

Rediscovery of the Elements

Helium



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Helium was first detected spectroscopically in the sun in 1868 by two independent astronomers at opposite ends of the earth — Pierre Jules César Janssen (1824–1907) in India and Joseph Norman Lockyer (1836–1920) in England. Priority disputes of elemental discoveries often could be contentious, but in this case mutual collaboration brought the two gentlemen together in a close friendship that lasted their entire lives.

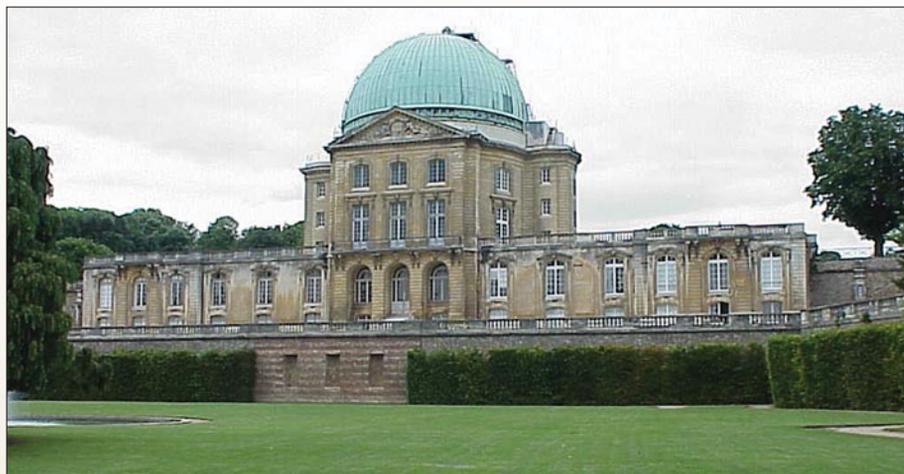
The French Globetrotter.¹ Throughout his life Pierre Jules César Janssen wandered about the world, visiting Peru to determine the position of the magnetic equator; Algiers to observe the transit of Venus; many mountaintops to set up solar observatories; scattered locations throughout Europe, Asia, Africa, and the Pacific Ocean to observe solar eclipses; and the United States and Canada, engaged in speaking tours (Figures 1 and 2).

The total solar eclipse that brought Janssen fame occurred on August 18, 1868, visible in Asia and with the unusually long duration of 6 minutes 57 seconds.¹ For an observation post Janssen chose Guntur, the center of a large cotton trade in the southeastern state of Andhra Pradesh, India. The French had established a colony here in the mid-1700s (before the British East India Company arrived in 1788), and



Figure 1. (LEFT) Janssen's memorial, erected in October 1920, at the top of a hill in Meudon, a southwest suburb of Paris (N48° 48.33 E02° 13.99). From this statue is a clear panoramic view of Paris (with the Eiffel Tower 7.5 km distant). At the base is an inscription celebrating some of Janssen's noted achievements, including his study of the total eclipse of the sun August 18, 1868, in Guntur, India. Janssen's generous and affable personality won him many friends on both sides of the Atlantic Ocean, from Thomas Alva Edison to Alexander Graham Bell.

Figure 2. (BELOW) Near the Janssen memorial (160 meters west) is the Meudon Observatoire (N48° 48.30 E02° 13.87). When Janssen returned from India in 1869, he supervised the construction of the new observatory. Lockyer, with no envy for his dear friend, actively supported the idea, stating that science should truly be without international boundaries. In 1876, Janssen set up his elaborate set of telescopes and laboratories at the Meudon estate, originally acquired by Louis XIV in 1695 for Le Grand Dauphin. The observatory was built onto an old château-fort (fortified castle) dating back to the 1500s.



Janssen found hospitality with the family of a French merchant, Jules Lefaucheur. This French host offered the complete facilities of his home including his roof for observation ("the highest and best situated in the village").² "I am having a screen of bamboos and mats made against the wind," Jules wrote to his wife Henriette.

"We have the whole of an immense room for our instruments. These families are proud and happy to receive us."¹ (This house was probably in the original French colony, now in Old Guntur along the Vijayawada Road in southeast Guntur, ca. N16° 17.5 E80° 27.3). Janssen, with his telescopes (four 16-cm refractors and 21-cm

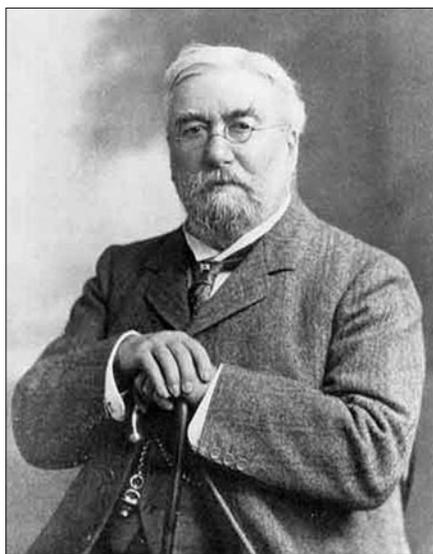


Figure 3. Norman Lockyer coined the name “helium” for the yellow line of its solar spectrum which had originally been confused with sodium (see Figure 7). He had to wait 26 years before his hypothetical element was confirmed by its terrestrial observation in uraninite (UO_2) where it was being produced by the α -decay of uranium.

reflector), was able to record the spectrum of the prominences (“flames”) of the sun. The line spectrum proved that the solar prominences were gaseous in nature, part of the solar atmosphere. Janssen clearly saw the red C and blue F spectral hydrogen lines and the yellow D line (assumed to be sodium). The next day he was able to devise a prism/slit system with which he could observe the sun in broad daylight and which “made eclipses obsolete for observing prominences.”¹

Janssen wrote letters to his wife, the Académie des sciences, the Bureau des longitudes, and several friends. His letters (September 19) did not reach Paris until October 24; they were read to the Académie on October 26.¹

Norman Lockyer, the “Literary Astronomer”^{3,4} (Figures 3,4). Readers of *The HEXAGON* will recognize Lockyer^{5f} as the founder of *Nature* in 1869, a prestigious scientific journal which prospers even today. Lockyer was originally in the Civil Service, with an auxiliary passion for the literary arts. He contributed both scientific articles and human interest stories to newspapers and journals in London. Soon he acquired a hobby in astronomy, which blossomed into a full career. Balfour Stewart (1828–1887), director of the Kew Observatory southwest of London, suggested to Lockyer that a spectral study of the solar “red flames” might be important.³ In 1868, Lockyer

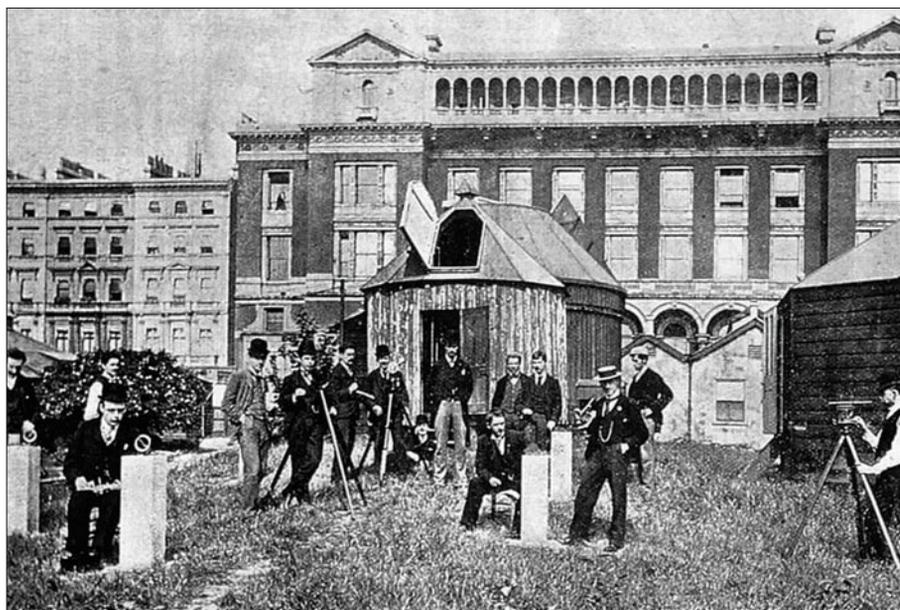


Figure 4. The Solar Physics Observatory in 1893. Norman Lockyer had moved to South Kensington in 1873 and had erected his observatory in temporary wood and canvas structures, in the garden of the Royal Horticultural Society. He oversaw the construction of the observatory in 1879 and became director in 1885. This was the future site of the present Science Museum (N51° 29.86 W00° 10.44). In 1913, his observatory was moved, first to Cambridge and then to Sidmouth, Devonshire where the Lockyer retirement home was located. Courtesy, Imperial College Library.

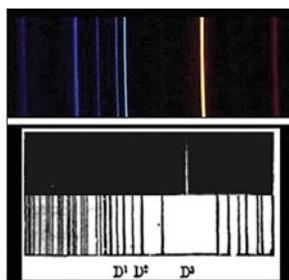


Figure 5. ABOVE: The spectrum of helium exhibits several lines, but prominently a yellow line (the D₃ line of Lockyer). Photograph by the authors. BELOW: Lockyer’s high resolution spectrum (X50 the scale of the upper spectrum) of the D₁ and D₂ lines (sodium; 589.592 and 588.995 nm) and of the D₃ line (helium; 587.562 nm).⁴

acquired a high quality spectroscope for his 6¼-inch refractor and immediately saw the blue, red, and yellow lines of his spectra on the morning of October 20 from his home observatory at 24 Fairfax Road, Hampstead, north London (N 51° 32.59 W00° 10.73). He immediately communicated his results to the Royal Society and to the Académie des sciences. By coincidence the Académie announced his results on the very same day as Janssen’s, on October 26, 1868.¹

Who should receive priority for the discovery? Janssen first observed the promi-



Figure 6. Cleveite. A variety of rare earth-uraninite, named²⁵ by Adolf Erik Nordenskiöld (the biographer of Scheele²⁶ and also the discoverer of crooksite²⁷) for Per Teodor Cleve (1840–1905). This sample is from Norway, from which helium was identified by both Cleve and Ramsay. From the elemental collection of the authors.

nences spectroscopically, but Lockyer had thought of the possibility first, two years earlier.⁶ The occasion was ripe for a bitter dispute, but Hervé Faye (1814–1903), professor of astronomy at l’École Polytechnique⁷, came to the rescue of everyone’s honor by eloquently proposing: “... instead of trying to proportion the merit of the discovery, and consequently diminishing it, would it be better to attribute impartially the whole honor to both of these men of science who, separated by some thousands of miles, have each been fortunate enough to reach the intangible and invisible by a method which is probably the most astonish-



Figure 7. Crookes' house at 7 Kensington Park Gardens (N51° 30.69 W00° 12.16), where he lived from 1880 to the end of his life. He had a complete laboratory here in which he performed the spectral identification of helium for Ramsay. (He previously lived on Mornington Road, 5 km northeast, where he discovered thallium in 1861.⁵⁾

ing that the genius of observation has ever conceived?"⁸ Janssen and Lockyer, both true gentlemen, accepted this compromise. Not only professional harmony, but also a strong friendship developed between the two that lasted 39 years.

The yellow spectral line. Lockyer was puzzled by the yellow spectral line in the solar chromosphere (a term Lockyer coined himself). Originally mistaken for the sodium line, it was not a doublet^{5f} nor did it appear at exactly the same frequency. Lockyer dubbed this line "D₃"⁴ to distinguish it from D₁ and D₂ lines of sodium (Figure 5). He sought the expertise of Edward Frankland (1825–1899), who had assumed the Chairmanship of the Royal College of Chemistry in 1865 when Auguste Wilhelm Hofmann^{5g} returned to Germany. It was logical to speculate that the D₃ line was generated by hydrogen under special conditions of temperature and pressure; however, the D₃ line could not be duplicated in the laboratory. Lockyer believed it was a new element, privately dubbing it "helium," admitting that he did not know whether it was a "metal like calcium or a gas like hydrogen." The first public reference to "helium"⁷ was by Sir William Thomson (Lord Kelvin) in 1871, the newly elected President of the British Association in Edinburgh, who gave credit to both Frankland



Figure 8. This building served as the chemistry building of the University of Uppsala 1850–1903 (now called the "Philologicum"), 3 Thunbergsvägen, on Carolinaparken, Uppsala, Sweden (N59° 51.24 E17° 37.69). Here P. T. Cleve independently isolated and identified helium from cleveite in 1895, taken from Karlskruva, Norway (N59° 20.84 E10° 52.45). Also in this building were discovered holmium and thulium by Cleve, and scandium by Lars Fredrik Nilson (1840–1899), all in 1879. The present modern chemistry complex ("Kemicum," founded 1904) lies 50 meters to the west.

and Lockyer.⁹ However, Frankland, perhaps cautious because of the many erroneous "newly discovered elements" arising from the high resolution spectra now available,^{5f} maintained³ that he did not want to have his name associated with this imaginary element (Note 1).

The discovery of terrestrial helium — prelude in Connecticut. New England has a complex geological history, with periods of mountain creation, folding, and erosion over the past billion years as the drifting continents collided, stretched, and separated. There was once a 30,000-foot mountain range along the present-Atlantic seaboard, which has eroded down to its present hilly environment with rich mineralogical treasures.¹⁰ One historic site is the Andrews (Old Hale) Quarry (a pegmatite outcrop with coarse-grain granite rich in heavy metals) 16 km southeast of Hartford (N41° 27.87 W72° 35.98), dating from the upper Ordovician age, 450 million years ago.¹¹

William Francis Hillebrand (1853–1925), eminent geologist and 27th president of the American Chemical Society in 1906, in 1889 analyzed a specimen of uraninite (uranium oxide) collected¹¹ from the Andrews Quarry by Frank Wigglesworth Clarke (1847–1931), geochemist and 22nd president of the ACS, 1901.¹² Hillebrand powdered the specimen in sulfuric

acid and noticed a gas being evolved. A casual observer would have attributed the gas to carbon dioxide (the field test for carbonates) — but Hillebrand noticed that the gas was evolving continuously and slowly, whereas carbon dioxide would have been generated rapidly. He collected the gas and identified it as nitrogen from its spectrum, with other unidentified lines signifying unknown impurities. This procedure was repeated for specimens from Norway, Texas, Colorado, and other sites, with the same results.

The British studies. Sir William Ramsay (1852–1916), the co-discoverer of atmospheric argon in 1895,^{5h} read the papers of Hillebrand¹³ and wondered if the gas might contain argon as well as nitrogen. He procured a sample of cleveite (Figure 6), isolated the evolving gas, and studied its spectrum. He soon realized the gas contained Lockyer's yellow spectral line.^{14a} He sent capillary samples of his gas to Lockyer and others to confirm his discovery; Lockyer was exuberant to see the "glorious yellow effluence" as he passed a current through his capillary of the gas.¹⁵ William Crookes (the co-discoverer of thallium⁵ⁱ) with his high quality spectral apparatus (Figure 7) confirmed the identification: a sharp yellow line at 587.45 nm, compared with the sodium doublet at 588.91 and 589.51.^{14b} Crookes then could say confi-



Figure 9. Owens College, at the corner of Quay [pronounced “Key”] Street and Byrom Street in Manchester, England (N53° 28.72 W02° 15.12), was the precursor of the University of Manchester. Owens College (1851–1873) was founded by Edward Frankland, who synthesized the first main-group organometallic compound in 1848²⁶ — a specimen of his diethylzinc is presently displayed in the exhibit hall of this building. In 1857, he was succeeded by Henry Enfield Roscoe, who had done a postdoctoral study with Robert Bunsen in Heidelberg,^{5b} (see Figure 10). Roscoe built up this university, overseeing its move to its present site in 1873 (1.8 km southeast), where Rutherford and his team later elucidated the structure of the atom.^{5d} Roscoe’s achievement in the chemistry of the elements was the first isolation of metallic vanadium (1869) at Owens College. Balfour Stewart was also appointed professor of physics here in 1870.

dently in 1895: “The spectrum of the gas is, therefore, that of the hypothetical element helium, or D₃.”^{14b} Lockyer’s helium was vindicated!

Communication between Hillebrand and Ramsay. Hillebrand *could* have made a case that he was co-discoverer of terrestrial helium — since he had observed it first — but in a noble display of courtesy, he wrote to Ramsay (April 4, 1895): “It doubtless has appeared incomprehensible to you that [the helium lines] should have escaped my observation. *They did not.* ... A suggestion was made by one of us... that a new element might be in question.” Hillebrand with great insight speculated that his measurement of the light gas might constitute an “infra-lithium group.” Hillebrand continued, “I have not the slightest thought of claiming or hinting at a prior discovery. I merely wish to absolve myself in your mind. ... from the charge of gross carelessness.”¹²

When Hillebrand’s papers appeared in 1890,¹³ the inert gases had not yet been discovered. Later Hillebrand said,¹⁶ “That is where I missed my chance.” It has been suggested by Hillebrand’s biographer that if argon had been known during his studies on uraninite, today

he undoubtedly would be recognized as the discoverer of terrestrial helium.¹²

The Swedish studies. Less than a month after Ramsay’s announcement of terrestrial helium,^{14a} a note appeared in *Nature*¹⁷ quoting a letter from Per Teodore Cleve (1840–1905) of Uppsala, Sweden. Cleve wrote that he had been informed by letter of Ramsay’s success the very same day that “one his pupils, Mr. Langlet [Nils Abraham Langlet, 1868–1936], tried to get the gas from cleveite in his laboratory” (Figure 8). Cleve observed that it was a “very light gas,” surmising “Will this gas fill the gap between hydrogen and lithium?” He noted that his helium gas was free from argon, in contrast to Ramsay’s impure samples. In subsequent publications¹⁸ Cleve established that he was, at the very least, a co-discoverer of helium, using the special talents of Tobias Robert Thalén (1827–1905), who had taken over the duties of Anders Jonas Ångström (1814–1874). Obviously Cleve’s helium preparations were superior to Ramsay’s — he had no lines of argon in his gas^{18a} and the density was “lower in value” than Ramsay’s^{18b} (in fact, Cleve’s value of 2.02 for the density of helium^{18b} is remarkably close to the

modern value of 1.99). Cleve stated in *Comptes rendus*, that his research showed that the “La présence de l’helium dans une substance terrestre est donc constatée”^{18a} — and he repeated it in Crookes’ *Chemical News*, “The presence of helium in a terrestrial substance is therefore established.”^{18c}

Ramsay would have no part of sharing the honors — he was working “speedily [so that he] could be the first in the field.”¹⁹ Flushed with the success of his recent discovery of argon,^{5b} Ramsay — with a loyal research group headed by Morris William Travers (1872–1961) — was hot on the chase for yet further inert gas discoveries.^{5b} In his biography of Ramsay,¹⁹ Travers barely mentioned Cleve at all (Note 2). However, today it is recognized that both Ramsay/Crookes and Cleve/Langlet deserve the credit for the discovery of [terrestrial] helium in 1895,²⁰ with acknowledgment that the defining spectral support was furnished by Crookes in the former case and Thalén in the second.²⁰

Travers’ biography of Ramsay gives the reason for his impure helium — Ramsay’s apparatus was fraught with leakage problems, and after the nitrogen and oxygen were chemically removed, residual argon from the air remained.¹⁹ The presence of argon did not bother Ramsay, because he originally expected it in Hillebrand’s gas from uraninite and the issue of contamination did not concern him. Ramsay’s problem with contaminants continued to plague him in future studies of radioactive materials.^{5h}

The source of terrestrial helium. Frederick Soddy (1877–1956), the co-discoverer of transmutation and radon (known at that time as “niton”) with Rutherford at McGill University in Montreal,^{5c} returned in 1903 to Great Britain to work for a year with Ramsay before moving on to Glasgow.^{5c} Soddy found in Ramsay’s laboratories that helium was a radioactive decay product of radium and radon. After using liquid air to separate out all other gases, Soddy collected a small sample of the remaining volatile residue in a micro-spectrum tube fashioned by the expert glassworker Ramsay. Soddy’s own words²¹ describe the laboratory event of July 8, 1903: “... all standing space was occupied. News had got round that this was the crucial moment when my transmutation prediction was to be tested. ... I gave Sir William [Ramsay] the ‘all-clear’ and he switched on the coil. ... I suddenly heard him cry out, ‘It’s helium. That’s D₃.’ ... It was helium! ... that single bright yellow line, which Lockyer, 34 years earlier, had discovered across 90 million miles of intervening space in the spectrum of the solar chromosphere.”

This was the first example of an already known element (radium) transmutating to another already known element (helium), and now it was clear why the helium was occurring in uranium and thorium minerals — it was a product of transmutation.

Epilogue. John William Draper (1811–1882), the first president of the American Chemical Society 1876–1877, was born in Saint Helens, Lancashire, England (17 km east of Liverpool). In 1832, he emigrated to the United States and earned a medical degree from the University of Pennsylvania in 1836. Although he became president of the New York University medical school, he is best known for his work in chemistry, photography, and astronomy. He observed in 1847 that at 525 C all materials glowed dull red (called the “Draper point”), shifting toward the blue with increasing temperature — thus anticipating the black-body radiation research of Gustav Kirchhoff (1824–1887) and Wilhelm Wien (1864–1928). He made the first female photographic portrait (of his sister, Dorothy Catherine Draper, 1807–1901) in 1840, and made the first photograph of the moon. He was making the first photographs of stellar spectra simultaneously with European astronomers, paralleling the work of Sir William Huggins (1824–1910).²² (Huggins in 1901 won the Henry Draper medal, awarded for research in astronomical physics).

While others rejected Lockyer’s helium, Draper did not doubt its existence for a moment; he further understood the implications that spectroscopy would vastly expand our knowledge of the universe. Eight years after Janssen’s and Lockyer’s discoveries, he stated in his Inaugural Address to the American Chemical Society:²³

“And now . . . through the vista that has been opened by the spectroscope, what a prospect lies beyond us in the heavens! I often look at the bright yellow ray emitted from the chromosphere of the sun, by that unknown element, Helium, as the astronomers have ventured to call it. It seems trembling with excitement to tell its story, and how many unseen companions it has. And if this be the case with the sun what shall we say of the magnificent hosts of the stars? May not every one of them have special elements of its own? . . . Infinite in influence, eternal in duration! what a magnificent spectacle!”

In the next issue of *The HEXAGON*, we shall visit the rediscovery of argon and the inert gases by Lord Rayleigh (John William Strutt), William Ramsay, and Morris Travers, as well as Ramsay’s ventures into radioactive chemistry. ☉

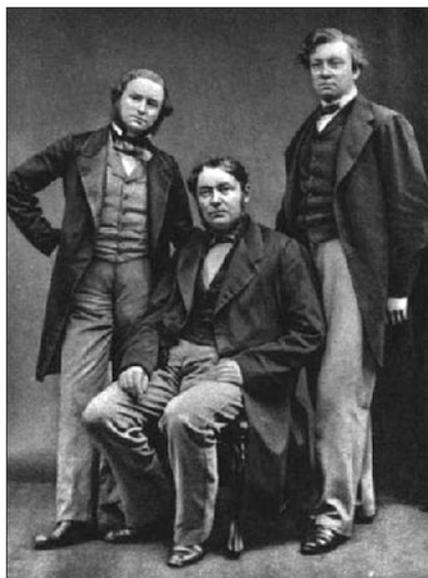


Figure 10. This famous photograph of Gustav Kirchhoff (left), Robert Bunsen (seated), and Sir Henry Roscoe (right) was taken in Manchester by Lady Roscoe, who was a professional photographer. The German scientists were visiting during the London International Exhibition of 1862, which coincidentally was held at the future site of Lockyer’s Observatory (Figure 4). Bunsen and Kirchhoff were the first to discover elements by spectroscopic studies (cesium and rubidium, 1860 and 1861) in Heidelberg.^{5b} Roscoe had been a postdoctoral student for Bunsen (1855–1856) in Germany and contributed to the idea of the Bunsen burner. The three remained close friends throughout their lives.

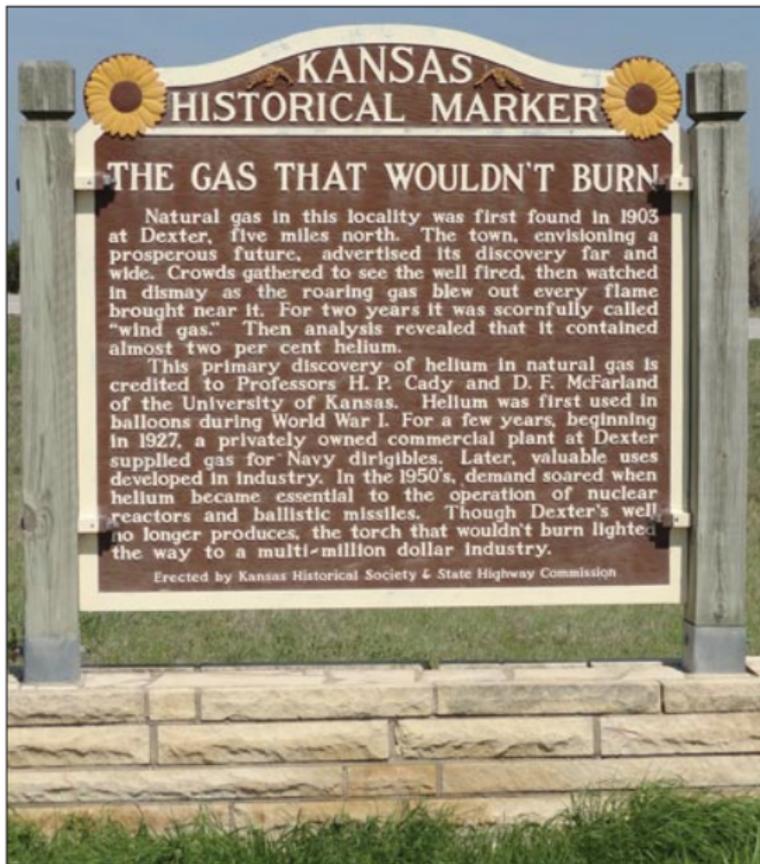
Notes

Note 1. Edward Frankland (1825–1899), a pioneer in organometallic chemistry, was the first chair of chemistry of Owens College in Manchester, England (1851) (Figures 9,10), before he was professor (1865–1885) of chemistry at the Royal College of Chemistry in London and where he assisted Lockyer in the spectral study of laboratory hydrogen gas. Some biographies erroneously label Frankland as a “co-discoverer” of helium, because of the allusion Lord Kelvin made (*vide supra*) to this research of Lockyer and Frankland.⁹

Note 2. In his full biography of Ramsay, Travers condescendingly included the contribution of Cleve in the second half of one short paragraph:¹⁹ “That no others ventured into the field [discovery of helium] requires immediate minor qualifications . . .” Travers claimed Cleve gave no details and that his work “was not continued.” In fact, Langlet with his pure helium went on to measure the specific heat and thereby proved helium was monoatomic.²⁴ Travers also erroneously claimed Cleve discovered cleveite (see Figure 6).

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Hamilton Perkins Cady (1874–1943) and David Ford McFarland (1878–1955) were on the chemistry faculty of the University of Kansas (Lawrence). Both were initiated into the Kappa Chapter of Alpha Chi Sigma of that university on April 20, 1910. McFarland was a geochemist who published the first report (1905) of the noncombustible gas of the Dexter Well. Using procedures of Ramsay, Rayleigh, and Dewar of England, Cady and McFarland made a detailed analysis and discovered helium as part of the inert fraction (mostly nitrogen) of “the gas that wouldn’t burn” (J. Amer. Chem. Soc., 1907, 29(11), 1523–1536). Cady was Chairman of the Chemistry Department at Kansas 1920–1940. This Kansas Historical Marker is found at the intersection of highways 166 and 15 (N37° 06.64 W96° 42.95), 4.6 miles south of the “Helium Park” in Dexter with the capped original well (N37° 10.80 W96° 43.04). Photo by Jenny Marshall.