Sir William Ramsay: Noble Gas Pioneer—On the 100th Anniversary of His Nobel Prize

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Abstract: On the occasion of the 100th anniversary of the awarding of the Nobel Prize in Chemistry on December 10, 1904 to Sir William Ramsay (1852–1916) "in recognition of his services in the discovery of the inert gaseous elements in air, and his determination of their place in the periodic system," this article reviews his life and career and discusses his most important contributions.

On December 10, 2004, the 100th anniversary of Sir William Ramsay's Nobel Prize in Chemistry, the Society for the History of Alchemy and Chemistry [1] will hold a joint meeting with the Department of Chemistry at University College, London, where Ramsay was Professor of Inorganic Chemistry. Alwyn Davis of UCL will present a lecture, "Ramsay, the Man, the Myth, the Bicycle," and a Royal Society of Chemistry Chemical Heritage Plaque to commemorate Ramsay's Nobel Prize for the discovery of the inert gases will be unveiled. The anniversary provides us with an excellent opportunity to review briefly Ramsay's life and career.

On December 10, 1904, the eighth anniversary of Alfred Nobel's death, Sweden's King Oscar II awarded the 1904 Nobel Prize in Chemistry [2] to Ramsay [3–9] (Figures 1 and 2) "in recognition of his services in the discovery of the inert gaseous elements in air, and his determination of their place in the periodic system" [10]. Ramsay was the first Briton to win the chemistry prize. In his presentation speech Professor J. E. Cederblom of Kungliga Tekniska Högskolan (the Royal Institute of Technology, KTH) and President of Svenska Kungliga Vetenskapsakademien (the Royal Swedish Academy of Sciences), after summarizing the events leading to the discoveries and enumerating some of Ramsay's most important achievements, praised the uniqueness of his discoveries at length:

> The discovery of an entirely new group of elements, of which no single representative had been known with any certainty, is something utterly unique in the history of chemistry, being intrinsically an advance of science of peculiar significance. The more remarkable is this advance when we recollect that all these elements are components of the atmosphere of the earth, and that, though apparently so accessible for scientific research, they have for so long a time baffled the acumen of eminent scientists, who from the time of Scheele, Priestley, and Lavoisier to our own day have been occupied in determining the chemical and physical properties of the air. The discovery, however, signifies far more than the simple addition of five new elements to the seventy odd that are already known. This is to no slight degree owing to the inert character of the new gases, which certainly renders their study very difficult, but at the same time places them in a very peculiar position among the other elements. In spite of repeated and indefatigable endeavours it has been found impossible in any authenticated case to induce chemical combination either with each other or with other known elements. Such a total inertness among elements was previously unknown; indeed it was almost generally believed that the power of entering into chemical reaction was a fundamental attribute which—though in a higher or lower degree—characterized all the elements. The discovery of the noble gases has removed this impediment to our knowledge, widened our far too narrow view of the nature of the elements, and for this reason, from a theoretical aspect, is of special interest [11].

History of Chemistry for Students and Practicing Chemists

In contrast to the situation in the humanities, where students are expected to steep themselves in the classics, the average science major, on graduating, has little, if any, knowledge of the history of his or her chosen discipline. Although we take this state of affairs for granted today, it has not always been the case [12, 13]. Johann Wolfgang von Goethe (1749–1832), himself an amateur scientist, declared, "Die Geschichte der Wissenschaften ist die Wissenschaft selbst." (The history of science is history itself," *Mineralogie und Geologie.*) Also, the first popular history of chemistry in the English language was written by Scottish chemist Thomas Thomson (1773–1852), an active practicing chemist [14]. August Kekulé (1829–1896) of benzene ring fame spent considerable time reading the classics of chemistry before making any original discoveries of his own. And several founders of the American Chemical Society, for example, Benjamin Silliman, Jr. (1816–1885), Henry Carrington Bolton (1843–1903), and Charles F. Chandler (1836–1925), were interested and active in studying the history of chemistry. But my favorite example of the value of studying the history of chemistry to practicing chemists as well as students is Ramsay and Rayleigh's discovery of argon, the first noble gas to be isolated.

The Discovery of Argon

Until the last decade of the 19th century, chemists thought that the air had been so thoroughly studied that no one dreamed that it could possibly contain hitherto unknown elements [15]. However, in 1785 English chemist Henry Cavendish (1731–1810) noticed that when he repeatedly passed an electric spark through a mixture of oxygen and air in the presence of alkali ("soap lees") part of the "phlogisticated air" (nitrogen) had failed to combine with the

* Series Editor contribution

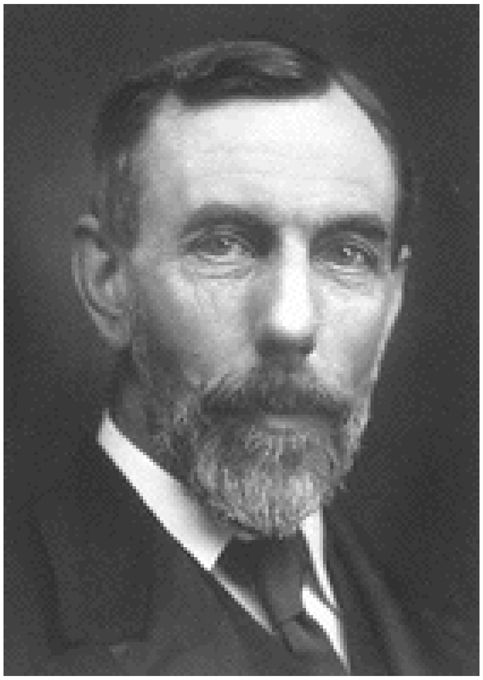

Figure 1. Sir William Ramsay (1852–1916). (Courtesy, the Nobel Foundation).

Figure 2. The Nobel Stamps of 1964. On December 10, 1964 the Swedish Post Office issued two new jubilee stamps to commemorate the Nobel Prizes in 1904—Sir William Ramsay (Chemistry); Ivan Petrovic Pavlov (Physiology or Medicine); Frédéric Mistral and José Echegaray y Eizaguirre (Literature); Lord John William Strutt Rayleigh (Physics). (Courtesy, the Nobel Foundation).

"dephlogisticated air" (oxygen) [16]. According to Cavendish, this residue was

> certainly not more than 1/120 of the bulk of the phlogisticated air [nitrogen] let up into the tube; so that if there is any part of the phlogisticated air [nitrogen] of our atmosphere which differs from the rest and cannot be reduced to nitrous acid, we may safely conclude that it is not more than 1/120 part of the whole [17, 18].

Although Cavendish suggested that, in addition to nitrogen, oxygen, carbon dioxide, and water vapor, air might contain another unreactive, colorless, odorless, insoluble gas, his experimental results were forgotten by most chemists. More than a century later—in the course of an investigation of the densities of hydrogen and oxygen to learn if their ratio confirms Prout's hypothesis (He found their ratio to be 1:15.882 [19].)—Lord Rayleigh (John William Strutt) (1842–1919) found that the density of nitrogen prepared from ammonia (NH_3) was less than that of nitrogen prepared from air. In a letter of September 7, 1892 to the journal *Nature* he reported his results and asked readers to suggest an explanation for the discrepancy, which was beyond experimental error, but no suggestions were received [20]. At a meeting of the Royal Society on April 19, 1894 he suggested that chemically prepared nitrogen might be contaminated with a less dense gas.

Ramsay then asked Rayleigh for permission to experiment with atmospheric nitrogen [15, 17, 21]. In his Nobel address, he stated:

> In my copy of Cavendish's life, published by the Cavendish Society in 1849 [22], opposite his statement that on passing electric sparks through a mixture of nitrogen with an excess of nitrogen,…I find that I had written the words "look into this." It must have been the latent memory of this circumstance which led me, in 1894, to suggest to Lord Rayleigh a reason for the high density which he had found for "atmospheric nitrogen" [2].

Contrary to Rayleigh's supposition, Ramsay believed that atmospheric nitrogen might contain a denser gas. In large-scale experiments he passed atmospheric nitrogen repeatedly over hot magnesium, which reacted to form solid magnesium nitride (Mg_3N_2) and left behind a small amount (about 1/80) of an unreactive gas. When he analyzed the gas spectroscopically, he observed, in addition to the lines of nitrogen, lines of a hitherto unknown gas. Sir William Crookes (1832–1919) later studied its spectrum and observed nearly 200 lines [23]. Rayleigh also repeated Cavendish's experiments and confirmed the presence of an unknown gas (1/107 of the original volume).

Ramsay and Rayleigh began to work together and exchanged letters almost every day. On May 24, 1894 Ramsay wrote, "Has it occurred to you that there is room for gaseous elements at the end of the first column of the periodic table?" On August 4 he wrote to Rayleigh that he had isolated the gas, and on August 6 Rayleigh replied that he too had obtained it "in miserably small quantities," and he suggested that they jointly announce their discovery [15, 24]. On August 7 Ramsay agreed, and on August 13, 1894 the pair announced their discovery to the British Association at Oxford of a new element in the atmosphere—the first inert gas—which at the suggestion of the chairman, H. G. Madan, they called "argon" from the Greek, meaning "the lazy one," because of its unreactivity [21, 25, 26]. Ramsay made a formal report of his and Rayleigh's results before an audience of at least 800 persons in a lecture at the University of London on January 31, 1895 [24]. Ramsay suggested that it be placed in a new group of zerovalent elements in the periodic table between chlorine and potassium [27]. The collaboration between Ramsay and Rayleigh was apparently an ideal one, for according to Ramsay's assistant Morris W. Travers (1872–1961), in all the correspondence between the two "there is no indication…of suspicion or sense of injustice on either side" [21].

The Discovery of the Other Inert Gases

During the next three years four other inert gases were discovered. In 1868 in India French astronomer Pierre-Jules-César Janssen (1824–1907) observed a total eclipse of the sun and made the first spectroscopic study of its chromosphere [28]. English astronomer Sir Norman Lockyer (1836–1920) found that a new yellow spectral line (D_3) noted by Janssen did not belong to any known element but to a hypothetical new element, which he named "helium" (Greek, sun) [29]. (The suffix "ium," characteristic of the names of metals, apparently indicated that Lockyer thought that the element was a metal.) For a quarter of a century scientists believed that although it might possibly exist on the sun, it had never been found on the earth. In fact, most spectroscopists doubted its existence, and some even ridiculed it [29].

In 1888–1890 American chemist William F. Hillebrand (1853–1925) treated the mineral uraninite with acid and noted the evolution of a gas that he thought was nitrogen [30]. Ramsay disagreed with Hillebrand's results and repeated the experiment with a similar uranium mineral, cleveite [31, 32]. He obtained nitrogen but also argon and another gas with different spectral lines. He sent samples of the unknown gas to Sir Norman Lockyer and Sir William Crookes. By March 1895 the new gas was shown to be identical with Lockyer's solar element—helium [27, 33]. At about the same time Swedish chemist Per Theodor Cleve (1840–1905) and his student Nils Abraham Langlet (1868–1936), independently of Ramsay, also discovered helium in cleveite. Ramsay had announced his discovery earlier, but the Swedes' gas was purer than Ramsay's, and they obtained a much better value for its atomic weight [34].

Because the atomic weights of helium and argon were found to be ca. 4 and 40, respectively, Ramsay believed that they might belong to a new group of the periodic system and consequently an intermediate member of the group with an atomic weight of ca. 20 might exist [35]. After abandoning their attempts to discover new gases by heating rare minerals, Ramsay and Travers decided to fractionate liquid air. They removed oxygen and nitrogen by reaction with red-hot copper and magnesium, respectively [36, 37]. On May 31, 1898 they examined the spectra of the inert residual gas and observed a bright yellow line with a greener tint than that of helium and a brilliant green line that did not coincide with any line of hydrogen, helium, argon, or mercury [21, pp 90–91]. They announced their discovery on June 6, 1898 and named the new gas krypton (Greek, hidden) [17, pp 251–255].

However, krypton was not the element intermediate between helium and argon that Ramsay and Travers were seeking but a denser one. Therefore, they continued their search for more than two years for the lighter gas by liquefying and solidifying their argon by surrounding three liters of it with liquid air boiling under reduced pressure, allowing the argon to volatilize, and collecting the more volatile portion, which distilled off first. According to Ramsay's laboratory notebook, the lightest fraction

> gave magnificent spectrum with many lines in red, a number of faint green, and some in violet. The yellow line is fairly bright, and persists at very high vacuum, even phosphorescence [21, pp 95–97].

Willie, Ramsay's 13-year-old son, asked his father, "What are you going to call the new gas? I should like to call it *novum*." (Apparently, at that time, teenagers were fluent in Latin. What a contrast with today!) Ramsay agreed but chose a similar, but better sounding name "neon" (Greek, new) for the gas discovered in June 1898.

By using a new liquid air machine provided by British chemist and industrialist Ludwig Mond (1839–1909), Ramsay and Travers were able to prepare larger amounts of neon and krypton. By repeated fractionation of krypton, on July 12, 1898 they isolated an even heavier inert gas that exhibited a bright blue glow in a vacuum tube. They named it xenon (Greek, stranger) [17, pp 251–255].

The last inert gas to be discovered was first called radium emanation, emanon (no name spelled backwards!), or niton. Pierre (1859–1906) and Marie Curie (1867–1934) noted that when air contacts radium compounds, it becomes radioactive. In 1900 Friedrich Ernst Dorn, Professor of Physics at the Universität Halle, explained this fact by showing that one of the disintegration products of radium was an inert gas, now known as radon [38–40]. In 1903, together with future (1921) Nobel chemistry laureate Frederick Soddy (1877–1956), Ramsay detected the presence of helium in the emanations of radium. In 1910 Ramsay and Robert Whytlaw Gray (1877–1958) determined its density and showed that it is the densest gas known [41].

We now fast-forward more than a half century. As chemical educators, we visualize ourselves as open-minded scientists uninfluenced by authority, who pride ourselves on viewing our scientific beliefs not as absolute truths but as tentative hypotheses that we are prepared to modify or abandon in the light of new discoveries. However, in July 1962, while attending a conference on Advances in the Chemistry of Coordination Compounds held at Ohio State University in Columbus, my open-mindedness was put to the test—and I flunked! [42]. Someone interrupted one of the lectures and announced that Neil Bartlett, a young (born 1932) and comparatively unknown lecturer at the University of British Columbia at Vancouver, had prepared a compound of an inert gas—xenon hexafluoroplatinate(V), $XePtF_6$ [43, 44].

For chemists of my generation the inertness of the inert gases was a watchword that we diligently and regularly taught to students in our introductory chemistry courses. A common witticism among us was that a book on *The Chemistry of the Inert Gases* would be a volume with blank pages. Therefore, faced with the news that one of chemistry's most cherished assumptions had been broken, I chose to assume that the announcement was a joke. After all, chemical educators, especially when away from their academic home grounds, have been known to delight in foisting all sorts of pranks on their unsuspecting colleagues. But the joke was on me when I found a detailed report about Bartlett's discovery in *Chemical & Engineering News* on my return from the conference. This discovery forced every teacher or textbook author of introductory chemistry to revise his or her previous treatment of atomic structure—a humbling experience that shows how far short we fall from our ideals.

In 1962 several inert gas fluorides were isolated [45–48], and soon many other inert gas compounds were prepared. Since then, inert gases are known as "noble gases," and many books, numerous reviews, a book-length bibliography, and an entire volume of *Gmelins Handbuch der anorganischen Chemie* have been devoted to the chemistry of a group of elements that not too long ago were universally thought to have no chemistry at all. Surely, a cautionary tale for all of us!

Ramsay and the Nobel Prizes

Ramsay was involved with the Nobel Prize in Chemistry since its very inception. In 1901, the year of the first competition [49], he was one of 11 chemists who nominated Jacobus Henricus van't Hoff (1852–1911), who won the prize that year. In 1902 he was one of five nominators of Marcellin

Berthelot (1827–1907). That same year, in which Emil Fischer (1852–1919) won the prize with five nominations, Ramsay received three nominations—from Adolf von Baeyer (1835–1917), Friedrich von Hefner-Alteneck (1845–1904), and van't Hoff. In 1903 Ramsay was one of three chemists who nominated Henry Moissan (1852–1907). Ramsay received four nominations that year, in which Svante A. Arrhenius (1859–1927) received the prize with 12 nominations. In 1904 Ramsay was one of six chemists who nominated Moissan, and Ramsay finally won the prize with 23 nominations, the largest number of nominations received by a single candidate up to that time. According to Robert Marc Friedman, "The 1904 prize to William Ramsay for his discovery of the inert so-called noble gases was probably as close to inevitable as any decision" [50]. From 1905 through 1916, the year of his death, with the exception of the years 1909–1911, Ramsay annually submitted nominations for the chemistry prize (two nominations in 1908 and 1912).

Also in 1904, the year in which Lord Rayleigh received the prize in physics with 11 nominations, Ramsay received one nomination for the physics prize—from Max Planck (1858–1947). In 1905 and 1906 Ramsay was one of the ten and eight nominators, respectively, of Joseph John (J. J.) Thomson (1856–1940) for the physics prize. In 1905 Philipp Lenard (1862–1947) won the prize, despite his receiving only two nominations. In 1906 Thomson won the prize.

Ramsay's Life and Work

The only child of civil engineer and businessman, William, and Catherine Ramsay (née Robertson), Sir William was born on October 2, 1852 in Glasgow, Scotland [3–9]. In spite of his family's scientific background, he was expected to study for the Calvinist ministry. He completed his secondary education at the Glasgow Academy and in 1866 entered the University of Glasgow, where he read the standard course in classics. He became interested in chemistry on reading about gunpowder manufacture in a textbook, and he attended lectures on chemistry and physics. Beginning in 1869, he also worked for 18 months as a chemist apprentice for Glasgow City Analyst Robert Tatlock (1855–1950).

From April 1871 to August 1872 Ramsay worked under Rudolph Fittig (1835–1910) at the Universität Tübingen on toluic and nitrotoluic acids, which earned him a Ph.D. degree at the age of 19. In 1872 he became Assistant in Chemistry under Georg Bischof at the Anderson College (now the Royal Technical College) in Glasgow and in 1874 Tutorial Assistant to John Ferguson at the University of Glasgow. He became Professor of Chemistry in 1880 and also Principal in 1881 at University College, Bristol. In 1881 he married Margaret Buchanan, who bore him a son and a daughter. In 1887 he succeeded Alexander W. Williamson (1824–1904) as Professor of Inorganic Chemistry at University College, London, where he set up a private laboratory and remained until his official retirement in 1912. He remained at his post until he was succeeded in March 1913 by Frederick G. Donnan (1870–1956). He then continued to work in his laboratory at his home in Hazlemere.

Ramsay was a scientist of exceptionally wide interests and talents. He was an experimentalist rather than a theorist. His earliest works involved organic chemistry, specifically picoline and the decomposition products of the quinine alkaloids (1878–1879). Beginning with the 1880s, he worked on physical chemistry topics such as stoichiometry, thermodynamics, surface tension, density, molecular weights, and the critical states of liquids and vapors. However, his most important achievements involved inorganic chemistry.

Honors and Awards

Only a few of Ramsay's honors will be cited here. In 1888 he was elected a Fellow of the Royal Society, and he received the society's Davy Medal in 1895. He was awarded the Smithsonian Institution's Hodgkins Prize (1895), the Chemical Society's Longstaff Medal (1897), and the Deutsche Chemische Gesellschaft's Hofmann Medal (1903). In 1902 he was created a Knight Commander of the Order of Bath (K.C.B.). In 1904, as we have seen above, he received the Nobel Prize in Chemistry.

Ramsay's Last Years

A cultured gentleman and patient teacher, Ramsay was admired and loved by almost everyone who knew him. He traveled extensively and was fluent in several languages, especially in both written and spoken German. He corresponded extensively with many German chemists and visited Germany several times [51].

In particular, Ramsay and 1902 Nobel chemistry laureate Emil Fischer (1852–1919) possessed scientific and personal common interests that created a strong bond of friendship between them. They were almost exactly the same age, being born only one week apart in the same year (Ramsay, October 2; Fischer, October 9). Both were Nobel chemistry laureates, each being the first recipient from his respective homeland. Each received high honors from his country, each had a great fondness and respect for the other's country, and each had a son who studied in the other's country.

It was a poignant tragedy that their relationship nurtured so carefully for more than two decades was brought to an abrupt end by the advent of World War I [52]. This war was the first "total war," in which not only armies but total populations were mobilized on behalf of the war effort. Inasmuch as science and technology had assumed a much greater role in waging war, scientists in particular were expected to play their part in ensuring victory. In October 1914 a powerful denunciation of allied claims of German wrongdoing, "An die Kulturwelt" (To the Civilized World), was signed by 93 of Germany's leading scientists and intellectuals, including 15 scientists, many of whom were Nobel laureates such as Emil Fischer [52]. In response, 117 British scholars, including Ramsay, signed a counter-manifesto, "Reply to the German Professors" [53].

As early as 1915 Fischer had considerable doubt about a German victory, had called for a resumption of international scientific cooperation as soon as the war was over, and campaigned to convince "the 93" to issue another manifesto calling for an end to the war. In contrast, Ramsay became caught up in the violent chauvinistic feeling of the time. He repudiated his former Germanophilism and made violently anti-German public statements, both in speeches and newspaper articles. His vituperative remarks became a source of surprise and alarm to his former colleagues in Germany. In the Deutsche Chemische Gesellschaft, which had awarded him its Hofmann Medal and to which he had been elected an honorary member in 1899, his intemperate conduct led to what was known as "der Fall Ramsay" (the Ramsay case).

In Ramsay's defense, his behavior was typical, rather than unique, and differed from that of other British chemists only in its degree of vehemence. Also in his defense, his extreme anti-German sentiments, especially as shown in his later statements, may have been a consequence of his mental state caused by the pain of his terminal nasal cancer and the knowledge that he was dying. Yet, although Ramsay's German colleagues were understandably upset by his statements, their view of his wartime activities, written following his death at his home in Hazlemere, near High Wycombe, Buckinghamshire, England on July 23, 1916, at the height of the conflict, were restrained and understanding. He was mourned internationally at the height of the conflict [7].

Unfortunately, neither Ramsay nor Fischer lived long enough to witness the remarkable rebuilding of the international scientific community during the 1920s. (Fischer committed suicide in 1919.) It is a tribute to both men that the spirit of cooperation that they helped to create in the prewar era and that they had exemplified in their own relationship with each other would outlast the bitterness of war and reemerge in peacetime [52].

The 1904 Nobel Prize in Physics

On December 10, 1904, the same day that Ramsay received his prize in chemistry, Sweden's King Oscar II awarded the 1904 Nobel Prize in Physics [54] to Ramsay's collaborator Lord Rayleigh (John William Strutt) [55], Professor of Natural Philosophy at the Royal Institution of Great Britain, "for his investigations of the densities of the most important gases and for his discovery of argon in connection with these studies" [56]. As was the case with Ramsay, Professor J. E. Cederblom delivered the presentation speech [57]. Perhaps some physicist with an interest in history has written or will write an article to commemorate Rayleigh's prize.

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