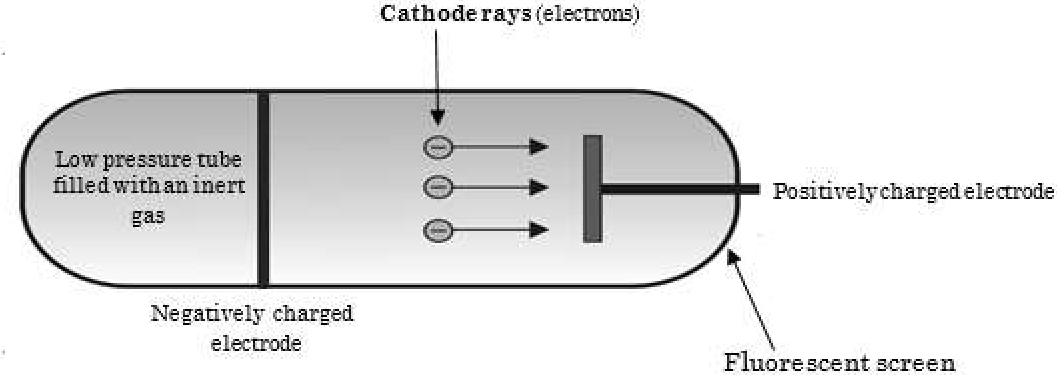
Anode rays were first observed when a perforated cathode (negatively charged) and an anode (positively charged) were subject to a high electrical potential (several thousand volts) in a gas discharge tube as shown below. Very faint luminous rays were observed extending from the holes in the rear of the perforated cathode and travelling towards the anode. Eugen Goldstein (pictured left) termed these rays *Kanalstrahlen* (channel rays) as they were emitted from the holes or channels of the cathode. Since they were attracted to the negatively charged anode, these streams of particles were clearly positively charged and Goldstein had discovered the *proton* although this was not explicitly recognised at the time.



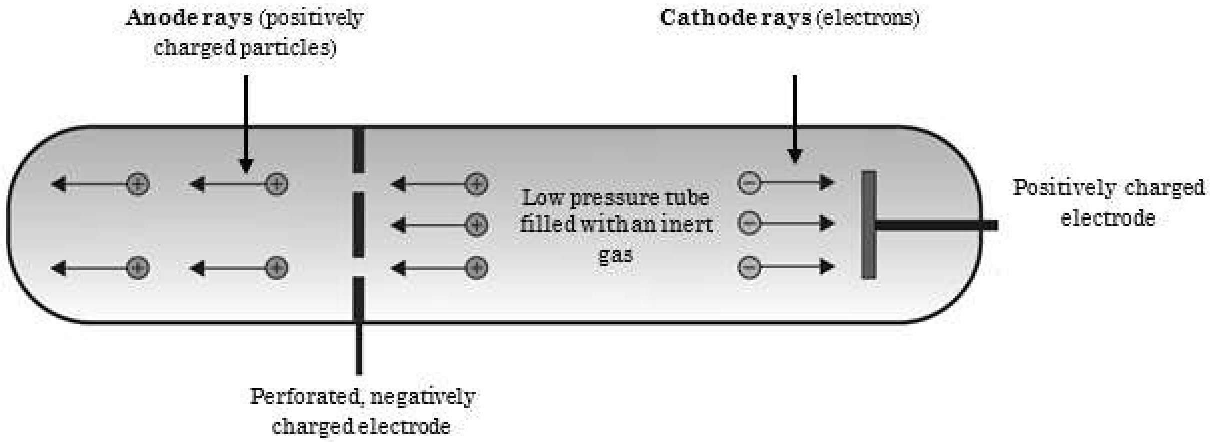
In 1897, Sir J.J. Thomson (right) performed a similar experiment (as shown below) and, placing a screen which would fluoresce (glow) when impinged by charged particles, observed cathode rays which, being attracted to the positively charged cathode, had to be negatively charged particles.

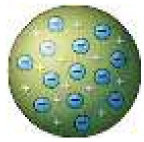


We now call them electrons.



We can combine these two experiments as shown below.





The discoveries by Goldstein and Thomson completely contradicted the notion of a hard, indivisible atom. Since both the, positively charged, protons and the, negatively charged, electrons (as we now term them) had to originate from the atom this led to Thomson's famous *plum pudding* model of the atom (right) in which it was envisaged that protons and electrons held each other together by electrostatic attraction and made up the complete volume of a solid atom which had to be neutral since atoms were not affected by a magnetic field and passed straight through on its path as if the electric field was not present. This also naturally led to the logical assumption that the number of positive particles and the number of negative particles in an atom were the same.

Thomson went one step further though and placed his apparatus in a magnetic field. This part of the experiment was really quite simple to perform since the gas discharge tube was merely placed between the two poles of an external magnet. Thomson observed that the cathode rays were deflected (their direction of motion altered) when passing through a magnetic field and he was able to calculate the mass of the electron. In 1907, it was observed that the anode rays could be deflected by a magnetic field in a similar way.

Most significantly, however, whilst the cathode ray beam remained uniform and simply changed its route when traversing the magnetic field, the anode ray beam was not deflected uniformly but split into a number of rays which were deflected to different extents rather analogous to the splitting of white light by a prism into the colours of the rainbow. This implied that all cathode rays were identical but that the anode rays were not all exactly the same.

We can now explain Thomson's experimental results on the basis that:-

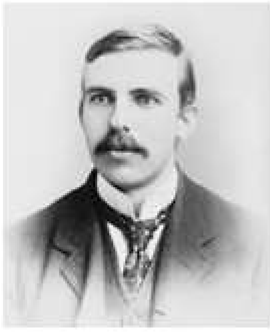
- Cathode rays are negatively charged electrons which are, of course, all exactly the same.
- The positively charged particles and, although not appreciated at the time, were the first indication of the existence of the nucleus and also of isotopes (nuclei of the same atomic number and so of the same positive charge but different masses).

This created a further puzzle since, by classical mechanical physics calculations, the masses of the particles constituting the anode rays could be calculated. It was consistently determined that the lightest particle was 1840 times greater than the mass of the electron. The ***proton*** had been discovered although the real significance of its role in atomic structure was not resolved until Rutherford's work in 1911.

The Discovery of the Existence of the Nucleus

In that year in Manchester, Rutherford assisted by, the soon to be famous in their own right, Hans Geiger and Ernest Marsden performed the classic '*gold foil*' experiment that led to the discovery of the existence of the atomic nucleus.

Hans Geiger



Lord Rutherford

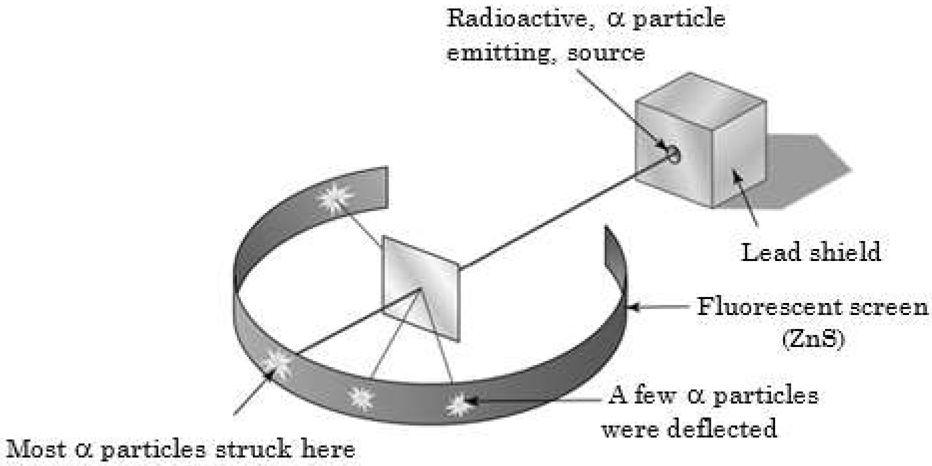
Ernest Marsden

In this experiment alpha particles (helium nuclei $^{4}He^{2+}$), which had been discovered as a consequence of the discovery of radioactivity, were aimed at a piece of gold foil.

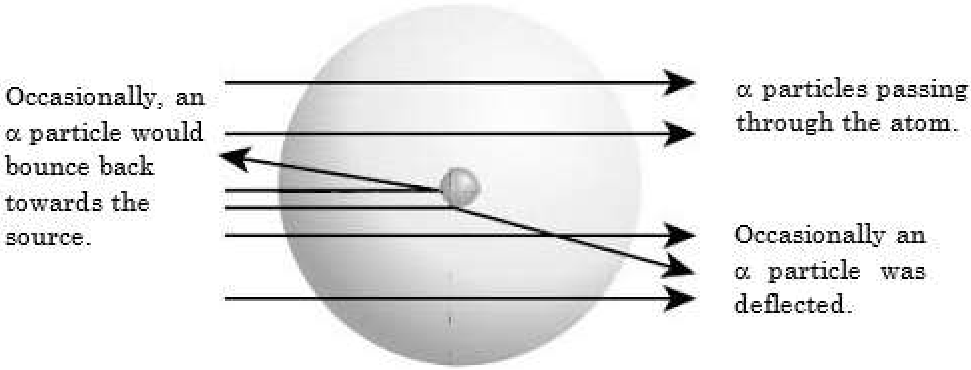
The entire apparatus was contained within a circular fluorescence screen which lit up briefly when hit by an alpha particle. It was predicted that if the atom was indeed completely solid then the alpha particles would be absorbed upon collision with an electron but repelled if they collided with a proton and none would reach a detector placed directly behind the gold foil.

This prediction is precisely what did *not* occur.

The result of the experiment was that the vast majority of the alpha particles passed straight through the gold foil. Most were deflected and passage through the gold foil changed their angle, but not the overall direction, of travel and reached the detector whilst a tiny fraction bounced off the foil and returned in various directions back towards the source of the alpha particles as illustrated below:



This led to the extraordinary conclusion that, since the alpha particles had encountered neither proton nor electron, they must have travelled through empty space and this completely contradicted the concept of a completely solid atom which was replaced by the nearly inconceivable conclusion that the atom was essentially empty space.



There were, however, two further problems to be resolved.

If the atom was almost empty, technically called *free space* in physics, then '***Why did some alpha particles bounce back***?' and '***Where are the protons and electrons as they must be there somewhere***?'

The only conceivable explanation was that there was a very small, positively charged, central part of the atom which was small enough that the atom was indeed still essentially free space. This small centre had to be positively charged since there was no other way the, positively charged, α particles could be repelled.

This answered both questions: most alpha particles passed straight through the free space but some were repelled by collision with the positive nucleus. Therefore the atom must comprise mostly empty space but contain a tiny, positively charged, nucleus.

Lord Rutherford was fascinated by the nucleus and radioactivity but was not particularly interested in the electron and concluded that the electrons simply existed outside the nucleus and circled it almost like a train of electrons.

On the basis of this dsicovery, the Japanese physicist, Nagaoka Hantaro (pictured right on a commemorative, 2003, stamp) rejected Thomson's *plum pudding model* and proposed his *Saturnian Model* which, essentially proposed that the atom comprised a small, but very dense, nucleus surrounded by a circle of travelling electrons and was inspired by the planetary model of our solar system.

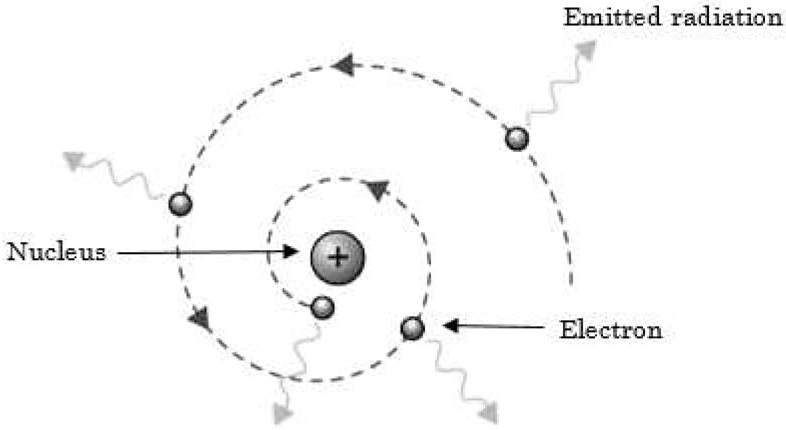
The nucleus comprised most of the mass of the atom and was surrounded by a revolving set of electrons bound to the nucleus by electrostatic attraction.

Nagoaka was half right and half wrong and this new concept of atomic structure was revolutionary and led to a surge of interest and experimentation since the physicists' modest belief that nothing could be discovered about the atom was now clearly incorrect.

It also produced what physicists enjoy most which is the opportunity to investigate and solve questions which had never previously been conceived.

More problems arose however since, according to classical electrodynamics, Rutherford's and Nagoaka's concept of electrons simply circling the small positively charged nucleus could not be correct for three reasons.

1. What was to stop the electrons simply being pulled into the nucleus by the positively charged protons?
2. A charge circling another charge would also spiral into the nucleus emitting radiation as it did so:



Neither of these events were observed and it also controverted the observation that moving electrons radiate energy which is, to this day, the reason why radio and tv aerials work.

3. The electrons revolving around the nucleus would repel each other and there was no explanation for the attractive power of the, positively charged, nucleus overcoming the mutual repulsion of the, negatively charged, electrons.

It also did not explain a very important analytical technique, the, qualitative, *flame test*. The main metals determined, essentially by lobbing some of the material into a flame and observing the newly produced colours are as follows:

Metal	Flame Colour	Metal	Flame Colour
Lithium	Red	**Barium**	Green
Sodium	Yellow	**Copper**	Blue – green
Potassium	Lilac	**Strontium**	Crimson
Calcium	Brick red	**Tin**	Blue – white

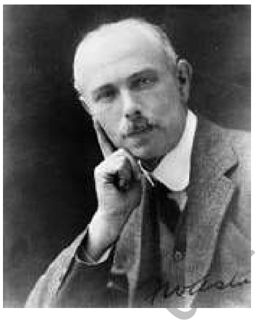
This could not be explained by any theory to this point but it inspired Niels Bohr's model of the atom.

The Rutherford model could not begin to explain this observation but it did lead to investigation by Niels Bohr (pictured left) whose conception of electrons existing in different levels i.e. different distances from the nucleus did explain that but still did not explain why the electrons did not spiral into the nucleus which is discussed later. Nevertheless Bohr's theory was incredibly important leading to the theory of quantum mechanics and, for our purposes, nuclear magnetic resonance.

All of this is discussed later.

The next matter to consider is F.W. Aston's discovery of the existence of isotopes through his invention of mass spectrometry.

Mass Spectrometry and the Discovery of Isotopes



In 1911, soon after Rutherford, Geiger and Marsden had discovered the existence of the nucleus, F.W. Aston (pictured right), a protégé of J. J. Thomson was invited to join him at the Cavendish Laboratory at Cambridge University to further investigate the *anode rays* which had been discovered by Eugen Goldstein in 1886. These were intriguing since the deflection of a single beam of cathode rays, electrons, produced a deflected beam but only one beam indicating that cathode rays were all exactly the same. In contrast, the anode rays were deflected by various amounts by the magnetic field indicating that the anode rays were ***not*** all the same.

There were still three problematic questions.

1. If the atom contained a positive nucleus and all nuclei of a particular element were identical then the deflection of all anode rays should produce one single deflected beam. This did not occur and in a magnetic field more than one deflected anode ray was detected.
2. The charges of the proton and the electron were both now known to be equal and opposite but adding up the masses did not explain the known masses of atoms which were inevitably greater than that predicted. This was before Moseley introduced the concept of atomic number and its significance had to wait several years. Likewise the existence of the neutron, the neutral particle with almost exactly the same mass of a proton, though its existence was conceived, had yet to be proven.
3. The relative atomic masses of all known atoms had been measured by other methods. Setting one atomic mass unit as that of the lightest, hydrogen, and ignoring the mass of the electron since being so small it would disappear in the rounding up or down of the mass, all other atoms should be whole number multiples of the mass of hydrogen. No elements had relative atomic masses that were exact multiples of the relative mass of a hydrogen atom.

Aston was intrigued by the relative atomic mass of, the relatively recently discovered element, neon and the relative atomic mass of the chlorine molecule.

Compared to hydrogen, whose relative mass was set at 1 atomic mass units (amu), or even relative to oxygen whose relative mass had been measured to be sixteen times greater than that of a hydrogen atom, the relative atomic mass of neon was 20.2 amu.

This was inexplicable, as was the relative atomic mass of the chlorine atom (35.5 amu) and that of the chlorine molecule, Cl_2, (71 amu) and it was Aston's genius to conceive of the idea of chemically identical atoms of the same element but of different mass and also to design an experiment to establish the truth or falsity of this idea.

These two achievements opened a whole new line of investigation into the structure of the atom and also a new way of analysing the composition of organic molecules.

The importance of these achievements cannot be overstated.

Aston knew that positive ions could be accelerated when passing through an electric field and could be deflected by a magnetic field and it was his inspiration to combine the two fields in succession.

However, having conceived of a system where ions could be accelerated by an electric field and deflected according to their mass/charge (m/z) ratio there were still practical difficulties to be overcome: the atoms had to be ionised, the entire apparatus must operate in a vacuum otherwise the ions would be absorbed by the other gases present and the ions had to be detected. In addition the entire glassware apparatus had to be constructed.

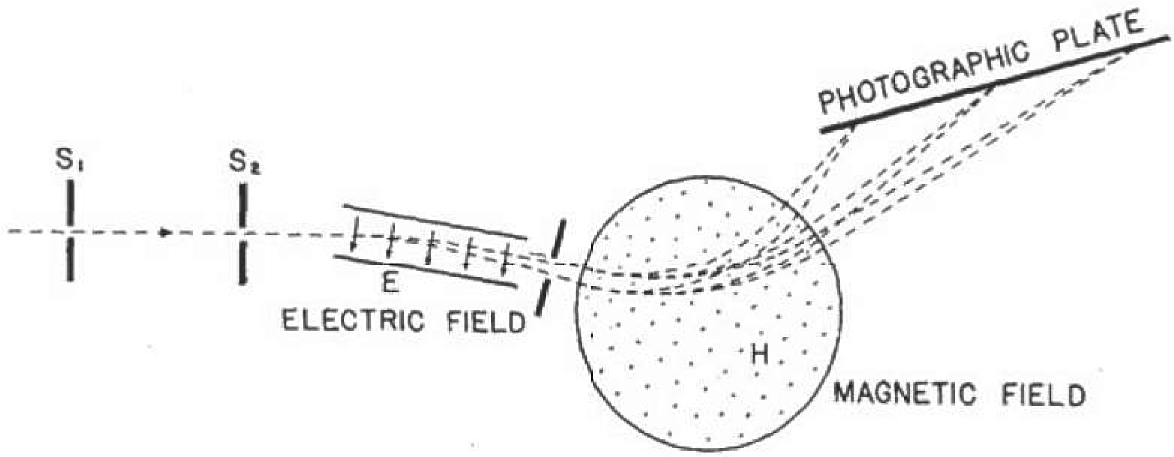
There were no issues with constructing an electric field since that was created by simply connecting two metal plates to an electricity supply (battery) and the magnets were easily obtained. The beam was focused by passage through a negatively charged plate with a central hole. Likewise there was no problem with the glassware as Aston, since his student days, had been a keen glassblower and blew his own apparatus.

The element was vaporised by simple heating and ionised by glow discharge (a plasma formed by passage of an electric current through the gas) whilst the pressure within the apparatus was reduced by a vacuum pump.

Finally the ions were detected by the exposure of a calibrated photographic plate which was developed according to, by then, well established photographic processes. Since the ions were individually deposited on the photographic plate the intensity of the peaks was measured by measuring the height of the deposits with a Vernier scale.

Although modern instrumentation is more sophisticated with peaks now being detected electrically, even lower vacuum pressures and more precise measurements and it is also computer controlled, the essential principles remain unchanged from Aston's first mass spectrograph which is illustrated below.

Aston's mass spectrograph

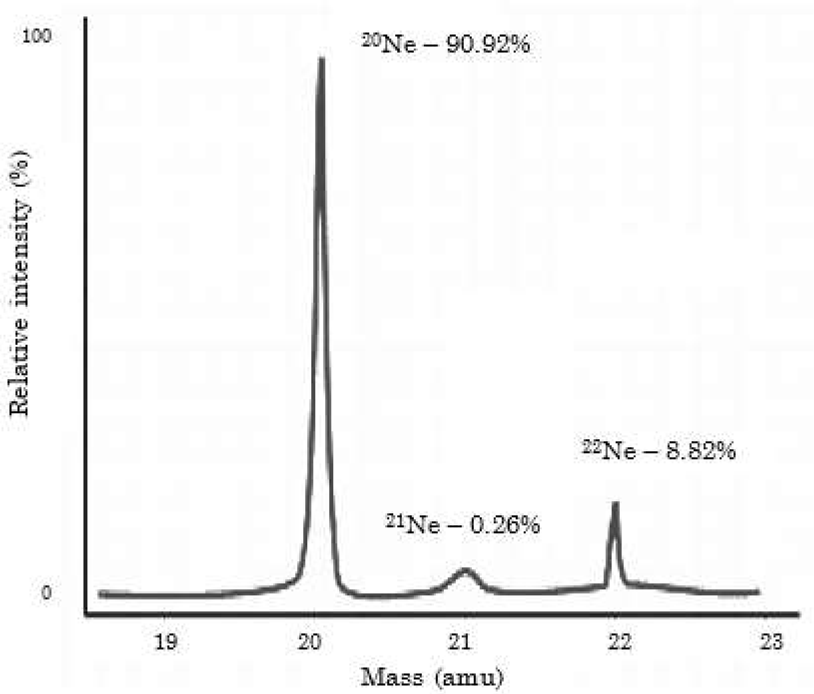


Aston's spectrograph was a great success and demonstrated for the first time the existence of isotopes, chemically identical atoms with the same number of protons but differing numbers of neutrons.

Two examples demonstrate its importance: the relative atomic masses of neon and chlorine, as discussed below.

Neon

Aston demonstrated that the relative atomic mass of neon was 20.2 atomic mass units (amu) because it is comprised of three isotopes of relative atom mass 20, 21 and 22 in the relative proportions: 90.92%, 0.26% 8.82% as shown.



The relative atomic mass is calculated by multiplying the mass of each atom by its abundance and summing the totals. To calculate the relative abundance is straightforward: sum all the peak heights and then divide the height of each peak by the total.

For neon the total abundance of the peaks is 114 + 0.2 + 11.2 = 125.4 and so the relative abundances of the three peaks are as follows:

Mass/charge:	**20**	**21**	**22**	
Peak height:	114.00	0.32	11.06	
Relative peak height:	114.00/125.4	0.32/125.4	11.06/125.4	
=	90.92	0.26	8.82	%

The relative peak height displayed above is the relative abundance of the ions.

To calculate the contribution each of these ions makes to the overall relative atomic mass is achieved simply by multiplying the relative abundance of each peak by its mass and summing the three results e.g.

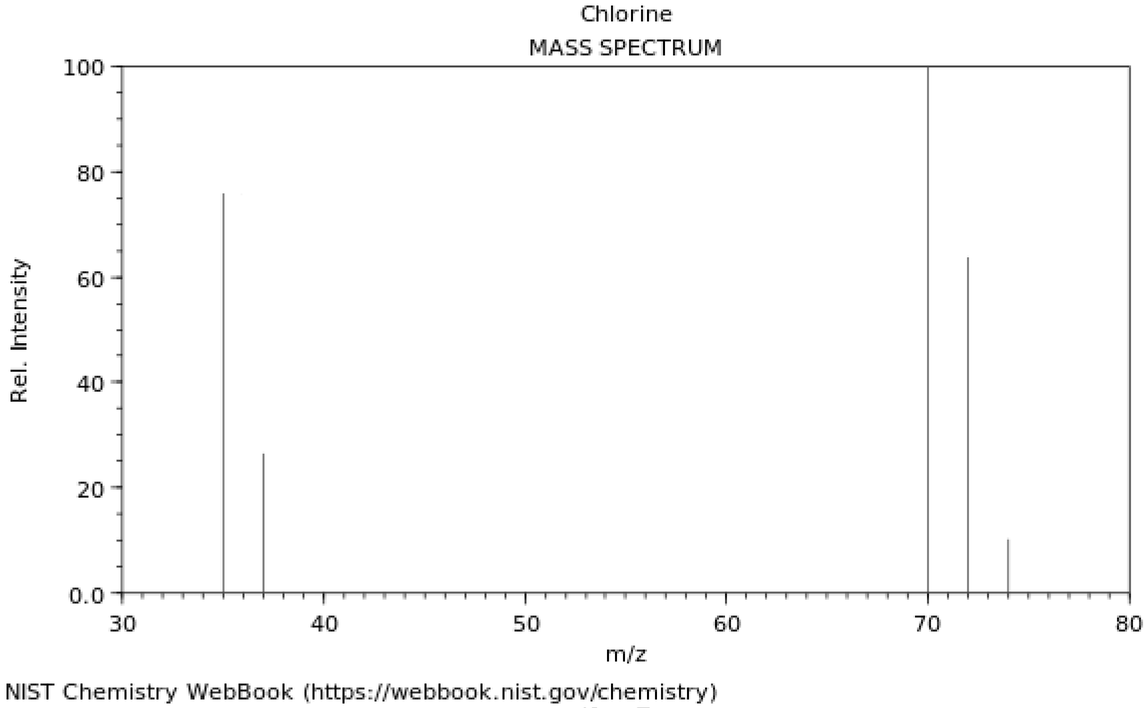
$RAM_{Ne} = (\mathbf{20} \times \mathit{90.92/100}) + (\mathbf{21} \times \mathit{0.26/100}) + (\mathbf{22} \times \mathit{8.82/100})$

$= 18.18 + 0.06 + 1.94 = 20.18$ amu

So with rounding the relative atomic mass of neon is measured to be 20.2 is explained.

Chlorine

The spectrum of neon, above, is displayed as it would have been drawn as a graph on the basis of the measurements of the spots on the photographic plate. The, measured, relative atomic mass of the chlorine atom was also a source of mystery as it is 35.5 amu. Aston discovered two isotopes of chlorine ^{35}Cl and ^{37}Cl in the proportion 3:1 as shown below and which is portrayed in the modern, conventional, format.



The relative atomic mass (A_r) of chlorine is measured and calculated as follows:

$$\mathbf{RAM_{Cl}} = (\mathbf{35} \times \mathit{75/100}) + (\mathbf{37} \times \mathit{25/100}) = 26.25 + 9.25 = \mathbf{35.5\ amu}$$

This also explained why the relative molecular mass of the chlorine (Cl_2) is 71 since gaseous chlorine consists of the following molecules: $^{35}Cl^{35}Cl$; $^{35}Cl^{37}Cl$; $^{37}Cl^{37}Cl$ in the proportions 9:6:1 meaning that the relative molecular mass may be calculated as follows:

$$\mathbf{M_r(Cl_2)} = (\mathbf{70} \times \mathit{9/16}) + (\mathbf{71} \times \mathit{6/16}) + (\mathbf{72} \times \mathit{1/16})$$

$$= 39.38 + 26.63 + 4.5 = 70.5 \approx \mathbf{71\ amu}$$

The explanation for the mass of the atom exceeding the mass of the protons and electrons contained within it was given in 1932 by James Chadwick with his discovery of a neutral particle of similar mass to the proton. The significance of the proton (atomic) number is discussed next followed by a discussion of the discovery of the neutron which, although occurring many years apart, answered the following two questions which are of significance for this volume:

1. Is the number of protons of any significance or just an interesting observation of no consequence?
2. Why are the relative masses of atoms greater than the sum of the relative masses of the protons and electrons?

Moseley's Determination of the Significance of the Atomic Number

Is the number of protons of any significance or just an interesting observation of no consequence?

The significance of the number of protons was discovered in 1913 by Henry Moseley (pictured below in 1910), who was tragically killed at Gallipoli, but whose inspirations resolved the issues about Mendeleev's Periodic Table.

X-rays had been discovered by Wilhelm Röntgen. In 1895, whilst investigating the cathode rays that had been discovered by J.J. Thomson, Röntgen noticed crystals on a nearby bench were glowing. He covered his cathode ray tube with black paper and when he again applied a high voltage across the tube the crystals fluoresced, i.e. glowed again.

The clear conclusion was that the tube was emitting a previously unknown type of light and which were rays which could pass through most substances, only being blocked by thick pieces of lead. This explosive news, of course, led to the medical x-ray diagnostics and numerous industrial applications.

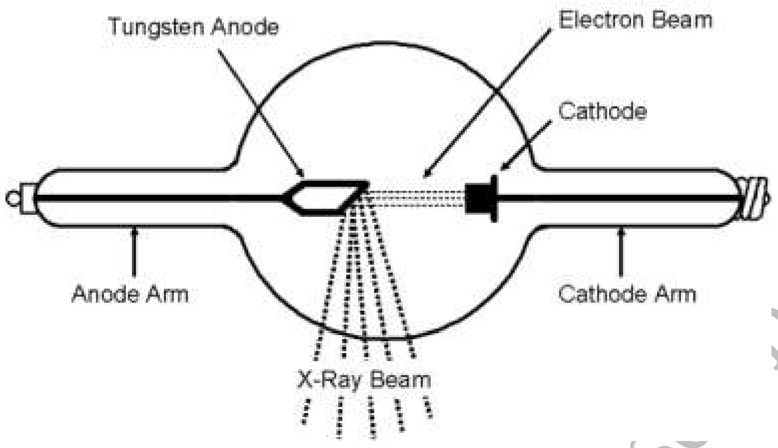
Indeed, one of Röntgen's first papers included an x- ray image of the hands of his wife, Bertha.

This invention caught the public imagination and led to some bizarre inventions such as a machine for determining exact feet measurements with many shoe shops advertising their x-ray machine for precise shoe fittings and, even more extraordinarily, radioactive toothpaste which, a by-product of the production of mantles for gas lamps, was advertised as imparting health benefits, including antibacterial action and contributing to the strengthening the defences of teeth and gums.

The production of x-rays for experimentation and industrial application was hampered however until 1913, since x-ray tubes were prone to breakage under the high voltages necessary for scientific application. This was solved by the invention of the Coolidge x-ray tube which could withstand voltages of up to 100 kV and was reliable as the vacuum was extremely low.

The principle was the same but with electrons emitted now and not absorbed on their journey, they were a reliable source of x-rays.

Moseley was fascinated by the invention and switched his studies to the interaction of x-rays and metals. He discovered that each element produced a unique x-ray spectrum and this discovery in itself led to the the entire discipline of x-ray spectroscopy which has been used for numerous applications from the detection and quantification of tiny quantities of impurities in metals through to the study of the interaction of molecules with metallic surfaces. A schematic diagram of the apparatus is shown below:



With the encouragement of William Henry and William Lawrence Bragg, father and son who uniquely shared the Nobel Prize for Physics in 1915 for their invention of the analytical technique of x-ray crystal diffraction, Moseley measured the x-ray spectra of thirty nine different elements.

William Henry Bragg noted that Moseley had missed a couple of peaks in the x-ray spectrum of platinum, and guided Moseley to realise that the x-ray spectrum was characteristic of the individual metal. After attempting numerous correlations, Moseley determined that the square root of the frequency of particular peaks was directly proportional to the number of protons in the nucleus as shown overleaf in the graph taken from Moseley's original paper. Even more significantly, Moseley grouped the lines into groups denoted K, L and M lines and, working with Niels Bohr's exposition of the electronic distribution of atoms, he was able to differentiate between the groups and assign some lines as arising due to transitions from inner to outer shells.

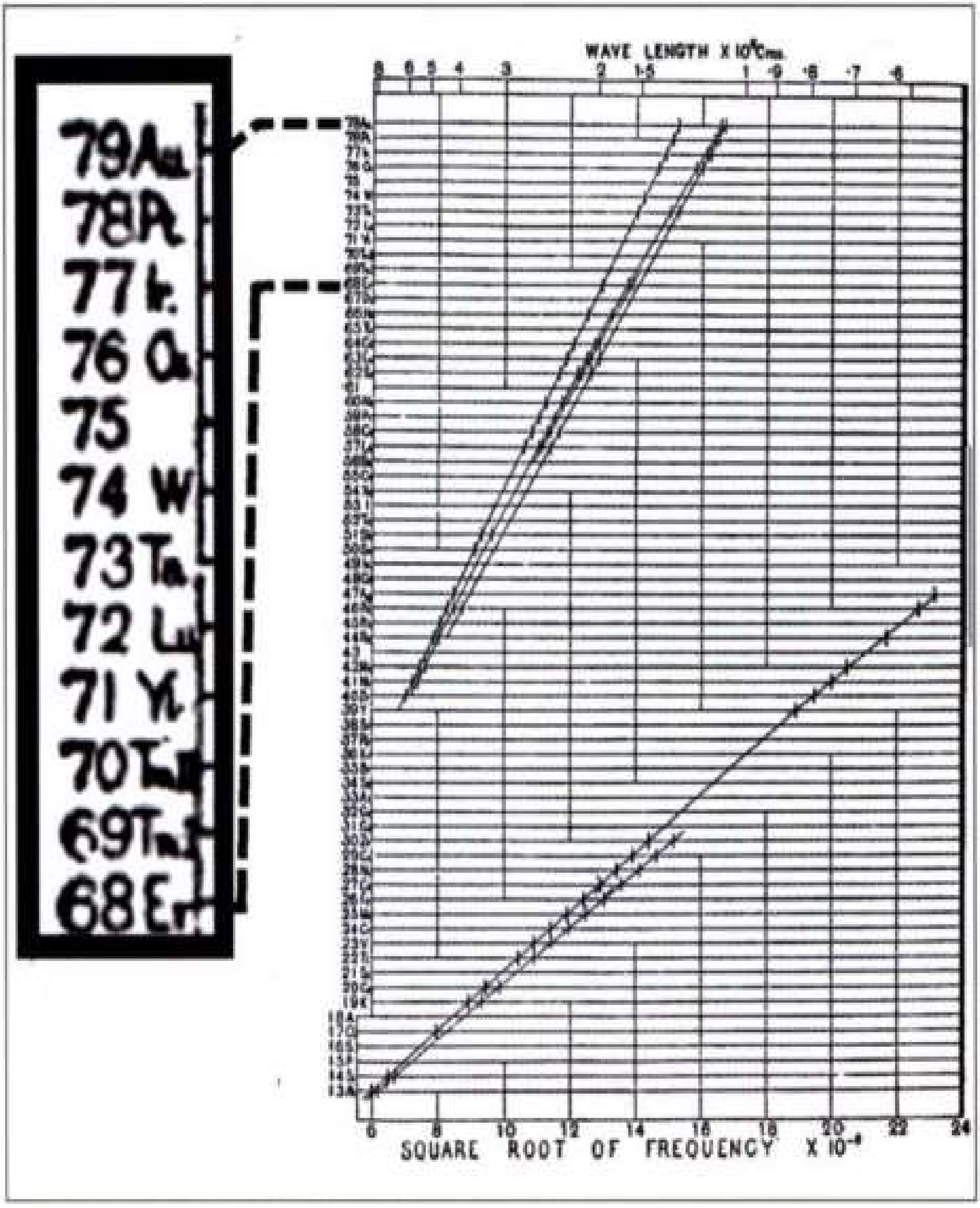
Again, it is impossible to underestimate Moseley's discovery who resolved three issues:

a. He identified that the number of protons was a fundamentally significant property and created the concept of the *atomic number*.
b. His work corresponded with the calculations and insights of Niels Bohr (discussed later) into electronic arrangements.
c. Moseley also explained some discrepancies in Mendeleev's Periodic table of the Elements. Mendeleev, whose name is known by all chemistry students for his periodic arrangements of the elements, was not the first to try to create patterns but he was the first to leave gaps hence predicting the existence and properties of as then unknown elements. However, Mendeleev himself made a couple of deliberate mistakes. He had assembled the elements in order of atomic weights (as the masses were then termed) but ignored this when convenient as, for example, with cobalt and nickel. Mendeleev assigned these two metals in that order on the basis of their properties and ignored the fact that cobalt, being slightly heavier than nickel, should have been placed after nickel.

Moseley's work resolved this since by placing the elements in order of the number of protons, *atomic number*, he reconciled the chemical properties with the element's atomic number and further demonstrated that the number of protons, ***atomic number***, is *the* fundamental property of an atom.

With these discoveries, Henry Moseley became world famous almost overnight but his death at Gallipoli, at the age of twenty six, robbed the world of untold future discoveries and his demise led to the rule that scientists of great esteem and achievement should not be permitted to serve in places of danger.

The graph of proton number versus square root of frequency in Moseley's first published paper on atomic number is reproduced below.



We can now also answer the second question:

Why are the masses greater than the sum of the masses of the protons and electrons?

The Discovery of the Neutron

James Chadwick's most elegant experiment answered the question:

Why are the masses greater than the sum of the masses of the protons and electrons?

Writing this in April 2020, one conundrum is analogous to the current concept of dark matter and neutrinos. Dark matter, still a theoretical explanation for the apparently missing, 95%, mass of the universe appears impossible to detect and it is the same with neutrinos. Neither dark matter nor neutrinos appear, *to us*, to interact, with the world. If they exist then they must do so even if just passing through and in some way we have yet to conceive.

The early 20th century problem was how to explain why a neutral atom containing equal numbers of positively charged protons and negatively charged electrons is more massive than the summed masses of the protons and electrons. It was clear that the remaining mass must be due to an uncharged particle. This particle would ignore and would not be accelerated by an electric field and would pass through a magnetic field as if the field did not exist. It must exist but how to detect it?

The answer was a beautifully simple and ingenious experiment designed by Sir James Chadwick (pictured left) in 1932. Chadwick was yet another former student of Lord Rutherford, and for his discovery of the neutron he received the Nobel prize for Physics, an almost unheard of, three years later.

Many physicists, including James Chadwick, reasoned that a neutral atom that contained equal numbers of of positive particles, *protons*, and negatively charged particles, *electrons*, but whose mass exceeds the total mass of those particles must contain some other, uncharged, particles. Since the mass of the electron was 1/1840th the mass of a proton, it would either contain 1840 neutral particles for every proton or there must be another particle. That particle, if of roughly the same mass as a proton, would only require a handful rather than thousands of neutral particles and seemed more sensible and realistic. The question was: ***How can we detect a particle which is oblivious to both electric and magnetic fields and appears to not interact at all with any other known substances***?

The solution was brilliantly simple and extremely elegant.

Chadwick reasoned, as described above, that it was highly unlikely that the missing mass was due to tens of thousands of small particles. He was also aware that one of the emissions of radioactive materials were the equivalent of helium nuclei: a doubly charged ion but with a relative mass of four indicating that these particles contained these unknown particles as well as protons.

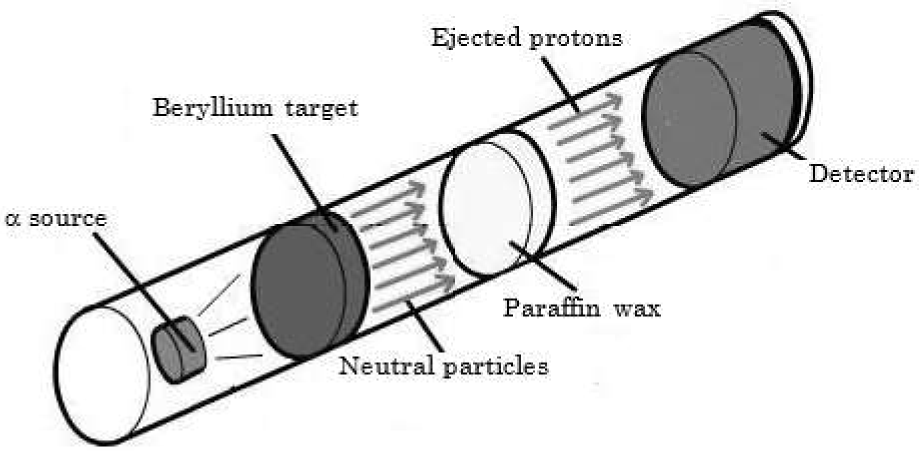
$$^{4}_{2}He^{2+}$$

It is often described as *the* helium nucleus. Some find that confusing since there has been no helium present. In reality, the α-particle is merely the ***same*** as a helium nucleus.

Chadwick hypothesised that the hidden mass of the nucleus was due to particles of the same mass of a proton since that reasoning required the existence of only two neutral particles of the same mass as the neutron. If they had the same mass as the electron then there would need to be 3,280 of them. Two particles seemed arther more realistic!

His elegant experiment was to direct the beam of radioactive emissions towards a beryllium film in an evacuated system. Classical, Newtonian, mechanics calculations suggested that the momentum of the emitted alpha particles would be sufficient to eject particles of similar size to the proton. The problem, again, was how to detect the neutral particles which were unaffected by electric or magnetic fields.

Again, the solution was derived from classical mechanics: the emitted neutral particles would, in turn, due to the conservation of momentum, eject protons from material upon which it impinged. Due to their charge, the protons could then be detected and the paths taken also enabled an assessment of the mass of the neutral particle. Chadwick selected a thin film of paraffin wax as illustrated below and the experiment was triumphantly successful since protons ejected from the beryllium target were detected.



The conclusion was that the neutral particle was of approximately the same mass as a neutron and explained many observations quite perfectly. For example, the α-particle was now known to constitute of two protons and two neutrons and explained the existence of all isotopes whose existence had been discovered almost twenty years earlier by F. W. Aston.

We can turn to the arrangement of electrons around the nucleus and Niels Bohr's model of the hydrogen atom.