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Sir William Ramsay and the noble gases

ALWYN G. DAVIES

ABSTRACT

Sir William Ramsay was one of the world's leading scientists at the end of the 19th century, and in a spectacular period of research between 1894 and 1898, he discovered five new elements. These were the noble gases, helium, neon, argon, krypton, and xenon; they added a whole new group to the Periodic Table of the elements, and provided the keystone to our understanding of the electronic structure of atoms, and the way those electrons bind the atoms together into molecules. For this work he was awarded the Nobel Prize in Chemistry in 1904, the first such prize to come to a British subject. He was also a man of great charm, a good linguist, and a composer and performer of music, poetry and song. This review will trace his career, describe his character, and give and account of the chemistry which led to the award of the Nobel Prize.

Keywords: *William Ramsay, noble gases, helium, neon, argon, krypton, xenon, radon, Nobel Prize*

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Introduction

The final decade of the 19th century was a period of ferment in physical science. In 1869, Mendeleev had formulated the Periodic Table. In 1895, Röntgen discovered X-rays; in 1896, Becquerel

Figure 1 *Portrait of Sir William Ramsay, 1905.*

discovered radioactivity; and in 1897, J.J. Thompson discovered the electron.

In 1887, William Ramsay arrived in London as Professor of Chemistry at University College London (UCL) with a background which enabled him to make his own major contribution to these developments. This review will sketch briefly his career and character, and then the chemistry which resulted in his being awarded the Nobel Prize in Chemistry in 1904 (see Note 1[1–3]).

Ramsay's career

William Ramsay was born in Glasgow in 1852, the only child of a family of the Calvinist faith and with a background in science. On his father's side there had been a history of the manufacture of dyestuffs and dyers' chemicals, and on his mother's side, of medicine. His father's brother, Sir Andrew Ramsay became Professor of Geology at UCL in 1848 then, later, the Director General of the Geological Survey.

He went to a local preparatory school, and at the age of eight he broke a leg playing football, which resulted in his introduction to

Figure 2 *William Ramsay, aged 8, with this father and mother.*

chemistry. In his own words: ''*During my convalescence I read Graham's chemistry, chiefly, I must admit, because I wanted to know how to make fireworks. I remember that my father gave me small quantities of potassium chlorate, phosphorus, sulphuric acid, and some small flasks and beakers and a spirit lamp, and with these I amused myself during several weary months*''. The picture of a boy handling such a lethal mixture of chemicals in his bedroom is quite frightening.

He then went to Glasgow Academy. There was little science teaching there, but he continued dabbling in chemistry at home. He taught himself French or German by translation: he already knew much of the New Testament in English by heart and took to church on a Sunday a copy of a French or German version, which he read during the long sermons.

In 1867, he went to Glasgow University at the age of 15, registering in the first year for classical languages, natural and moral philosophy, logic and mathematics. William Thomson, later

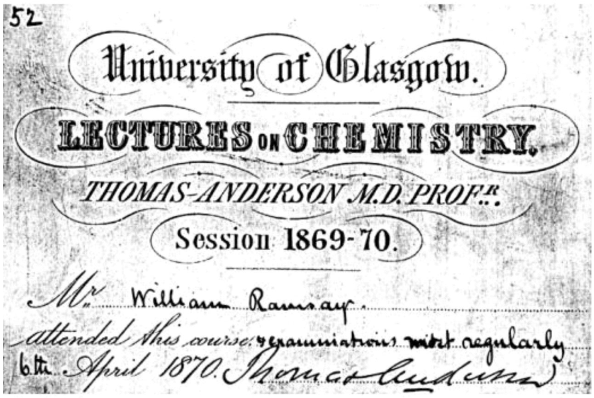

52
University of Glasgow.
LECTURES ON CHEMISTRY.
THOMAS ANDERSON M.D. PROF.R.
Session 1869-70.
Mr William Ramsay
attended this course & examinations most regularly
6th April 1870. Thomas Anderson

Figure 3 *Ramsay's certificate of attendance at Professor Anderson's lectures, 1869–70.*

Lord Kelvin, was professor of philosophy, and may have influenced Ramsay in changing in the second year to focus on chemistry. This was despite John Ferguson, the professor of chemistry's assistant and successor, warning him that chemistry was completely worked out and that was nothing more to be discovered. He attended Professor Anderson's chemistry lectures (Figure 3), and, after May 1869, worked part time in the laboratory of the Glasgow analyst, Robert Tatlock.

He intended to go to Heidelberg to work with Bunsen for a PhD, but the Franco Prussian war intervened and in 1871 he went to Tübingen, without taking a degree at Glasgow, to work with Fittig, and he obtained a PhD degree with the thesis title *Investigations on the toluic and nitrotoluic acids*.

He returned to Glasgow in 1872, first as Professor's Assistant in Anderson College (later the Royal Technical College, and now Strathclyde University), then, in 1874, to a similar position in Glasgow University.

In 1878 he was applying for chairs in chemistry as they came onto the market, and was beginning to get discouraged. The breakthrough in his career came in 1879 when he was successful in his application for the chair of chemistry at University College, Bristol. He said that he got the chair by one vote because one of his testimonials was written in Dutch, and he impressed the appointing committee with his knowledge of the language. His salary was £300 a year, plus a share of the students' fees, with the guarantee that the total would not be less that £400 a year. His lodgings cost 18s a week and he found that he could live very well on £2 12s 6d a week.

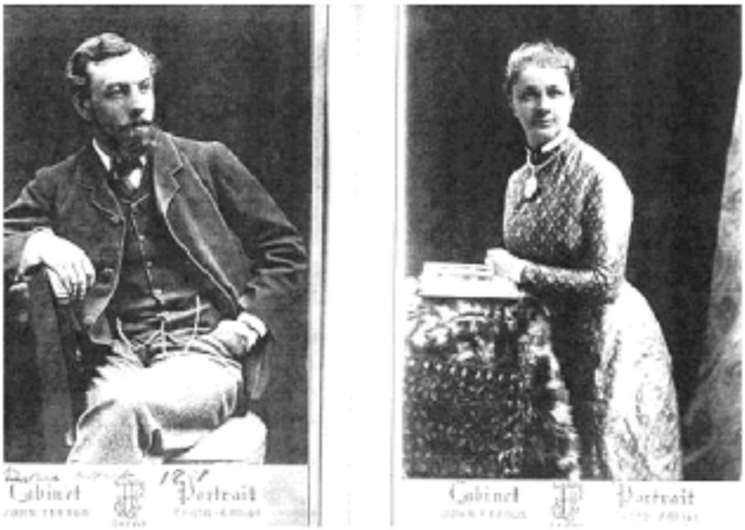


Figure 4 *William and Margaret Ramsay, 1891.*

Two years later he was offered the post of Principal of the College, which he accepted on the condition that ''*I am first a chemist. I won't take it if it seriously interferes with my prospect of doing scientific work*''.

In that year he also married Margaret Buchanan from Glasgow (Figure 4). She had the same easy charm as her husband and they were the ideal host and hostess, and, like her husband, she was an good linguist.

It was at Bristol that his research laid the foundation for his discovery of the noble gases. He became interested in the physical equilibria between solids, liquids, and gases. He learned glass blowing from his assistant Sidney Young (later Professor Young FRS) and became expert in designing and building apparatus, and in handling small amounts of gases; they published papers together in *Philosophical Transactions of the Royal Society* (communicated by Ramsay's uncle Andrew) and in *Journal of the Chemical Society*.

In February 1887, Carey Foster, who was head of the Physics Department at UCL, wrote to Ramsay to say that Alexander Williamson, who was head of the Chemistry Department, was going to resign, and Ramsay applied for the post. He was 34 years of age, and quoted a list of 21 publications, largely in *Journal of the Chemical Society*, *Proceedings of the Royal Society*, and *Philosophical Magazine*.

Carey Foster warned him that he knew of more than one case where the College had not approached referees, and advised him to rely on open testimonials, and he submitted the following impressive list.

Referees

Hugo Müller, President of the Chemical Society.
Sir Lyon Playfair, M.P., K.C.B., FRS.
Professor Jowett, Master of Balliol.

Testimonials:

President of University College Bristol	Chairman of University College Bristol
Professor Crum Brown (Edinburgh)	Professor Julius Thomsen (Copenhagen)
Professor Ira Ramsen (John Hopkins)	Professor George Liveing (Cambridge)
Professor John Ferguson (Glasgow)	Professor Wilhelm Ostwald (Riga)
Professor Sir William Thomson (Glasgow)	Professor Waage (Christiana)

Williamson held both the chairs of Chemistry and of Practical Chemistry, and it was possible that the two chairs (and the salary) might be split, one going to W.H. Perkin who was also a candidate. The interview apparently was very pleasant; Williamson, who had criticised some of Ramsay's work, was supportive, and Ramsay was appointed as the single professor at a salary of £700 a year.

The Ramsays bought a house at 12 Arundel Gardens, in Notting Hill, and he wrote to his sister: ''*I go to town and on a bicycle, right along Bayswater Road to Oxford Street and to Gower Street. This morning I was at College in eighteen minutes*''. An English Heritage Blue Plaque was opened on the house on 9 February 2011, and a convoy of bicycles retraced his journey to college (in about 40 minutes). This was to be the Ramsays' house for 15 years till they moved to 19 Chester Terrace, Regents Park, in 1903.

On Ramsay's appointment, the resignation of the other staff was automatic. Foster Morley was not reappointed, but Plimpton and Rideal remained and Norman Collie was recruited. Ramsay also had two assistants and a demonstrator.

The Laboratory which Ramsay left at Bristol was small but well-equipped; the one which he met at UCL was large but in poor condition and cluttered with the accumulated, and largely unlabelled, residues of many years. Ramsay's initial task was to clear the laboratories and remodel them to his satisfaction.

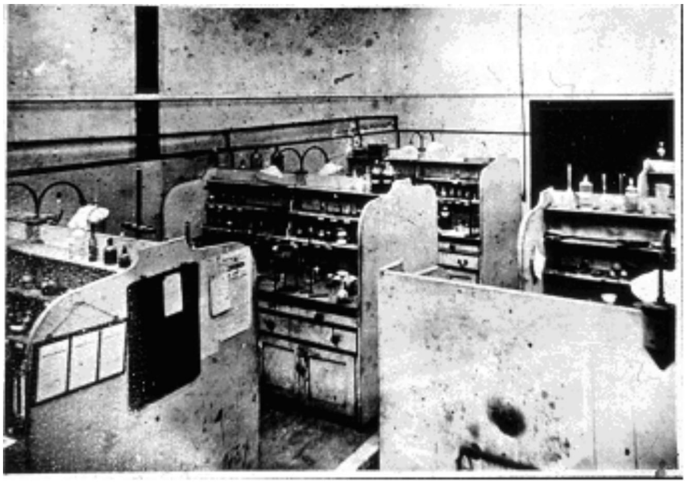


Figure 5 *The "horse boxes".*

The chemistry department was located in the ground floor and basement of the North wing (which is now the Slade School of Art), and also a shed at basement level, fitted with benches which were called horse-boxes (Figure 5), Collie and Plimpton having one bay each.

Ramsay's character

He was a man of great charm, and picked up languages quickly. He was fluent in French, German, Italian, Norwegian, Swedish, and Dutch, and apparently could get by in a dozen languages. The only language that he said beat him was the pronunciation of Scottish Gaelic. This facility helped him to become intimate friends with the other leaders of chemistry at the time, such as Arrhenius in Sweden, Ostwald and Fischer in Germany, and van't Hoff in Holland (all of whom, in due course, won the Nobel Prize in Chemistry), and he stayed with them on his frequent trips to the continent, and they with him when they visited London. We have his guest book covering the years 1889 to 1906, and it contains signatures of people from 18 overseas countries–USA, Barbados, France, German, Czechoslovakia, Russia, Turkey, China, Japan, India, Australia, New Zealand, and Tasmania–including Otto Hahn, Emil Fischer, and Demitrii Ivanovich Mendeleev. He conversed with Mendeleev in German. In 1900, the Russian Academy of Sciences had an engraving made of Mendeleev; 20 copies were made and distributed according to Mendeleev's wishes, and one came to Ramsay (Figure 6).

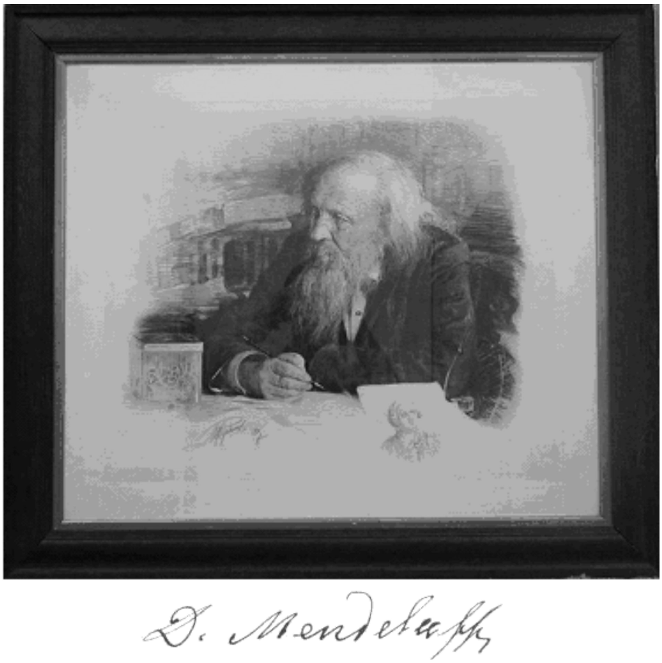
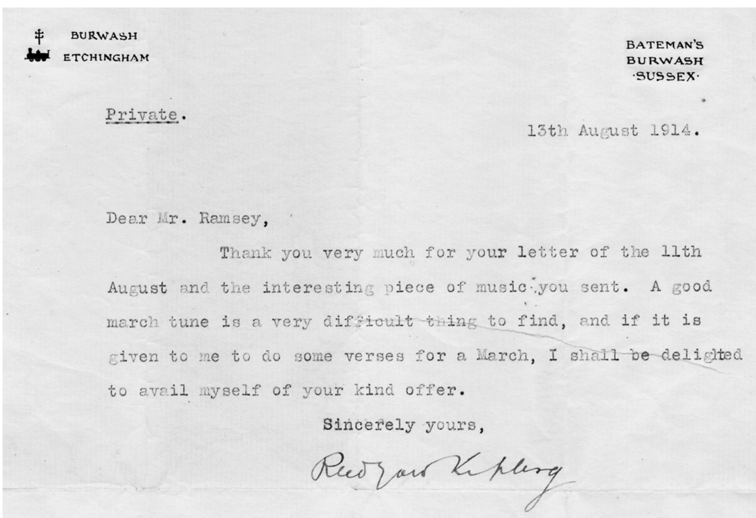


Figure 6 Etching of Mendeleev. The signature is copied from Ramsay's guest book, 1897.



BURWASH
ETCHINGHAM

BATEMAN'S
BURWASH
·SUSSEX·

Private.

13th August 1914.

Dear Mr. Ramsey,

Thank you very much for your letter of the 11th August and the interesting piece of music you sent. A good march tune is a very difficult thing to find, and if it is given to me to do some verses for a March, I shall be delighted to avail myself of your kind offer.

Sincerely yours,

Figure 7 *Rudyard Kipling's letter to Ramsay 13 August 1914.*

He composed and performed music, poetry and song. Figure 7 shows a letter from Rudyard Kipling to Ramsay, dated 13 August 1914, 9 days after Britain had declared war on Germany. Ramsay had composed a march tune, and Kipling was proposing to write the words to go with it.

We have in the UCL archives a letter from Margaret Beale (Groshshank) who was a child in Sussex in the 1890's when the Ramsays sometimes came to her home for weekends and parties. She says ''The long formal full-dress dinner parties ceased to be tedious if the Ramsays were there ... Sir William whistled to his own piano accompaniment ... to us young people he was the most delightful, humorous, and understanding of friends''.

The Chemistry Department at UCL has held an annual Laboratory Dinner since Ramsay's day, and he would supply some of the entertainment singing his own compositions, and playing the piano. A note on a 1910 menu says ''*there was a short interlude when Sir William Ramsay went to the piano and whistled Annie Laurie and other Scottish songs to his own accompaniment*''.

His following composition from 1902, very neatly encapsulates the discovery of nuclear fission.

The Death Knell of the Atom

Old time is aflying, the atoms are dying;
Come, list to their parting oration:-
We'll soon disappear to a heavenly sphere
On account of our disintegration.

Our action's spontaneous in atoms uranious
Or radious, actinious, or thorius;
While for others the gleam of a heaven-sent beam
Must encourage our efforts laborious.

For many a day we've been slipping away
While the savants still dozed in their slumbers
Till at last came a man with gold leaf and can
And detected our infinite numbers.

So the atoms, in turn, we now clearly discern,
Fly to bits with the utmost facility,
They wend on their way, and in splitting display
An absolute lack of stability.

Tis clear they should halt on the grave of old Dalton
On their way to celestial spheres
And a few thousand million – let's say a quadrillion
Should bedew it with heavenly tears.

There's nothing facetious in the way that Lucretius
Imagined the chaos to quiver,
And electrons to blunder, together, asunder
In building up atoms together.

In 1900 he travelled to India at the time of the Laboratory Dinner to advise on the setting up of the Indian Institute of Science, and recorded his speech on a wax cylinder which was played at the dinner. Unfortunately, efforts to find that recording have as yet been unsuccessful.

He was foremost an experimentalist. He tried to visit the teaching laboratories every day and carried on his watch chain a platinum spatula for poking the students' precipitates. He smoked and always rolled his own cigarettes, scorning the machine-made ones as being unworthy of an experimentalist. Henry Terry, no mean smoker himself, expressed his admiration of Ramsay's technique.

He was a keen teacher and believed in the value to teaching through experiment. We have the book of notes which H.E. Watson took in Ramsay's Intermediate Chemistry Lectures, in 1904–05, and in the front he has written the following:

> ''*No mere notes however convey the fascination of the course or the method of its delivery; still less can they describe the innumerable experiments, ranging from the isolation of argon from the air, to the vocal effects of hydrogen when inhaled, which accompanied it. Practically every laboratory preparation described was carried out on the lecture bench, and a sample of every substance mentioned was to be seen. Any unusual properties were demonstrated*''

This continued up to the last lecture which he gave at UCL to the Intermediate class. This was on cyanides and complex cyanides and one of his experiments was to dissolve gold in sodium cyanide. The gold leaf kept sticking to his fingers, and when he finally succeeded he said ''*gold doesn't usually stick to one like that*''.

Ramsay isolated argon first in August 1894 and already on 14 November he demonstrated the isolation in his undergraduate lecture. His love of hands-on research comes through in the song which he composed and sang at the Lab Dinner in 1898.

The Atmospheric Gases, O! (Air–Green grow the rushes, O!)

There' nought but air on every han',
In every breeze that passes O;
What guides the windmill or a fan,
An' 'twere na for the gases O.

Chorus:
Here's tae their masses O,
Their atomic masses O,
The happiest hours that ere I spend
Are spent among the gases O.

The wardly race may riches chase
And riches still may fly them O
And tho' at last they catch them fast
Their hearts can ne'er enjoy them O.

Gie me a cannie hour at e'en
A pint o' liquid airie O,
A tube or twa 'o impure Neon,
I'll never ha'e a carie O.

In liquid sate, I'll fractionate
Wi' Travers and wi' Baly O,
And we are sure we'll make it pure
And weigh it on the scalie O.

And Xenon tae, we'll catch and weigh
And find its refractivity,
And now it's done, we' ripe for fun
To join you in festivity.

Sae lads o' mine, pour out the wine,
Fill bumpers in your glasses O.
Wi' three times three, come join wi' me,
''The atmospheric gases O.''

He was a strong advocate for the equality of women and men. When Armstrong was President of the Chemical Society in 1888, he proposed, unsuccessfully, that women should be admitted to membership. He complained of having to deliver his lectures twice, once to the men's class and once to the women's, but the classes were amalgamated in 1890. A photograph of his staff and research group in 1899 shows the presence of five women and 45 men–a proportion which many chemistry departments had not reached 50 years later.

In his obituary of Ramsay, Frederick Soddy said ''*At University College he was looked up to in a way that can scarcely be expressed. He was at once genial, approachable, and great–any one of which alone is an infallible passport to the student's heart–and repaid their trust and affection as complete as that of a Scottish chieftain to his clan*''. The spirit in his research group can be judged from a story told by Travers about a student who had discarded a large sample of argon which had been made at the cost of much labour, thinking that it was air. *I explained to him the nature of his crime, and said to him, ''Now you had better go and tell the Chief'', using the name by which Ramsay was always spoken of. Off went the student looking very glum, but as I had anticipated, he came back smiling, ''Well, what did the Chief say about it?'' The student replied, ''All he said was, 'You had better go and tell Dr. Travers.' ''*

Frederick Donnan said of Ramsay ''*Nothing was ever postponed. What an ordinary very active man would do on Monday morning, Sir William Ramsay did on Saturday afternoon*''. Yet he was modest about his achievements. He ascribed his success to his large flat thumb that could close off the end of an eudiometer tube of a gas enclosed over mercury, and said that ''*it is all pure luck and plugging away*''.

When asked what his main contribution to science was, he said that it was not the chemistry but the chemists which he had produced.

A list is given below of 28 people – and the list is most probably incomplete – who worked with him and later occupied chairs of chemistry in universities ranging from Canada to New Zealand. This was at a time when there were few universities and most of these had at most one professor of chemistry; his disciples had a major influence spreading his standards of teaching, scholarship, and research throughout the world.

13 Of these 28 men became Fellows and two became Foreign Members of the Royal Society. Three obtained Nobel Prizes in their own right: Frederick Soddy (1921 for radioactivity and isotopes), Otto Hahn (1944, for nuclear fission), and Jaroslav Heyrovsky (1959, for electrochemistry). Stafford Cripps, who worked and published with Ramsay, defected to politics; he was Ambassador in Moscow during the war and a member of Churchill's wartime cabinet, and then Chancellor of the Exchequer in Atlee's post-war government.

Ramsay's students who subsequently occupied Chairs of chemistry

29 Professors, 13 FRS, 2 For.MRS, 3 Nobel Prizes, 1 Member of the Cabinet

H. Bassett (Reading)
E.C.C. Baly FRS (Liverpool)
A.T. Cameron (Manitoba, Canada)
J.N. Collie FRS (UCL)
F.G. Donnan FRS (UCL)
Sir James Dobbie FRS (Bangor)
Sir Alfred Egerton FRS (Imperial College)
A. Findlay (Aberdeen)
O. Hahn For.MRS, (Berlin Nobel Prize)
J. Heyrovsky For.MRS (Prague Nobel Prize)
J.H.K. Inglis (Dunedin, New Zealand)
Professor C. James (New Hampshire, USA)
Professor A.M. Kellas (Middlesex Hospital)
W.C. McC. Lewis FRS (Liverpool)
Sir David Masson FRS (Durham)
R.B. Moore (Purdue, USA)
R.T. Plimpton (Middlesex)
S. Smiles FRS (Kings College London)
F. Soddy FRS (Oxfd Nobel Prize)
B.D. Steele FRS (Queensland)
A.W. Stewart (Belfast)
M.W. Travers FRS (Bristol)
W.B. Tuck (Middlesex)
Sir James Walker (Edinburgh)
H.E. Watson (Bangalore, India)
N.T.M. Wilsmore (W. Australia)
R. Whytlaw-Gray FRS (Leeds)
S. Young FRS (Bristol)
Sir Stafford Cripps FRS (Cabinet)

Figure 8 *Ramsay and Rayleigh in Terling Place during the weekend 22–24 September 1894.*

Ramsay's chemistry

The background to the discovery of the noble gases was the search for accurate atomic and molecular weights. Prout in 1815 had proposed that all bigger atoms were agglomerates of hydrogen atoms. All atomic weights should then be simple multiples of that of hydrogen, and if hydrogen is given the atomic weight 1, those of all the other atoms should have integral numbers. This was approximately true–carbon 12, nitrogen 14, oxygen 16, and so on, but perhaps not exactly so, and the apparent deviations from whole numbers interested scientists for the rest of that century. Chemists attempted to improve the accuracy of the methods for determining atomic weights, usually by methods of chemical analysis.

Lord Rayleigh (Figure 8) followed a different approach. He was a physicist, with an appointment at the Royal Institute but he also had a private laboratory at his house at Terling Place in Essex where most of the work which is described here was carried out. He set out to determine accurate atomic weights of the elemental gases by measuring their densities, and in 1892 he began to communicate his results. On 19 April 1894 he lectured on the topic at the Royal Society, and Ramsay was in the audience.

Rayleigh reported that he had dealt successfully with hydrogen and oxygen, but nitrogen presented a problem. The gas derived from air by removing the oxygen with red hot copper appeared to be denser than nitrogen derived from chemical sources such as ammonia or nitrous oxide. The difference was small – about one part in 230 – but repeatable and convincing. Ramsay was in the audience and, after the lecture, he and Rayleigh discussed the problem, and they set out, in parallel to try to answer it.

Rayleigh looked initially for a light impurity (presumably hydrogen) in the chemical nitrogen, then changed tack and looked for a heavy impurity in aerobic nitrogen. Ramsay believed from the start that the answer was a heavy impurity, and his assistant, Williams set out to find it, but Ramsay himself could not join him until teaching and examinations were over in July. The different methods used by Ramsay and Rayleigh are shown in Figures 9 and 10.

Argon

Rayleigh followed the method which Cavendish had used in 1785. Air was confined in a tube, ***A***, over alkali, ***B***, and a spark could be thrown between two electrodes, ***D***, in the gas (Figure 9). The oxgen reacts with the nitrogen to give nitrogen oxides which are acidic and dissolve in the alkali. Further oxygen was added as necessary, until there was no further diminution in volume. Excess oxygen was removed with pyrogallol and any residual gas should be the

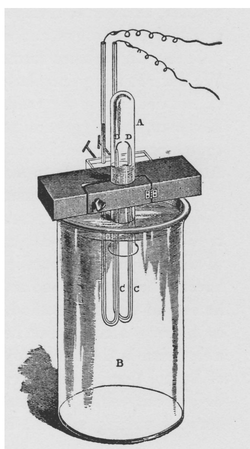


Figure 9 *Rayleigh's apparatus for isolating argon.*

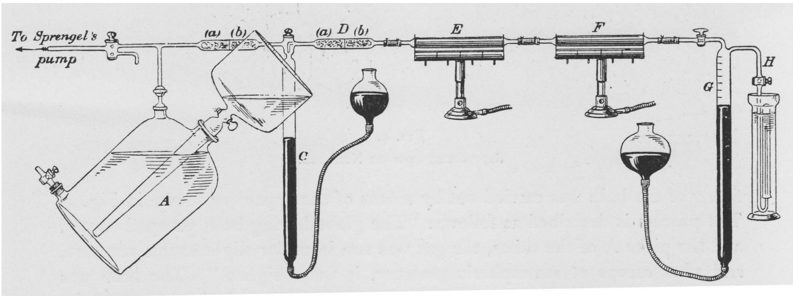


Figure 10 *Ramsay's apparatus for isolating argon.*

suspected impurity. After 9 days of sparking, from 50 mL of air, Rayleigh obtained 0.3 mL of inert gas.

Ramsay, with his experience in building apparatus for handling gases, could be more ambitious, and his apparatus, which was regularly being improved, is shown in Figure 10. The Bunsen burners, which are modified to spread the flame along the length of the tube which they carry, were of Ramsay's design and are called Ramsay burners,

Nitrogen (from air from which the oxygen had been removed with red hot copper) in the large gas holder ***A*** was transferred to the first gas burette ***C*** and then passed over P_2O_5 and slaked lime in ***D*** (to remove water and CO_2), then over heated Cu/CuO in ***E*** (to remove any residual oxygen, and any hydrogen from the reaction of H_2O and Mg), and then over red hot magnesium in ***F*** where the nitrogen reacts to form solid magnesium nitride. The gas was passed back and forth over the magnesium until there was no further reduction in volume, then pumped out to a reservoir and the process repeated. In this way, about 10 to 11 L of nitrogen were reduced to 104 mL.

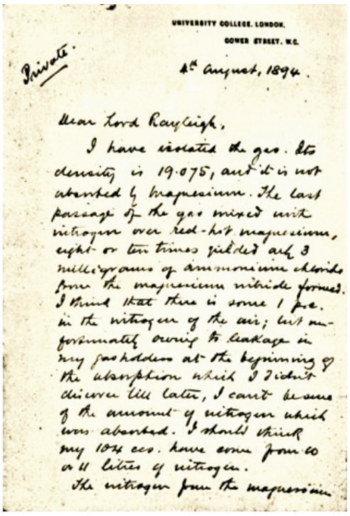
On 4 August 1894, Ramsay wrote to Rayleigh (Figure 11): ''*I have isolated the gas at last. Its density is 19.075 ...*''

On 6 August, Rayleigh replied: ''*I believe that I too have isolated the gas, though in miserably small quantities...*''.

On 7 August, Ramsay writes: ''*To take the last part of your letter first. I think joint publication would be the best course...*''.

When Ramsay went into work on Monday 7 August, he found that that the gas burette had cracked and most of the gas was lost.

The apparatus was continuously improved. In particular, an ingenious pump, based on a Sprengel pump, which Norman Collie had designed, was fitted so that the nitrogen could be continuously recirculated over the magnesium. It was this apparatus


UNIVERSITY COLLEGE, LONDON.
GOWER STREET, W.C.

Private.

4th August, 1894.

Dear Lord Rayleigh,

I have isolated the gas. Its density is 19.075, and it is not absorbed by magnesium. The last passage of the gas mixed with nitrogen over red-hot magnesium, eight or ten times yielded only 3 milligrams of ammonium chloride from the magnesium nitride formed. I think that there is some 1 p.c. in the nitrogen of the air; but unfortunately owing to leakage in my gasholder at the beginning of the absorption which I didn't discover till later, I can't be sure of the amount of nitrogen which was absorbed. I should think my 104 ccs. have come from 10 or 11 litres of nitrogen.

The nitrogen from the magnesium

4th August, 1894

Dear Lord Rayleigh,

I have isolated the gas. Its density is 19.075, and it is not absorbed by magnesium.....

6th August , 1894

Dear Prof Ramsay,–

I believe that I too have isolated the gas, though in miserably small quantities...

Figure 11 *Ramsay's letter to Rayleigh, 4 August 1894, reporting his discovery of argon, and Rayleigh's reply.*

which Ramsay used when he demonstrated the isolation of about 70 mL of argon to his class on 17 November. The photograph of Ramsay and Rayleigh in Figure 8 is taken shortly after this, when Ramsay stayed with Rayleigh at Terling Place for the weekend of 22–24 September. Ramsay characterised the gas by sealing it at reduced pressure in a tube fitted with a pair of electrodes, called a Plücker or Geissler tube. If a high potential is applied across the electrodes, the gas shows a discharge which can be broken up by a grating or prism into a line spectrum which is characteristic of the gas. Argon showed the spectrum which is illustrated in Figure 11, and is characterised by a strong blue line. Many of Ramsay's original Geissler tubes still exist at UCL and still give the characteristic spectra of their contents. Two are shown in Figure 12, and the discharge for one for is shown later in Figure 16. The blackening of the tubes is caused by evaporation, after prolonged discharge, of the electrodes.

Sir William Crookes, who had a private laboratory at his house at 7 Kensington Park Gardens, close to where Ramsay lived, was a skilled spectroscopist and Ramsay depended on him for measuring accurately the wavelengths of his spectra. The gas was called argon, from the Greek $\alpha\rho\gamma o\nu$ which is a word used in the New Testament to describe ''*the labourers who stood idle in the market place*'', to denote its inertness. On 13 August a brief preliminary announcement was made at the British Association meeting in Oxford; full details were not published until the New Year because Ramsay and

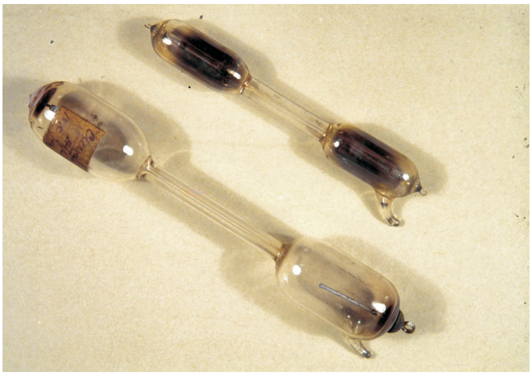


Figure 12 *Two of Ramsay's original Geissler tubes.*

Rayleigh had submitted it for the Hodgkin's Prize (which they won) of the Smithsonian Institute which was worth $10,000 (£2,000) but was only given for unpublished work. In December, Dewar at the Royal Institution confirmed that treatment of atmospheric nitrogen with red hot magnesium produced a gas with distinct low-temperature physical properties but he suggested that this was not a new element but instead was a new allotrope of nitrogen, N_3, corresponding to ozone, O_3. The Times reported ''*With these grave uncertainties brooding over the discovery, it is remarkable that Lord Rayleigh and Professor Ramsay should prefer to keep silence, though all doubts might have been settled in almost as many days as months have elapsed since the meeting of the British association*''

Ramsay gave full details of the work at a lecture to the Royal Society on 31 January 1895. It is said that there were 800 people at the lecture, and at the end, the audience rose in acclamation[5].

Figure 13 shows the state of Mendeleev's Periodic Table of elements at that date. The properties of the elements vary from strongly metallic in Group I (the alkali metals) to strongly non-metallic in Group VII (the halogens), and there is no obvious place for Ramsay's argon with an atomic weight of about 40. Its announcement was met with incredulity by much of the scientific community.

Helium

On the day after Ramsay's lecture (1 February 1895) Sir Henry Meirs, who was the chief mineralogist at the British Museum, wrote to Ramsay saying that an American geologist, Hillebrand, had

I	II	III	IV	V	VI	VII	VIII
H 1.0							
Li 6.9	Be 9.0	B 10.8	C 12.0	N 14.0	O 16.0	F19.0	
Na 23.0	Mg 24.3	Al 27.0	Si 28.1	P 31.0	S 32.1	Cl 35.5	
K 39.1	Ca 40.1	Sc 45.0	Ti 47.9	V 50.9	Cr 52.0	Mn 54.9	Fe 55.8 Co 58.9 Ni 58.7
Cu 63.5	Zn 65.4	Ga 69.7	Ge 72.6	As 74.9	Se 79.0	Br 79.9	
Rb 85.5	Sr 87.6	Y 88.9	Zr 91.2	Nb 92.9	Mo 95.9	??	Ru 101.1 Rh 102.9 Pd 106.4
Ag 107.9	Cd 112.4	In 114.8	Sn 118.7	Sb 121.8	Te 127.6	I 126.9	
Cs 132.9	Ba 137.3	*Contemporary tables broke down beyond Ba because of the lanthanides.*					

Figure 13 *Mendeleev's Periodic Table in 1894 (with modern atomic weight values).*

Figure 14 *Ramsay's remaining sample of cleveite from which helium was first isolated.*

reported that some uranite minerals, notably cleveite, gave off a gas when treated with acid or fused with sodium carbonate. Hillebrand thought that the gas was nitrogen, but Meirs and Ramsay thought it might be argon from some compound of argon in the mineral. Ramsay bought 1 g of cleveite from a mineral dealer, Gregory, in 88 Fitzroy Square for 3s 6d, and boiled it in sulfuric acid, and collected a gas which gave a yellow line in the discharge spectrum, which belonged to neither nitrogen nor argon. He sent a specimen to Crookes who confirmed that it was the same line that was obtained by Janssen from a spectrum of the sun's corona during an eclipse in India in 1868. Its wavelength was 587.59 nm, close to that of the D lines of sodium, D_1 at 589.50 and D_2 598.90, so Janssen called it the D_3 line. It appeared to belong to no known element, so Lockyer and Frankland proposed that it belonged to an unknown element which they called helium. This was the second noble gas, helium[6] (see Note 2 [7–11]).

The discovery of helium and argon led to intense speculation about their position in the Periodic Table. Ramsay had written to Rayleigh on 24 May 1894 ''Has it occurred to you that there is room for gaseous elements at the end of the periodic table ..'' but he put in the same Group VIII the triads Fe–Co–Ni and Ru–Rh–Pd. His conviction that there must be a missing intermediate inert gas was based on the large difference of about 36 between the atomic weights of helium and argon. In other groups of elements as then recognised, the difference between the first and second members was usually about 16 (*e.g*. F 19, Cl 35.5 differences 16.5; O 16, S 32, difference 16; C 12, Si 28.3, difference 16.3). It seemed that with He 4 (before lithium) and Ar 40 (before potassium), if these were the first and third members of a new Group, there should be an inert gas of the same family, with an atomic weight of about 20 (before sodium).

In August 1897, in his presidential address to the Chemistry section of the British Association, he said: ''*There should be an undiscovered gas between helium and argon, with an atomic weight 16 units higher than helium, and 20 units lower than that of argon, namely 20 . . . here is a supposed unknown gas, endowed no doubt with negative properties, and the whole world to find it in*''.

He apparently did consider the existence of inert gases heavier than argon, but in Travers' words ''The prediction of the gases of higher atomic weight was more in the nature of an extrapolation than the prediction of the gas intermediate between helium and argon'', and a heavier gas (krypton) turned up unexpectedly when he was looking for the lighter gas (neon). (see Note 3 [12,13]).

They spent two years in fruitless attempts to prepare compounds of argon, and to find the supposed missing gas in minerals, mineral springs, volcano vents, and animal and vegetable materials. The only success was that argon was always found in the gases from mineral springs, and traces of helium were found in many minerals.

Neon, and krypton and xenon

In 1898 they decided that the gas that was missing between helium and argon must be hiding in the air, and they managed to isolate it, and also the two further gases, krypton and xenon, because liquid air had become available as a result of work by Dewar at the Royal Institution and Olszewski in Poland. Dewar was a competitor rather than a collaborator, but Dr W. Hampson, working with the Brin Oxygen Company (which later became the British Oxygen Company) had built a liquid air machine early in 1898. Ramsay and Travers stockpiled 18 litres of argon with the intention of condensing it in liquid air when it should arrive, and then fractionally evaporating the argon.

Hampson provided them with about three quarters of a litre of liquid air on 24 May 1898. On 31 May, the residue of 10 mL which had not boiled away was then purified from oxygen, nitrogen, and carbon dioxide. The spectrum and density of the remaining 26.2 mL of gas showed the presence of argon but also a new gas, krypton,

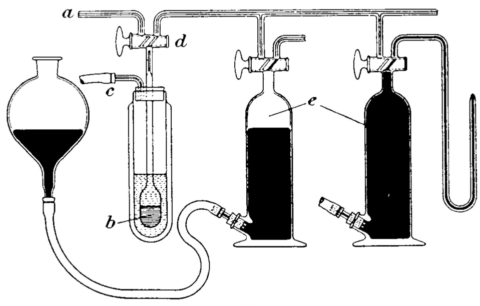
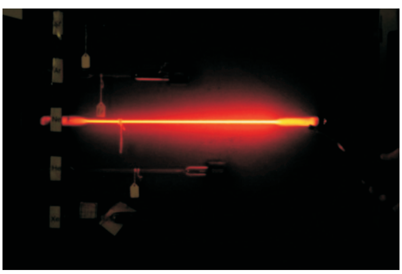


Figure 15 *Ramsay's apparatus for isolating neon.*

with a density of 40. In looking for a lighter inert gas, they had unexpectedly found a heavier one[14].

On Saturday afternoon, 11 June, Hampson provided them with a further sample of liquid air. They condensed argon in the bulb *b* (Figure 15) by causing the liquid air to boil off under reduced pressure through *c*. The argon was then allowed to warm up, and seven fractions of the argon were collected in turn in *e*, and transferred to sample tubes. On the next day, the Sunday, 12 June 1898, Ramsay, Travers, Baly, and Walker met at the UC gates at 10 a.m. Ramsay and Travers transferred the most volatile fraction into a discharge tube; it gave a blaze of crimson light. They had separated neon from the impure argon. They purified it, determined its density as 14.67, its specific heat ratio C_p/C_v (1.66) which showed it to be monatomic, and its spectrum. At 6 p.m. Ramsay and Travers went to Ramsay's home, had dinner, wrote the paper, and posted it after midnight to the Royal Society the pillar box at the corner of Arundel Gardens[15]. As Travers said, ''*It had been a full and exciting day*''.

The least volatile residues of Hampson's liquid air were condensed at *b* in the apparatus shown in Figure 17. Careful fractionation gave the final gas in the air, xenon[16].



"This time we had no need to decide whether or not we were dealing with a new gas. The blaze of crimson light told its own story". - Travers

Figure 16 *The discharge in one of Ramsay's original Geissler tubes of neon.*

In the middle of July, the fifth of the noble gases was isolated.

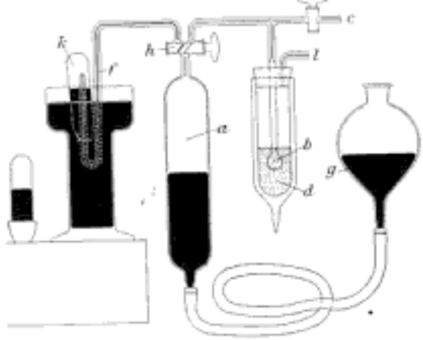


Figure 17 *Ramsay's apparatus for isolating xenon.*

Group VIII of the Periodic Table is now nearly complete as shown in Figure 18; the percentages in air are Ne 0.0029%, Ar 1%, Kr 0.0001%, and Xe 0.000009%.

Radon

At McGill University, Rutherford and Soddy has shown that heavy elements such as thorium and radium gave off a gas, which they called emanation, in minute quantities, which appeared to be chemically inert, and might be a further noble gas that could fill the gap below xenon in the Periodic Table. They attempted to determine its density, which would give the atomic weight, but they could not get a reliable value.

Only Ramsay had the technique of handling such small amounts of gases, and in 1903, Soddy joined Ramsay. The gas showed no discharge spectrum, but after a time, the spectrum of helium developed. This was the death knell of the indestructibility of the atom, as we saw earlier in Ramsay's song (and this led to Soddy's interpretation of the changes in atomic weight and atomic number that accompany α and β radiation, and his Nobel Prize in 1921).

The only way to confirm that the emanation, that they first called niton, and later radon, was a noble gas, was to determine its density, and Whytlaw-Gray in Ramsay's laboratory built the balance which was sensitive to 10^{-8} g and is shown in Figure 19. It was a modification of a design by Steele, one of Ramsay's students, who had by then moved to Australia. The beam, 7.5 cm long, was made of silica rods, about as thick as pin, and carried a mirror reflecting light onto a vertical screen 3 m away. *B* And *K* are adjustable silica

I	II	III	IV	V	VI	VII	VIII
H 1.0							**He 4.0**
Li 6.9	Be 9.0	B 10.8	C 12.0	N 14.0	O 16.0	F19.0	**Ne 20.2**
Na 23.0	Mg 24.3	Al 27.0	Si 28.1	P 31.0	S 32.1	Cl 35.5	**Ar 39.9**
K 39.1	Ca 40.1	Sc 45.0	Ti 47.9	V 50.9	Cr 52.0	Mn 54.9	Fe 55.8 Co 58.9 Ni 58.7
Cu 63.5	Zn 65.4	Ga 69.7	Ge 72.6	As 74.9	Se 79.0	Br 79.9	**Kr 83.8**
Rb 85.5	Sr 87.6	Y 88.9	Zr 91.2	Nb 92.9	Mo 95.9	??	Ru 101.1 Rh 102.9 Pd 106.4
Ag 107.9	Cd 112.4	In 114.8	Sn 118.7	Sb 121.8	Te 127.6	I 126.9	**Xe 131.3**
Cs 132.9	Ba 137.3	*Contemporary tables broke down beyond Ba because of the lanthanides.*					

Figure 18 *The Periodic Table in 1898, showing the noble gases, in* **bold**, in group VIII (with modern atomic weight values and the modern symbol for argon of "Ar" instead of the contemporary "A").

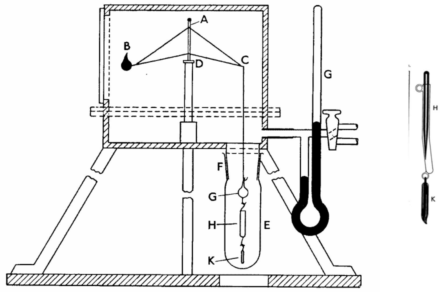


Figure 19 Whytlaw-Gray's balance.

weights. *G* Is a bulb of air which acts as a counterpoise, the buoyancy of which can be changed by changing the pressure in the balance case. The argon was confined in the capillary *H*, and the balance zeroed. The tip of the tube was then broken, and the balance rezeroed by changing the pressure which was read with a cathetometer. One of many complications is that the radon is decomposing to helium with a half life of 3.8 days. A number of further corrections have to be applied. They found that 6.58×10^{-5} mL of radon weighed 6.55×10^{-7} g; an average of five such experiments gave the A.W. of argon as 222, completing the collection[17].

In 1904, Ramsay was awarded the Nobel Prize in Chemistry, with the citation ''*in recognition of his services in the discovery of the inert gaseous elements in air*''.

At the same ceremony, Rayleigh was awarded the Nobel Prize in physics. Figure 20 shows Ramsay's Nobel Certificate.

Figure 20 Ramsay's Nobel certificate.

Note 1

This article is based on a lecture given at University College London on February 9, 2011, on the occasion of the unveiling of an English Heritage Blue Plaque on the house at 12 Arundel Gardens, where Ramsay lived from 1887 until 1902. References have been kept to a bare minimum. Further details of Ramsay's life and work, are given in books[1–3]. Traver's biography of Ramsay[3] can be particularly recommended. Mellor's treatise[4] gives an extensive list of references.

Note 2

In fact the D_3 line of helium was observed in 1882 by an Italian volcanologist, in gas from the lava of Mount Vesuvius[7–8].

Soon after Ramsay isolated the helium from cleveite, Clève, after whom the mineral was named, reported the isolation of the gas by a similar method[9–11].

Note 3

Many other predictions were made by others of missing members of the series. Many of these were very wide of the mark but a remarkably prescient one was made in 1895 by Julius Thomsen of Denmark[12,13]. He based his argument on the principle that there was a change in valence of one unit between adjacent elements in the Periodic Table. Then in going from the electronegative halogens in Group VII, with a valence of -1, to the electropositive alkali metals in Group I, with a valence of $+1$ there should be an intermediate group of inactive (electrozero) elements, Group VIII, with a valence of zero. He predicted that the atomic weights of these elements should be 4, 20, 36, 84, 132, 212, and 292, whereas the currently accepted values are He 4.00, Ne 20.18, Ar 39.95, Kr 83.80, Xe 131.29, Rn 222, and Uuo 294. Only three (or four) atoms have been prepared of ununonium (Uuo, Element 118). It was prepared in 2002 by the collision of californium-249 atoms and calcium-48 ions and has a half-life of $\sim$0.89 ms.

The timing of Thomsen's prediction is interesting. Ramsay communicated the identification of helium to the Royal Society on Thursday 27 March 1895. The dateline on Thomsen's paper in *Zeitschrift für Chemie* is April 1895.

Thomsen could hardly have known of Ramsay's helium when he submitted the paper, and there is no mention of helium (or of Ramsay) in the paper. Indeed, he says that he conceived of the Group of inert elements many years before, and it was only the discovery of argon which encouraged him to publish: ''*The discovery of argon as well as some small communications by Lecoq de Boisbaudran and Sedgwick encourage me to publish some thoughts which were forced upon me many years ago that I had not previously wanted to publish in order not to emburden science with hypotheses that can not be adequately demonstrated*''

Equally interesting is the question of when Ramsay knew of Thomsen's prediction. The paper was published in both Danish[12] and German[13]. Ramsay could read both languages, and it seems unlikely that he could have remained unaware of the *Zeitschrift für Chemie* paper for long. Further to that, he must have been acquainted with Thomsen who had written a testimonial for him when he applied for the post at UCL. It would seem reasonable that Thomsen might have communicated his thoughts to Ramsay, but there appears to be no mention of this in the papers, and as late as 1908 Ramsay was still putting transition metals along with the noble gases in Group VIII.

Acknowledgement

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