Henry Cavendish (1731–1810), the discoverer of hydrogen (phlogiston) in 1766, studied atmospheric gases for many years. In 1785, he wondered “...whether there are not in reality many different substances confounded together by us under the name of phlogisticated air [nitrogen].”1 By means of electrical sparking, he reacted phlogisticated air with dephlogisticated air (oxygen) to form nitrous air (nitrogen oxides) and “continued to spark till no further diminution took place...only a small bubble of air remained unabsorbed, which certainly was not more than 1/120 of the bulk of the phlogisticated air.”1

Lord Rayleigh.2 John William Strutt, 3rd Baron Rayleigh (1842–1919) (Figure 1), was the second Cavendish Professor of Physics (1879–1884) at the University of Cambridge (following James Clerk Maxwell, 1831–1879). Rayleigh is well known for his publications on Rayleigh scattering (explaining the blue color of the sky) and Rayleigh waves (e.g., surface earthquake waves). He received the Nobel Prize in Physics in 1904 for “his investigations of the densities of the most important gases and for his discovery of argon.”

The discovery of argon was prompted by an attempt to corroborate the postulate of William Prout (1785–1850), who had proposed3 that the atomic weights of the elements were multiples of the primary substance hydrogen. Rayleigh accurately weighed samples of purified hydrogen, oxygen, and nitrogen to determine if in fact hydrogen was a common denominator (Figures 2, 3). He obtained reproducible values for hydrogen and oxygen, but with nitrogen he noticed a discrepancy: atmospheric nitrogen gas weighed more than artificially produced gas. He sent a letter to Nature4 where he queried: “I am much puzzled by some recent results as to the density of nitrogen, and shall be obliged if any of your chemical readers can offer suggestions as to the cause...” Rayleigh’s data showed, for a 1800-cc flask, 2.3102±0.0002 grams for atmospheric nitrogen and 2.2990±0.0006 grams for nitrogen synthesized from ammonium nitrite and other inorganic precursors. Several persons responded, including James Dewar (1842–1923), inventor of the eponymous flask; William Crookes (1832–1919), discoverer of thallium5; and William Ramsay (vide infra). Crookes was the
only one with a specific suggestion, which recalled Cavendish’s earlier research: add oxygen to the nitrogen and spark, remove the resulting nitrogen oxides with caustic potash (KOH), measure the density; repeat until the density does not change.²

William Ramsay: Sir William Ramsay (1852–1916) (Figure 4), the co-discoverer of argon, won the 1904 Nobel Prize in Chemistry simultaneously with Rayleigh for “the discovery of the inert [noble] gaseous elements in air, and his determination of their place in the periodic system.” Ramsay became professor at University College, London, in 1887 (Figure 5), replacing Alexander Williamson (1824–1904, who had proved the divalency of oxygen in 1850.³). Upon reading Rayleigh’s publication in Nature, Ramsay asked him if he could carry out his own investigative studies on the problem. Both agreed that the discrepancy was probably due to a heavier impurity in the atmospheric nitrogen, because all known lighter gases, such as hydrogen, methane, ethylene, etc., had been diligently removed (helium was not yet discov-
The two decided on different tacks: Rayleigh would remove nitrogen from air by sparking in the earlier fashion of Cavendish (Figure 6); Ramsay would remove nitrogen from air by reaction with hot magnesium (Figure 7).

The collaboration. Never was there a more improbable partnership: the impatient Ramsay and the ultra-cautious Rayleigh. It was “not in the character of Rayleigh to do things in a hurry,” while Ramsay would “make hasty conclusions with a minimum of data.” Friends of Rayleigh resented Ramsay’s aggressive style; Lady Rayleigh in her private notes relates how Lord Kelvin was “furious at Ramsay’s interference” in the “greatest discovery of the century [argon].” It is true that Rayleigh and Ramsay could be irritated with each other; however, each respected the other and they understood that the collaborative approaches of a physicist and a chemist could be beneficial. Rayleigh was impressed with Ramsay as an experimenter and his prompt energetic attack on a problem, while Ramsay revered his elder, even declaring that “Rayleigh was the greatest man alive.”

On August 4, 1894, Ramsay wrote Rayleigh: “I have isolated the gas at last . . . and it is not absorbed by magnesium.” He determined the density of the gas “X” to be 20.01 (on a scale where oxygen = 16). Rayleigh replied two days later, “I believe I too have isolated the gas, though in miserably small quantities.” They both recognized that “X” was chemically unreactive and suggested that it belonged to a new family in the Periodic Table.

At the 64th meeting of the British Association [for the Advancement of Science] at Oxford on August 13, 1894, the two scientists presented a preliminary announcement of the existence of a new gas in the atmosphere. The chairman, Henry George Madan (1838–1901), suggested the name “argon,” from Greek argoz (“idle,” “indolent”) from its chemical inertness (Note 1). Considerable doubt existed regarding the nature of this new gas—it was simply difficult for people to believe that under their noses existed a previously unknown substance making up a substantial portion of the atmosphere. The very notion of an element that did not react chemically was antithetical to the views of some—James Dewar believed it was simply a form of nitrogen, perhaps N3.

The next year a complete story could be presented. On January 18, 1895, a special meeting of the Royal Society was held at its Burlington House on Picadilly (today the home of the Royal Society of Chemistry) with an audience of 800. A complete review of the research by Rayleigh and Ramsay was given, including a determination of the ratio Cp/Cv (heat capacities at constant pressure and volume) of 1.67 which indicated a monatomic gas. Then a report by Karol Stanislaw Olszewski (1846–1915) of Krakow, Poland was presented (by Ramsay) of the cold temperature behavior of the gas: specific values of the melting point (-189.6°), boiling point (-187.0°), critical temperature (-121°), and critical pressure (50.6 atm) were determined, establishing the gas as a simple substance (the modern respective values are -189.2°, -185.7°, -122.4°, 48.0 atm). Finally, William Crookes reported on the spectrum, which was characteristic and unique.

Helium and future plans. Barely two months after Ramsay’s complete description of argon, he announced (March 29, 1895) his discovery of terrestrial helium. As a courtesy, Ramsay had asked Rayleigh to help work out the discovery, but Rayleigh declined—he did not think “working in double harness was very congenial to his habit of mind.”

Thus, Ramsay was free to launch his own private pursuit of possible other inert gases. At the 67th meeting of the British Association [for the Advancement of Science] in Toronto,
Morris William Travers
Karol
argon. The excitement of a possible entire new Ramsay in 1894, just after the discovery of University College, London, joined the group of (1872–1961), (Figure 8), an undergraduate of "Undiscovered Gas." ed 20 for the atomic weight for the Döbereiner's Law of Triads and boldly predict- of atomic weights from the Periodic Table. He was simply underscored the difficulties in predicting Periodic Table to predict this new element. Ramsay was concerned about uncertainties in predictions from the Periodic Table. He was aware of the predictions of Locq de Boisbaudran, who, impressed by the prophesy of his element (gallium) by Mendeleev, used extrapolations from the Periodic Table to predict a much lower atomic weight (36.40) for the "element [argon] between chlorine and potassium." In reality, the atomic weight of argon was much greater (40), even larger than that of the following element, potassium (39), in the Periodic Table. In fact, "reversals" of atomic weights had been observed twice before in the Periodic Table (viz., Te/I and Co/Ni)\(^5\), which simply underscored the difficulties in predicting of atomic weights from the Periodic Table. Ramsay preferred the simplicity and success of Döbereiner’s Law of Triads and boldly predict- ed 20 for the atomic weight for the "Undiscovered Gas."

Morris Travers. Morris William Travers (1872–1961), (Figure 8), an undergraduate of University College, London, joined the group of Ramsay in 1894, just after the discovery of argon. The excitement of a possible entire new group of elements fascinated Travers and he became Ramsay’s junior partner through the discovery of a whole series of inert gases.

Ramsay had been preoccupied with his "undiscovered gas," but other inert gases were serendipitously discovered first. By 1898, Ramsay and Travers had been preparing argon on a large scale by separating it from the atmosphere with liquid air, now prepared in quantity by the new process developed in 1895 by William Hampson (1854–1926).\(^1\) One day a liter of argon, neglected because of other tasks, evaporated over the period of a week. A sudden inspiration of Ramsay led to the study of the residual liquid. Although it exhibited spectral lines of argon, also visible were two new lines, a green and a yellow-green line. It was a new gas! Ramsay named it krypton, for “hidden.”\(^7\)

During another evening, on a hunch Travers stayed late to collect a bubble of residual gas in the pump (which was usually discarded). Ramsay arrived the next day to find they had another gas with new blue lines. They named this gas xenon, for “stranger.”\(^7\)

Next, upon liquefaction of a sample of air, the remaining uncondensed gas was studied. Along with the yellow line of helium, it also exhibited brilliant red lines, a "blaze of crimson light." It was named neon for "new."\(^7\) Although the other heavier gases—argon, krypton, and xenon—could be separated and isolated by a series of fractional low-temperature distilla- tions, the volatile neon could not be separated from helium. Thus, the atomic weights and other physical properties were known for all the inert gases except neon.

There was only one solution: prepare liquid hydrogen, which would condense neon but not helium. The separation of neon from helium attests to the genius and tenaciousness of Travers—he received no help whatsoever from Dewar, who had earlier prepared liquid hydrogen (May 10, 1898) but published no details.\(^1\) Travers, who had always loved to tinker with appliances, took it upon himself to design and build a hydrogen liquefier from scratch.\(^1\) By July 7, 1900, he was successful, and the helium-neon mixture condensed out 15 mL of neon, whose boiling point of 27°K (-246°C) was only 7 degrees higher than that of hydrogen, 20°K (-253°C). On July 10, 1900, after a final series of purifications, the atomic weight was determined to be 19.98, incredibly close to the prediction at the Toronto meeting\(^2\) in 1897, (the modern value is 20.18). Ramsay exclaimed, as he performed the final calculation beside Travers, “No one will repeat this work for many years to come.”\(^7\) His words were most prophet- ic—this was the last experiment that Travers carried out with Ramsay (Figure 9).

In 1904, Travers assumed a professorship at the University College, Bristol (now the University of Bristol). In 1907, he set up the Indian Institute of Science, Bangalore, India. He returned to England in 1914, and thereafter was involved in many industrial enterprises involving fuel technology and cryogenics.\(^14\)

The science of cryogenics. Karol Olszewski (vide infra) and Zygmunt Florenty Wróblewski (1845–1888) had first condensed oxygen and nitrogen in 1883 at Krakow, Poland.\(^4\) These cryogenic techniques depended upon a cyclic compression and then adiabatic expansion. A decade later, William Hampson in London, and Carl von Linde (1842–1934) in Munich, developed methods of producing liq- uid air in quantity; they filed their patents almost simultaneously in 1895.\(^5\) Linde had a long history of research in refrigeration, and his business developed into an international endeavor; “Linde Industrial Gases” is successful worldwide even to this day.

The pioneering work of Hampson and Linde depended not only on adiabatic expansion, but also on the Joule–Thomson effect, where a real (nonideal) gas experiences van der Waals inter- molecular effects. Liqifying hydrogen was par- ticularly difficult, because the Joule–Thomson effect at room temperature actually warms the lighter gases (e.g., helium, hydrogen, and neon) upon expansion. In order to take advantage of a negative Joule–Thomson effect, hydrogen gas must first be cooled below the "inversion" tem- perature (-68°C).
Hampson was a fascinating individual—originally trained in the classics and law, he was self-educated in engineering. He stunned the scientific community by suddenly presenting his own invention of a compact refrigeration unit (size of a washing machine) that in 20 minutes would produce liquid air in liter quantities (Linde’s unit was four times as large and took hours to prime). Hampson was a quiet, unambitious, generous person; he personally delivered flasks of liquid air to Ramsay’s laboratories, literally enabling the discovery of the inert gases. Hampson then passed on to adult education, writing popular books in science and mechanics, later progressing into the medical field where he invented the precursor to the heart pacemaker. Then he moved on to social and economic issues, like Frederick Soddy.

James Dewar’s contributions Sir James Dewar (1842–1923) at the Royal Institution (the home of Sir Humphry Davy and Michael Faraday) is perhaps best known for his Dewar flask and for his liquefaction of static (liquid, not mist) hydrogen. A chemist by training, he did not deeply understand theoretical physics, and his success with liquid hydrogen has been described as the result of “brute force.” He made an intense effort to liquify helium, but in 1908 he lost out to Heike Kamerlingh Onnes (1853–1926; Nobel Prize in Physics, 1913) of the University of Leiden (Netherlands), who went on to discover superconductivity in 1911. Once it was clear even to Dewar that the inert gases were real, he made an effort to find the “undiscovered element” first hypothesized by Ramsay, but he lost this race as well, even though he had liquefied hydrogen before Travers.

James Dewar never published details on his cryogenic appliances, leading to ill feelings from others, especially Hampson who claimed that Dewar plagiarized his own methods to liquify hydrogen. Hampson even went so far as to state that the “Dewar flask” was actually a “modification and popularization” of the vacuum flask originally invented by Crookes. Hampson felt insulted when Dewar said, “My results would have been attained had Dr. Hampson never existed...” With a “strong affinity for disliked people,” Dewar led a “monastic” life, bitterly criticizing Rayleigh and Ramsay’s discoveries. Dewar maintained that it was “not science” to present merely a swath of gaseous mixtures; he wrote letters to The Times that Ramsay’s gases were fiction and that “argon” was only an allotrope of nitrogen, a perfect analogy of the next member of the same chemical family, phosphorus, which also displayed allotropic forms.

Ramsay’s entry into radioactive chemistry. Frederick Soddy (1877–1956) returned from McGill University in Canada to England in 1903 to work with Ramsay, taking advantage of Ramsay’s expert techniques of micro-management with gases. Soddy wanted to know specifically: Was radon (known at that time as “niton”) a member of the “argon family”? A supply of radium was now available (Figure 10) and Soddy was able to collect sufficient quantities of this radioactive gas and prove that indeed radon did belong to the new family of inert gases.

The phenomenon of transmutation, discovered by Soddy and Rutherford and observed in the generation of helium in Ramsay’s laboratories, impressed Ramsay greatly. After Soddy left his laboratory for Glasgow, some very strange results began to appear from Ramsay’s laboratory. Ramsay’s successful prophecy of the “undiscovered element” neon had been a heady triumph, and with his breezy, unruffled manner he went on to make some preposterous claims: radium not only produced radon and helium, but also catalyzed copper to produce lithium and argon, neon from water, carbon from thorium, etc. The announcements in the sixpence newspapers captured the imagination of the gullible layman with convincing news that transmutation occurred at everyone’s doorstep: “The philosopher’s stone has been found, and it turns out to be a gas!” Even Mary Elvira Weeks (author of Discovery of the Elements) was taken in; she stated Ramsay’s “later work on radioactivity is regarded as even more remarkable than his discovery of the inert gases.”

Leaders in nuclear chemistry were quite upset; Rutherford said Ramsay, plagued with laboratory contaminations, was “more anxious for scientific notoriety than accuracy.” Bertram B. Boltwood queried, “I wonder why it hasn’t occurred to him that radium and thorium are a mixture of the elements?”

Adding to the indignation of scientists, Ramsay’s attitude regarding women particularly offended Ernest Rutherford and Madame Curie—Ramsay said that “all the eminent women scientists have achieved their best work when collaborating with a male colleague” and that “lady scientists would better serve by being nurses or secretaries to scientists or doctors.” Hertha Ayrton (1854–1923), a respected researcher in her own right and one of the women specifically mentioned in Ramsay’s interview, retorted that all of Ramsay’s own work also had been done “when collaborating with a male colleague.”

Perhaps justice was served when Madame Curie and her Norwegian colleague Ellen Gleditsch (1879–1968) proved with a very careful set of experiments, using platinum apparatus instead of glass, that Ramsay’s lithium and other “transmutation products” were contaminants from his glassware. Rutherford and Ramsay were jubilant—“I do hope,” Boltwood wrote to Rutherford, “now that Ramsay has been treed, that you won’t [sic] call off the dogs, but that you keep hammering at him until you have brought him down. He should be absolutely discredited in all matters radioactive, for he entered the field under false colors and has been playing to the grandstand ever since.” Madame Curie suggested to Ramsay that he might repeat his experiments; Ramsay blithely replied, “I am not going to repeat the experiment on Cu-Li transformation. All I can say is that we succeeded in bringing about this transformation and she didn’t.” But the evidence mounted: the neon and argon was contamination from the atmosphere, the carbon

Figure 10. This monument originally stood at Frankfurter Straße 294 in the center of Braunschweig, Germany (N52° 15.43 E10° 30.77). It reads: [in German] Hermann A. Buchler, 1815–1900, founder of the firm Hermbuchler London, sugar refinery and quinine works, Braunschweig, Buchler & Co., 1858–1958. [in Latin] For many years. It was here that Friedrich Oskar Giesel (1852–1927) initiated the side venture of radium production; Rutherford, Soddy, and Ramsay obtained their radium from him. This monument now stands at the new site of Buchler, Harzbütteler Straße 3, Thune, 8.3 km north (N52° 19.80 E10° 30.39). Giesel was the co-discoverer of actinium in 1902.
was from oxalate contamination. Soon the radioactive experiments were dropped and Ramsay’s radioactive research was forgotten by others.

**Ramsay’s final days.** In 1912, Ramsay toured America, including a visit to Houston, Texas. Here he participated in the opening of Rice Institute (October 10–12), presenting three inaugural addresses among a group of seven international scholars and scientists invited for the special occasion. Ramsay’s talks are interesting as they represent the limits of the classical nineteenth century science to understand the electron, chemical bonding, and radioactivity—all on the eve of Moseley’s atomic numbers (1913–1914), Bohr’s quantum atom (1913), Soddy’s radio-elements (1914), and Gilbert N. Lewis’ (AXX, Sigma ’13) covalent bonding (1916) (Note 2).

Returning to England, Ramsay gave his last lecture at the University College, London, in June 1912. Always esteemed at his University and popular with his students, a special ceremony was held on March 18, 1914, where the Milbanke painting (Figure 4) was presented to him. Lady Ramsay remarked that the expression on her husband’s face in the painting was “that which he has when he is interrupted at his work by a visitor and wants to look as pleasant as possible.” The ceremony[26] highlighted his being the “only man to discover a complete Periodic Group of elements.” He and Lady Ramsay retired to the country (High Wycombe, Buckinghamshire, 50 kilometers west of London), where he passed away two years later.

In a future issue of *The HEXAGON* we will return to Connecticut,[27] the origin of yet another element discovery.

**Acknowledgments**

The authors are indebted to the gracious hospitality of Lord and Lady Rayleigh (John Gerald Strutt, 6th Baron) of Terling, who gave a personal tour of the historic laboratories on their estate and furnished much important information about his famous great-grandfather scientist.

**Notes**

1. Henry George Madan (1838–1901) also had suggested the names for the newly discovered satellites of Mars (Phobos and Deimos). Madan was originally trained in the classics, but became a chemist (M.A. at Oxford) and was head of the Science Department at Eton College. Henry was the brother of Falconer Madan (1851–1935), whose granddaughter, Venetia Burney (1918–2009), first suggested the name of the dwarf planet Pluto.[27]

2. These Rice inaugural talks include several factual errors, e.g., that Becquerel characterized uranium radiation as “a-rays”; and embarrassingly Ramsay was still insisting that radon (“niton”) catalyzed copper to lithium, thorium to carbon, and water to neon. Ramsay never understood the phenomenon of radioactive decay; even Travers admitted Ramsay was “a mere tyro” concerning transmutations.[28] Soddy relates a story where Ramsay pinched a large fraction of his precious radium bromide and to his “absolute horror” held it in a Bunsen burner to determine its flame color (carmine), thus “permanently spoiling the laboratory for any delicate laboratory work.”[29]

**References**


17. W. Hampson, *Nature* (a) 1897, 55(1430), 485; (b) *1898*, 58(1491), 77; (c) *1898*, 58(1495), 174.


26. ______, *Nature*, 1914, 93(2317), 91. [The date of the ceremony was March 18, 1914.]