

Francis Aston and the mass spectrograph

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Received 18th June 1998, Accepted 28th July 1998

The chemical determination of atomic weights gives the *average* weight for an aggregate of a large number of atoms. Although this is useful in many applications, the determination of the masses of *individual* atoms gives further important information, in particular the stability of the atoms or more precisely of their nuclei. The first accurate determination of the masses of individual atoms was made by Aston in 1919. His measurements demonstrated the existence of isotopes in non-radioactive elements and paved the way for our present picture of the nuclear atom.

Early life

Francis William Aston was born on 1 September 1877 at Harborne, Birmingham. He was the third child of a family of seven. His father and paternal grandfather were metal merchants and farmers, and Francis was brought up on a small farm. From an early age he showed a keen interest in mechanical toys and scientific apparatus. He had a 'laboratory' over a stable and amused his sisters with home-made fireworks and large tissue-paper hot-air balloons. These were dispatched with stamped addressed postcards, which were sometimes returned from great distances.¹

Aston entered Malvern College in September 1891 and two years later went to Mason College (which subsequently became the University of Birmingham), where he studied chemistry and physics. The professor in physics was John Poynting (of Poynting's vector). While at Birmingham Aston acquired skill with tools and glass-blowing which proved invaluable in his later work. Faced with the need to earn a living after graduating he took a course in fermentation chemistry and in 1900 started work in a brewery in Wolverhampton. In his spare time he experimented at home, designing and building new forms of Sprengel and Töpler vacuum pumps. This experience was again to stand him in good stead later on.

In 1903 Aston returned to Birmingham University and physics. He worked on the properties of electrical discharges in

gases and measured the variation of the length of the Crookes dark space with current and pressure. In 1908 his father died, and he used a legacy to travel round the world. On his return he was appointed a lecturer in Birmingham University, but after one term he received an invitation from Joseph (J. J.) Thomson to come to the Cavendish Laboratory at Cambridge as his assistant. Poynting, a close friend of Thomson, had recognised Aston's great gifts as an experimenter and recommended him for the post. Aston accepted the invitation and thus began a career that had momentous consequences for chemistry and nuclear physics.

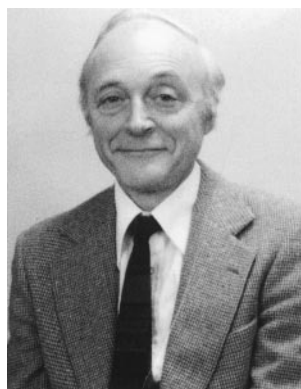
Historical background to Aston's work

To appreciate the significance of the work Thomson was doing and Aston's subsequent role we need to go back in the history of chemistry. In 1803 John Dalton put forward an atomic theory, which laid the foundations of modern chemistry. One of the postulates was that atoms of the same element are similar to one another and equal in weight. About ten years later William Prout suggested that the atoms of the elements were made up of aggregates of hydrogen atoms. If this were true the weights of atoms would be expressed as whole numbers, *i.e.* integers, and, on the basis of Dalton's postulate that all the atoms of an element had the same weight, atomic weights would also be whole numbers. However, experiment showed that although the atomic weights of many of the elements were whole numbers, far more than could be attributed to chance, there were a few, for example, magnesium, atomic weight 24.3, and chlorine, atomic weight 35.5, which were not. Therefore, Dalton and Prout could not both be correct, and around 1900 it was Dalton's rather than Prout's hypothesis that was accepted.

In 1896 Henri Becquerel discovered radioactivity, and from then until the outbreak of the first World War many radioactive substances were found. An interesting feature was that two and sometimes three of the substances with quite different modes of decay appeared to be chemically similar. For example, in 1906 Bertram Boltwood found that once salts of thorium and ionium were mixed they could not be separated by any chemical means.² Another example was radium B and lead; not only were their chemical properties the same, but Ernest Rutherford and Edward Andrade found that they had identical X-ray spectra.³ In 1913 Frederick Soddy⁴ proposed the word *isotopes* to describe these chemically similar materials, because they occupy the same place in the Periodic Table of the elements. He observed 'They are chemically identical, and, save only as regards the relatively few physical properties which depend upon atomic mass directly, physically identical too'.

Thomson's work on positive rays

In 1886 Eugen Goldstein was investigating the properties of the electric discharge obtained when a large voltage is applied across a pair of electrodes in a vessel containing a gas at low pressure. He found that if a channel or canal was cut through the cathode a beam of light appeared on the side remote from the anode. He called the beam *Kanalstrahlen*, canal rays.⁵ In



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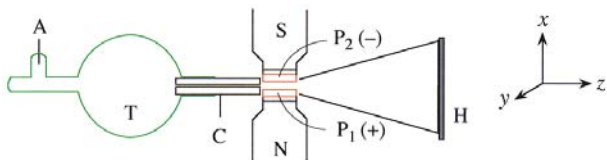


Fig. 1 Diagram of Thomson's positive ray apparatus.

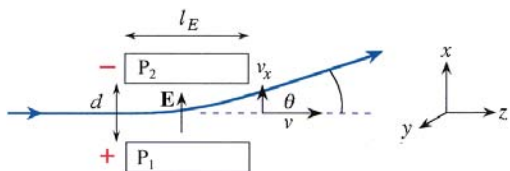


Fig. 2 The deflection of positively charged particles by an electric field.

1898 Willy Wien⁶ managed to deflect the beam with a strong magnetic field, in a direction which showed it was due to a stream of positively charged particles. They are in fact the positive ions resulting from the atoms in the gas that have lost one or more electrons. In 1907 Thomson⁷ started to investigate the positive rays. He measured the mass of the particles by deflecting the rays with electric and magnetic fields. His apparatus was the forerunner of Aston's mass spectrograph and it is instructive to consider it first.

The essentials of the apparatus are shown in Fig. 1. The discharge occurs in the spherical tube T. The anode A is located in a side arm, and the positive rays pass through the cathode C, which is a fine tube. The rays then pass between the poles N and S of an electromagnet, the pole pieces P₁, P₂ of which are insulated from the magnet by thin sheets of mica. By this means a potential difference may be applied across the pole pieces, giving an electric field **E** in the same direction as the magnetic field **B**, this direction being at right angles to the path of the particles. The particles finally strike the screen H, where they produce a fluorescent spot. In the absence of the two fields the particles travel in a straight line, and the spot is in the centre of the screen in line with the fine tube in the cathode.

Take a set of right-handed axes *x*, *y*, *z*, with the initial direction of the particles as the *z* axis, and the common direction of **E** and **B** as the *x* axis. We consider the electric and magnetic deflections separately. The deflection produced by the electric field is shown by the diagram in Fig. 2. The particles coming from the left with velocity *v* enter the region between the pole pieces P₁ and P₂, across which a potential difference *V* is applied. If the pole pieces are a distance *d* apart this gives an electric field $E = V/d$, which causes an acceleration eE/m , where *e* is the charge and *m* the mass of the particles. If l_E is the length of the plates, the particles spend an approximate time l_E/v between the plates, and when they emerge from the plates they have acquired a component of velocity in the *x* direction given by

$$v_x = eEl_E/mv. \quad (1)$$

Since $v_x \ll v$, the angle through which the particles are deflected by the field is approximately

$$\theta = \frac{v_x}{v} = \frac{eEl_E}{mv^2}. \quad (2)$$

A magnetic field **B** whose direction is at right angles to the path of the particles deflects them into a circular path of radius *R* as shown in Fig. 3. The force due to **B** is *Bev*, and its direction is at right angles to the directions of both **B** and **v**. The acceleration in the circular path is v^2/R . Thus

$$mv^2/R = Bev, \quad \text{i.e. } mv = BeR. \quad (3)$$

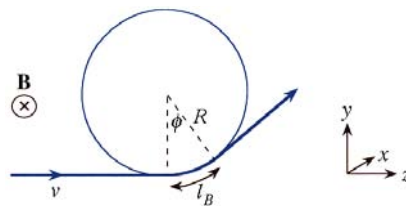


Fig. 3 The deflection of positively charged particles by a magnetic field. The direction of the field is down, perpendicular to the plane of the diagram.

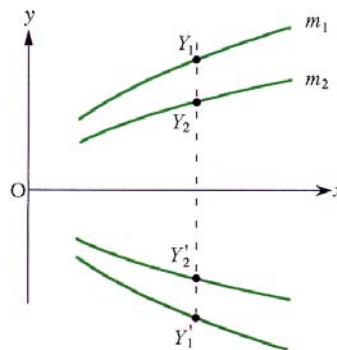


Fig. 4 Parabolas obtained with Thomson's positive ray apparatus. The ratio of the masses of the particles for the two parabolas is given by $m_1/m_2 = (Y_2 Y_2' / Y_1 Y_1')^2$. The parabolas with negative *y* are obtained by reversing the magnetic field.

The particles are deflected in the *y* direction through an angle

$$\phi = \frac{l_B}{R} = \frac{eBl_B}{mv}, \quad (4)$$

where l_B is the length of the path in the magnetic field.

Now let **E** and **B** act together. The screen H, which contains the *x* and *y* axes, is shown in Fig. 4, with the position O of the spot for the undeflected beam as the origin. The field **E** deflects the particles in the *x* direction by an amount proportional to the angle θ , while **B** deflects them in the *y* direction by an amount proportional to the angle ϕ , both the angles being small. The coordinates of the spot are therefore

$$x = c_1 \frac{eE}{mv^2}, \quad y = c_2 \frac{eB}{mv}, \quad (5)$$

where c_1 and c_2 are constants depending on the geometry of the apparatus. Eliminating the velocity *v* between these two expressions gives

$$\frac{y^2}{x} = c_3 \frac{e}{m} \frac{B^2}{E}, \quad (6)$$

where the constant c_3 depends on the geometry of the apparatus. Thus, for a beam of ions with the same value of e/m and varying velocities, the pattern on the screen is a parabola, Fig. 4. Particles with different velocities arrive at different points on the parabola.

If ions with different masses are present there will be several parabolas corresponding to the different e/m values. The value of *e* is the electronic charge, 1.60×10^{-19} C, or a simple multiple of it. For singly charged ions the *y* value of the parabola at a constant value of *x* is proportional to $1/\sqrt{m}$. So the ratio of two masses is given by the square of the inverse ratio of the two *y* values at the same value of *x*. This is independent of the form of the apparatus and of the values of **E** and **B**. If an atom of mass *m* loses two electrons in the discharge tube, the doubly charged ion appears on a parabola corresponding to a singly charged ion of mass $m/2$. A photographic record is made of the

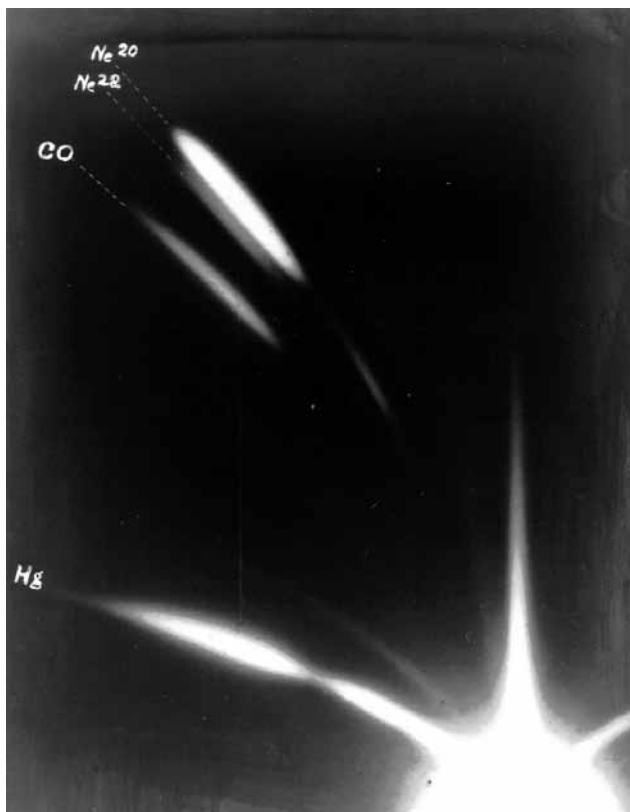


Fig. 5 Positive ray parabolas of neon obtained by Thomson in 1912.

traces. If the mass is known for one of the parabolas, measurements of the y values at constant x give the values of all the other masses. The axis Ox is not marked on the photograph. The magnetic field is therefore reversed for the second half of the exposure, which puts the pattern in the $-y$ region and allows the y values to be measured.

When Aston arrived at the Cavendish Laboratory in 1909 Thomson's positive ray apparatus was already working. With his assistance the apparatus was greatly improved, and by 1912 parabolas corresponding to mass differences of 10% could be resolved. In November of that year some gas containing neon was analysed. The photograph, Fig. 5, showed a strong parabola corresponding to a mass of 20 (on the scale oxygen = 16) and a much weaker one at a mass of 22.⁸ Various possibilities for the 22 parabola were considered. One was that it was due to doubly charged CO_2 . However, when the gas was passed through liquid air, the parabola at 44, due to singly charged CO_2 , disappeared, while the one at 22 was not affected. Another speculation was that the 22 trace was due to a compound NeH_2 .

From density measurements the atomic weight of neon was known to be 20.2. So the novel, and at the time revolutionary, suggestion was made that neon could exist in two forms, which were isotopes, just like the isotopes suggested by Soddy in radioactive elements. If the isotope of mass 20 was 9 times more abundant than the one of mass 22, that would give the measured atomic weight of 20.2. In other words, neon did not consist of identical atoms of mass 20.2, but of two different atoms of mass 20 and 22, in line with Prout's hypothesis.

Aston set to work to see if he could separate the two constituents of neon. He first tried fractional distillation, but without success. He then tried diffusion through fine pores, using clay tobacco pipes, and after much labour obtained a small effect.⁹ Then, in his own words 'the whole of the lightest fraction was lost by a most unfortunate accident'. (It is said that he dropped the flask containing the specimen!) However, undeterred, he carried on with the heaviest fraction and ultimately obtained two samples with densities 20.15 and 20.28 on

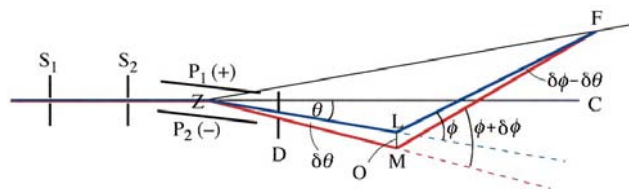


Fig. 6 The paths of the particles in Aston's mass spectrograph. The particles have the same mass value but varying velocities. The path of the fastest particles is shown in blue and that of the slowest in red. For clarity the electric and magnetic deflections are shown as abrupt changes in direction, rather than the actual continuous changes shown in Figs. 2 and 3.

the scale $\text{O}_2 = 32$. These results were just on the borderline of the experimental uncertainty.

The work was interrupted by the first World War. Aston was sent to the Royal Aircraft Factory, later the Royal Aircraft Establishment, at Farnborough. Frederick Lindemann, later Lord Cherwell, and George Thomson (J. J. Thomson's son) were also there. In after years Thomson recollected that Lindemann was sceptical of Aston's isotope hypothesis, preferring the idea of CO_2 or NeH_2 for the 22 parabola.¹⁰ He said that Lindemann was a much better theoretician than Aston and always won the argument, but Aston 'had faith and next morning was still of the same opinion'. In 1914 Aston crashed in an experimental aeroplane, but escaped unhurt. He worked at Farnborough as a chemist, studying among other things the properties of the doped canvas with which aeroplanes were then covered.

Aston's first mass spectrograph

After the war Aston returned to the Cavendish Laboratory. While at Farnborough he had meditated on an improved form of the apparatus to measure the masses of the positive ions, and in 1919 he built his first mass spectrograph.¹¹ Like Thomson's parabola apparatus it employed electric and magnetic fields to deflect the particles, but the two fields were in different regions along the path of the particles. Unlike Thomson's apparatus in which particles with the same e/m value, but different velocities, were distributed along the parabola, in Aston's spectrograph these particles were focused to the same point on the screen. This was a big advantage. The focused beam was much more intense, thus permitting finer slits to be used, which improved the resolution and accuracy of the instrument.

The principle of the instrument is illustrated in Fig. 6. The path of the positive particles emerging from the discharge tube is defined by a pair of narrow slits S_1 and S_2 . The particles then pass between a pair of plates P_1 and P_2 across which a potential difference is applied. The particles are deflected downwards by the electric field towards the negative plate P_2 . They are deflected continuously in the region between the plates, but as a first approximation we may assume that the paths come from a point Z in the middle of the plates on the line defined by S_1 and S_2 . A group of the rays is allowed to pass through a narrow diaphragm D , which selects those deflected through angles between θ and $\theta + \delta\theta$. They then pass between the poles of an electromagnet which has its north pole above the plane of the diagram. This deflects the particles in the opposite direction to that of the electric field.

The same notation is used as in the discussion of Thomson's apparatus. Eqns. (2) and (4) still apply. For particles of velocity v , charge e and mass m , the electric field \mathbf{E} gives a deflection θ , and the magnetic field \mathbf{B} gives a deflection ϕ . The position of the diaphragm D fixes the angle θ , and hence the velocity of the particles passing through. The spread $\delta\theta$ in θ gives rise to a spread δv in v , which in turn gives a spread $\delta\phi$ in the deflection produced by the magnetic field. The relations between $\delta\theta$, δv and $\delta\phi$ are obtained from eqns. (2) and (4). For a constant value

of elm , θ is proportional to $1/v^2$, and φ is proportional to $1/v$. Therefore

$$\frac{\delta\theta}{\theta} = -2 \frac{\delta v}{v}, \quad \frac{\delta\varphi}{\varphi} = -\frac{\delta v}{v}, \quad (7)$$

whence

$$\delta\varphi/\delta\theta = \varphi/2\theta. \quad (8)$$

The minus signs in eqns. (7) indicate that the faster particles, indicated by the blue path in Fig. 6, are deflected less in both the electric and the magnetic fields than the slower particles indicated in red. Since the electric and magnetic deflections are in opposite directions the rays passing through D are brought together at a point F.

It is readily shown that the angle between the line ZF and the initial direction ZC of the particles is equal to θ . Fig. 7 shows the mean paths of the particles. The angle between FZ and OZ is denoted by ρ , where O is the centre of the magnetic field. The angle GOF = φ , and ZFO = $\varphi - \rho$. Now ρ and $\varphi - \rho$ are small; in Aston's apparatus they were of the order of $1/10$ rad. The line LM in Fig. 6 is therefore almost perpendicular to the lines ZL, ZM, FL and FM, and, to good approximation, its length is given by

$$LM = a\delta\theta = b(\delta\varphi - \delta\theta), \quad (9)$$

where a and b are the lengths OZ and OF. Similarly, in Fig. 7, if ON is the perpendicular from O to the line ZF, its length is

$$ON = a\rho = b(\varphi - \rho). \quad (10)$$

Therefore, from eqns. (10) and (9),

$$\frac{a}{b} = \frac{\varphi - \rho}{\rho} = \frac{\delta\varphi - \delta\theta}{\delta\theta}, \quad (11)$$

whence

$$\frac{\varphi}{\rho} = \frac{\delta\varphi}{\delta\theta} = \frac{\varphi}{2\theta} \quad (12)$$

The last step follows from eqn. (8). Eqn. (12) shows that $\rho = 2\theta$, i.e. the angle FZC = θ . The position of the point F on the line ZB depends on the value of φ , and hence from eqn. (4) on the value of elm . So particles with different elm values come

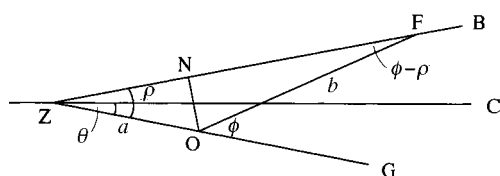


Fig. 7 Mean paths of the particles in Aston's mass spectrograph: Z is the centre of the electric field, and O the centre of the magnetic field; OZ = a , OF = b .

to a focus at different points along the line ZB. A photographic plate is placed along this line to record the traces.

The position of the focus point on the line ZB for a given elm value may be calculated from the values of E , B , and the geometry of the apparatus. However, the quantities required are the ratios of masses, and these are obtained most accurately by empirical methods. Aston first calibrated the instrument using a set of lines given by atoms and compounds with masses spread over a suitable range, and whose relative masses were known to the accuracy required. An example of such a set was: 6, C^{2+} ; 8, O^{2+} ; 12, C; 16, O; 28, CO; 32, O_2 ; 44, CO_2 . (The integer before each atom or compound is the effective mass number, i.e. the actual mass number divided by the number of charges on the ion.) This provided a set of points on a calibration curve. He filled in the gaps between the calibration points by taking the spectrum with the same set of ions, which were made to give lines at a different place by changing the value of the magnetic field.

Aston gave a preliminary account of the spectrograph in August 1919.¹¹ The instrument was an immediate success. The two isotopes of neon, mass 20 and 22, were easily resolved.^{12,13} Similarly, chlorine was found to be a mixture of isotopes of mass 35 and 37.¹⁴ By the time his first book *Isotopes* appeared in 1922 he had studied 27 elements.¹⁵ Among them were the following (masses, where oxygen is 16, in parentheses): lithium (7, 6), boron (11, 10), magnesium (24, 25, 26), argon (40, 36), krypton (84, 86, 82, 83, 80, 78) and xenon (129, 132, 131, 134, 136, 128, 130). The isotopes are given in the order of the intensities of the lines. Reproductions of the spectra for neon and chlorine are given in Fig. 8.

Although the discovery of many isotopes in light non-radioactive elements was of great importance, even more significant was Aston's result that the masses of all the particles are whole numbers. (The only exception was that of hydrogen whose mass was 1.008, see below.) This *whole number rule* as it was called gave a simple model for the atomic nucleus. The only particles known at the time were the proton and the electron, with relative masses of 1837. It was therefore proposed that the nucleus of an isotope of mass M and charge Z , both being integers, consisted of M protons and $M - Z$ electrons. Thus, for example, the nucleus of ${}^7\text{Li}$ consisted of 7 protons and 4 electrons, while that of ${}^6\text{Li}$ consisted of 6 protons and 3 electrons. Although this model gave the correct mass and charge of the nucleus, and satisfied the whole number rule, it had two grave defects. First, from the uncertainty principle, if an electron were confined to a region as small as an atomic nucleus, its momentum and hence energy would be much larger than the binding energy of the nucleus. Secondly, the spins of some of the nuclei were anomalous on this model. For example, the nucleus of ${}^{14}\text{N}$ would consist of 14 protons and 7 electrons, giving a total of 21 particles. Since the spin of both the proton and the electron is $\frac{1}{2}$, the spin of the nucleus with an odd number of particles would be half-integral; in fact the spin of ${}^{14}\text{N}$ is 1.

The discovery of the neutron by James Chadwick¹⁶ in 1932 removed these difficulties. The present model is that a nucleus of charge Z and mass number M contains Z protons and $M - Z$ neutrons. Isotopes are thus nuclei with the same number of protons and a different number of neutrons. They have the same chemical properties, but different nuclear properties.

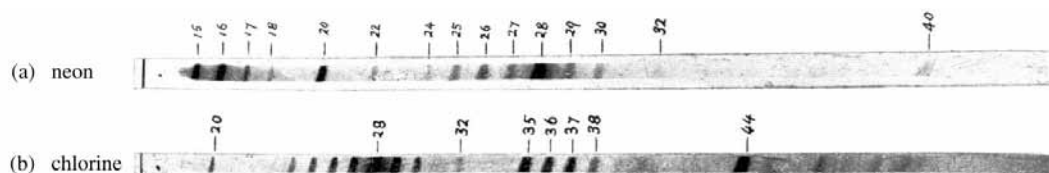


Fig. 8 Mass spectra obtained by Aston, 1919–1920, of (a) neon showing the 20 and 22 isotopes, and (b) chlorine showing the 35 and 37 isotopes.¹⁴ A number of other ions are present in both spectra. For example, the line at 28, prominent in both spectra, is due to CO. The lines at 36 and 38, present in the chlorine spectrum, are due to $H^{35}\text{Cl}$ and $H^{37}\text{Cl}$.

There are no electrons in the nucleus, and the nucleus ^{14}N contains 14, an even number, of particles of spin $\frac{1}{2}$.

Aston's first mass spectrograph could separate particles with a mass difference of 1 in 130, which may be compared with a value of about 1 in 10 for Thomson's parabola apparatus. The values of the masses were obtained with an accuracy of about 1 part in 1000.

The second and third mass spectrographs

Aston and other scientists soon grasped the reason for the departure of the mass value of hydrogen from an integral value, namely that it is the only atom with a non-composite nucleus. The masses of all the other atoms are reduced owing to the binding energy of their constituents, which results in hydrogen having a slightly higher mass relative to its mass number. The next step in mass spectrometry was therefore to improve the accuracy of the instrument to measure divergences from the whole number rule for all the atoms, which would give basic information on the binding forces within nuclei. For nuclei with mass numbers greater than about 20, the binding energy per nucleon is roughly constant, with a value between 8 and 9 MeV, which is about 1% of the energy equivalent of the mass of a nucleon. So to determine the binding energy to 1% the mass of the nucleus must be measured to an accuracy of about 1 part in 10^4 . Aston started designing an improved version of his spectrograph in 1921, though he continued to use the original instrument until it was dismantled in 1925.

In the second mass spectrograph finer slits were used and they were placed farther apart, thus more accurately defining the paths of the particles.¹⁷ The electric deflecting plates were curved, so that the particles remained midway between them as they were deflected. The electric deflection θ was doubled to $1/6$ rad. The potential for the deflection came from a set of 500 accumulators, each one built by Aston himself. They were charged twice a year and gave a voltage constant to better than 1 part in 10^5 during a single experiment. To achieve a constant magnetic field with minimum heating, the core of the magnet was wound with over 6000 turns of wire weighing over 100 kg. A current of 1 A through the coils produced a magnetic field of 1.6 T, which was sufficient to deflect the heaviest and most energetic particles through an angle φ of $2/3$ rad. (A detailed calculation shows that, when $\varphi = 4\theta$, the position of the line varies linearly with mass, which is convenient for interpolation.) The pole pieces of the magnet were greatly reduced by changing their cross-section from the circular shape of the first instrument to a sickle shape, thereby producing a magnetic field only in the region close to the particle beam. Aston demonstrated the improved resolving power of the second instrument by separating six isotopes of mercury with mass numbers ranging from 198 to 204.¹⁸ With the original instrument the lines appeared as an unresolved blur.

Aston's third mass spectrograph in 1937 incorporated further improvements.¹⁹ The widths of the collimating slits could be adjusted externally, obviating the laborious opening of the apparatus which was necessary for such adjustments in the first two instruments. The stability of the magnetic field was improved by monitoring its strength with a fluxmeter; in the previous instruments only the exciting current had been kept constant. Any variation in the magnetic field was compensated for by manual adjustment of a spiral mercury resistor. Another advance was in the greatly improved sensitivity of the photographic plates used to record the lines, which resulted after extensive trials carried out with the collaboration of the Ilford photographic company.

The biggest advance came in the use of the doublet method for comparing two masses. This consists of measuring the small difference in the masses of two ions with the same mass number

M . The mass of an atom X with mass number M is denoted by $m(^M\text{X})$. Since the value of m is close to the integer M , we may express it as

$$m(^M\text{X}) = M(1 + \delta), \quad (13)$$

where δ , known as the *packing fraction*, is small compared to 1.

As an example we show how Aston measured the mass of the hydrogen atom in terms of the mass of the carbon atom. He measured the difference in mass Δ_1 between the deuterium atom and the hydrogen molecule (doublet with $M = 2$), and the difference Δ_2 between the masses of the triatomic deuterium molecule and the doubly charged carbon atom (doublet with $M = 6$). Then

$$\begin{aligned} \Delta_1 &= 2m(^1\text{H}) - m(^2\text{H}) = \\ &= 2(1 + \delta_{\text{H}}) - 2(1 + \delta_{\text{D}}) = 2\delta_{\text{H}} - 2\delta_{\text{D}}, \quad (14) \end{aligned}$$

$$\begin{aligned} \Delta_2 &= 3m(^2\text{H}) - m(^{12}\text{C}^{2+}) = \\ &= 6(1 + \delta_{\text{D}}) - 6(1 + \delta_{\text{C}}) = 6\delta_{\text{D}} - 6\delta_{\text{C}}, \quad (15) \end{aligned}$$

$$\delta_{\text{H}} - \delta_{\text{C}} = (3\Delta_1 + \Delta_2)/6. \quad (16)$$

Aston's values for Δ_1 and Δ_2 were $(15.2 \pm 0.4) \times 10^{-4}$ and $(423.6 \pm 1.8) \times 10^{-4}$ respectively, giving $\delta_{\text{H}} - \delta_{\text{C}} = (78.2 \pm 0.4) \times 10^{-4}$.

At the time of Aston's measurements the atomic mass unit, denoted by u , was defined by taking the mass of the atom ^{16}O to be exactly 16, but in 1962 the definition was changed²⁰ so that the mass of the atom ^{12}C is taken as exactly 12, *i.e.* $\delta_{\text{C}} = 0$. Thus on the present scale Aston's value for the packing fraction of hydrogen was $\delta_{\text{H}} = (78.2 \pm 0.4) \times 10^{-4}$, giving $m(^1\text{H}) = 1.00782 \pm 0.00004 u$. The example shows the intrinsic advantage of the method of measuring the difference in mass of doublets with the same mass number. The mass differences Δ_1 and Δ_2 are measured to accuracies of the order of 1%, but the mass of the hydrogen atom obtained is accurate to 4 parts in 10^5 . It may be noted that Aston's value is in complete agreement with the present value,²¹ $m(^1\text{H}) = 1.00782504 \pm 0.00000001 u$.

The particles whose masses are measured in the spectrograph are ions that have lost one or more electrons, but the mass values quoted relate to the neutral atoms, *i.e.* the mass of one or more electrons is added to the measured masses. The mass of the electron, $5.486 \times 10^{-4} u$, is small but not negligible at the accuracy of Aston's measurements. On the other hand, the binding energies of the atoms in a molecule, being of the order of electronvolts, correspond to mass values of the order of $10^{-9} u$. So the mass of a diatomic molecule such as hydrogen may be taken to be twice the mass of the hydrogen atom.

Aston improved the resolving power of his spectrographs from 130 for the first instrument to 600 for the second and 2000 for the third. He claimed an accuracy of 1 in 10^4 for the second instrument and approaching 1 in 10^5 for the third. If we compare his mass values (changing them to the ^{12}C scale) with the present-day values, which are accurate to about 1 in 10^6 or better, the differences for the values obtained from the 1927 instrument are on average about 1.5 in 10^4 , and for the 1937 values about 2.5 in 10^5 . So his claimed accuracy is well substantiated. The third mass spectrograph, without the magnetic field components, is in the Museum of the Cavendish Laboratory; it is shown in Fig. 9. Aston's first mass spectrograph is in the Science Museum in South Kensington.

Other workers and modern developments

Although Aston is recognised as the pioneer in mass spectroscopy there were other major workers in the field from 1918 onwards. Arthur Dempster, at the University of Chicago, con-



Fig. 9 Aston's third mass spectrograph, now in the the Museum of the Cavendish Laboratory. The discharge tube is on the right. The white discs are for adjusting the widths of the slits S_1 and S_2 . The magnet, not shown, acts over the region of the tube in the left-hand wooden support. The photographic plate is placed in the focus plane just before the left end of the tube to record the spectra. The overall length of the instrument, excluding the discharge tube, is 105 cm.



Fig. 10 Aston working with his apparatus for the separation of the isotopes of neon by fractional distillation, 1914.

structed a mass spectrograph in 1918²² and in the next few years found isotopes in magnesium, lithium, potassium, calcium and zinc. His instrument involved bending monoenergetic ions into a semicircular path by a uniform magnetic field, which gives direction focusing, *i.e.* ions diverging in direction at the entrance to the magnetic field are brought to a focus after completing a semicircle. Kenneth Bainbridge, at the Franklin Institute, Swarthmore, improved on Dempster's instrument by using a velocity filter before the magnetic analyser, thereby removing the need for a monoenergetic source.²³ With his apparatus he made the first measurement of the mass of the deuterium atom²⁴ and also provided one of the first experimental demonstrations of Einstein's mass-energy relation.²⁵

The detailed motions of ions in electric and magnetic fields were calculated by Richard Herzog and Josef Mattauch in Vienna²⁶ and others in the early thirties. The results led to the design of high-resolution double-focusing instruments in which ions with both a spread in velocities and a spread in initial directions were brought to a focus. Instruments making use of double focusing were built by Alfred Nier at the University

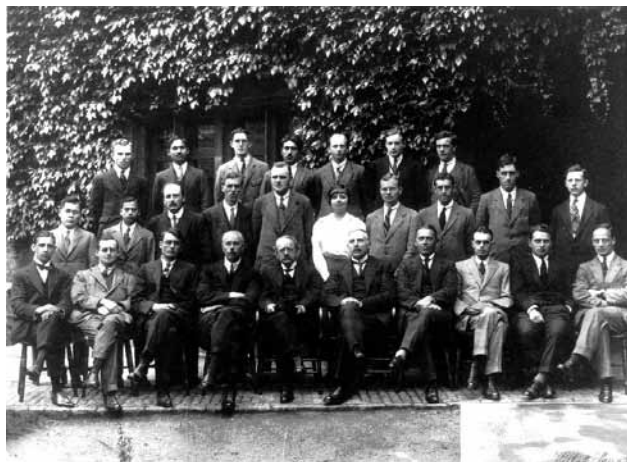


Fig. 11 The research students and staff of the Cavendish Laboratory in 1922, the year that Aston was awarded the Nobel Prize. Aston is fourth from the left in the front row, Thomson is fifth, and Rutherford, the Cavendish Professor, is sixth. Edward Appleton is second from the right in the front row, Patrick Blackett is second from the right in the second row, and Peter Kapitza is at the right-hand end of the back row.



Fig. 12 Aston working with his third mass spectrograph, *ca.* 1937.

of Minnesota²⁷ and several other workers.²⁸ Further improvements came from replacing photographic plates by electrical detectors and from advances in vacuum technology.²⁹ The value of 2000 for the resolving power of Aston's third mass spectrograph has been extended to values exceeding 10^5 , and accuracies of the order of 1 part in 10^8 or 10^9 have been obtained.³⁰

Mass spectroscopy is now applied in several branches of chemistry, biology, geology, and physics. In many of these applications the classical method of electrostatic and magnetic deflection described in this paper has been replaced by timing methods. The highest precisions are obtained by cyclotron resonance in which the frequencies of ions rotating in a uniform magnetic field are measured and analysed by Fourier transform techniques. Sophisticated ionisation methods have been developed for the analysis of complex biomolecules and macromolecules.³¹

Aston's later life

Aston's first mass spectrograph brought him immediate acclaim. He was appointed to a Fellowship in Trinity College, Cambridge in 1920 and was made a Fellow of the Royal Society in 1921. He was awarded the Nobel Prize in Chemistry in 1922 for, in the words of the citation, 'his discovery, by means of his mass spectrograph, of isotopes in a large number of non-radioactive elements, and for his enunciation of the whole

number rule'. In proposing the toast of the laureates at a dinner in December of that year, Svante Arrhenius, the Director of the Nobel Institute, commented that never before had the Nobel Prize been handed over to a group of such distinguished laureates, which, besides Aston, included Niels Bohr, Albert Einstein, and Frederick Soddy. The last two were the 1921 prize winners in Physics and Chemistry respectively, but the awards were made in 1922.

Aston never married and for the last 35 years of his life lived in Trinity College. Outside his work his main interests were sport, travel and music. He was a keen cross-country skier, and played tennis up to tournament class. He played golf in a famous foursome with Ernest Rutherford, Ralph Fowler, and Geoffrey (G. I.) Taylor. He was an enthusiastic cyclist, once cycling 200 miles in 22 h. He was also an excellent photographer and combined this hobby with his love of travel to help at several solar eclipse expeditions. He was an omnivorous reader, Sherlock Holmes being his favourite. An acquaintance once described him as the highest lowbrow that he had ever met.

Aston died on 20 November 1945. In an obituary in *Nature*³² G. P. Thomson wrote 'Aston was a man in whom a great zest for life was combined with a simplicity of character almost approaching naivety. Though a good occasional lecturer, he had no gift for teaching, and a few early attempts were not persisted in. His attitude to physics was essentially that of the experimenter and visualizer. He preferred the model to the equation, the concrete to the abstract. He was a Conservative in politics as in life, and though he would admit that a change might be good, he preferred it to happen as gradually as possible'.

In summary, Aston was not only a one-experiment man, he was effectively a one-instrument man. However, what he measured was of the highest importance and he did it extremely well. To quote G. P. Thomson once more,³³ 'Aston was a superb experimenter. His first mass spectrograph was a triumph; few but he could have got it to work at all'.

Acknowledgements

Fig. 8 is reproduced from the *Philosophical Magazine*, 1920, by permission of Taylor & Francis. Figs. 5 and 9 to 12 are from the Photographic Archives of the Cavendish Laboratory.

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