Rediscovery of the Elements

Daniel Rutherford, Nitrogen, and the Demise of Phlogiston

James L. Marshall, *Beta Eta 1971*, and Virginia R. Marshall, *Beta Eta 2003*, Department of Chemistry, University of North Texas, Denton, TX 76203-5070, *jimm@unt.edu*

Figure 2. Map of Edinburgh, Scotland. The chemical discoveries of Black and Rutherford were performed at the "Old College" in Edinburgh, which is not identified on this modern map, because it demolished and replaced by buildings of the "New College," on South Bridge (N55° 56.85 W03° 11.17). Rutherford, later a professor of botany at the University of Edinburgh, maintained the Botanic Gardens at "Leith Walk" (see Figures 4,5); today's Royal Gardens are located 2 km west. The locations of the homes of Black and Rutherford are known, but they no longer exist. The modern campus is 2.7 km south of the "New Campus."

In the previous *HEXAGON* "Rediscovery" article, the life and work of Joseph Black (1728–1799) was introduced.[1g] As a graduate student at the University of Edinburgh, Scotland, Black discovered fixed air (carbon dioxide) and characterized magnesium as a substance separate from calcium, and thus may be considered the discoverer of that calcareous element. Afterwards, he became professor at the University of Glasgow, where he developed the concept of latent heat. He returned to the University of Edinburgh in 1766 as the head of chemistry. (Figure 1).

Black as a professor at Edinburgh. Upon his return to Edinburgh (Figure 2), Black turned away from fundamental research and instead concentrated on industry and teaching. An active participant in the Scottish Enlightenment, he was sought out by scientists throughout Europe for guidance in chemical curricula and industrial research.[2a] He mentored several graduate students, one of whom succeeded him as chair of chemistry,[2b] Thomas Charles Hope (1766–1844), who first fully characterized strontium, discovered in a mine in northwest Scotland.[1a] Other students of Black attained prominent positions at Oxford University.[2b] Another of his students was Daniel Rutherford (1749–1819), (Figure 3) who was the son of John Rutherford (1695–1779), one of the founders of the Medical Institute at Edinburgh.[1g] Daniel later became Professor of Botany at the University of Edinburgh (Figures 4-6), but never rose to the prominence of his father John or of Joseph Black. However, while a student of Black, he found his mark as the discoverer of "malignant air," later to be known as nitrogen.

The characterization of "malignant air." Daniel Rutherford described the discovery of this new air in his 1772 M.D. dissertation ("Inaugural dissertation on the air called fixed or mephitic").[3] In his dissertation research, Rutherford "destroyed" ordinary air (i.e., removed the oxygen) by burning charcoal, candle, or phosphorus, or by respiration with a living mouse. In the cases where mephitic air (fixed air, or carbon dioxide) was produced, he removed this with alkali, following the procedure of his mentor Joseph Black.[1g] Rutherford concluded that the remaining "malignant air,"[3]

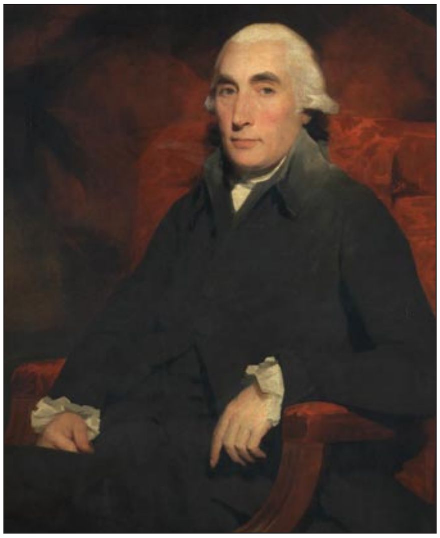

Figure 1. Joseph Black's original painting, from which most black and white engravings are reproduced. It was painted (ca, 1790) by Sir Henry Raeburn, titled "Professor Joseph Black (1728–1799)" Courtesy, Hunterian Museum and Art Gallery, University of Glasgow.

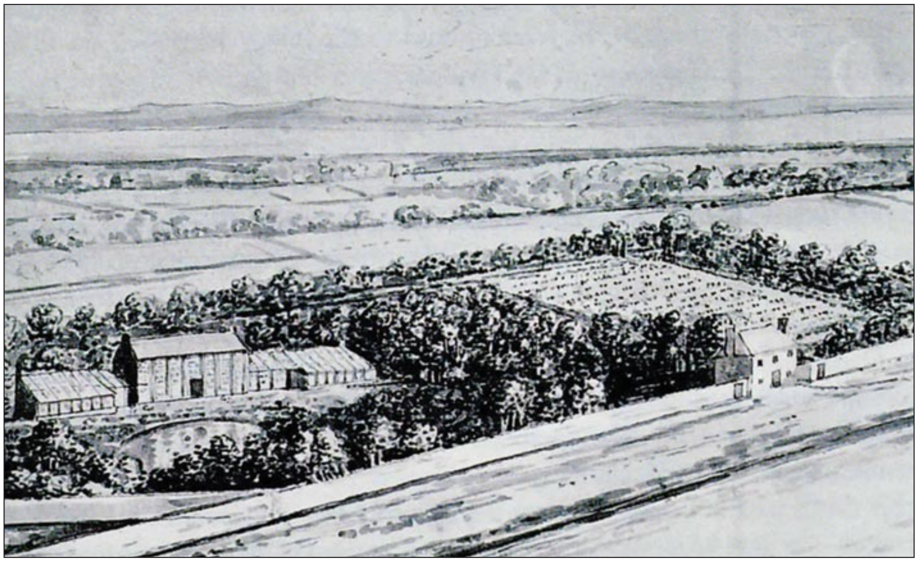

Figure 4. This is a north view of the Leith Walk Gardens at the time of Rutherford, who maintained them when he became Professor of Botany in 1786 at the University of Edinburgh.18 The road in the foreground (left-right) is Leith Walk, which exists today (see map, Figure 2). The field to the right has rows of rhubarb, grown for medicinal purposes; the seeds were obtained from St. Petersburg, Russia. Only a tiny remnant of the original garden exists today (see next figure). Courtesy, Royal Botanic Garden, Edinburgh, Scotland.

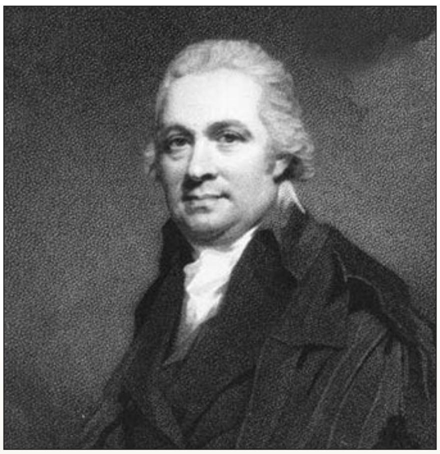

Figure 3. Engraving of Daniel Rutherford, after a painting by Sir Henry Raeburn, from ref 6.

Figure 5. Leith walk today: Hopetoun Crescent, an arc extending from Leith walk (road) of a grassy grove of trees with benches for resting (N55° 57.69 W03° 11.05). Inset: Sign on fence.

must be "atmospheric air saturated with phlogiston" since it "cannot be converted into mephitic air by combustion."[3] Rutherford never gave his air a specific name, but did speculate that it was "pure phlogiston united to common air" seeming to "form *another species of air*" [authors' italics].

Rutherford was impressed with the "poisonous" nature of mephitic air, which lay low in caverns and asphyxiated small animals on the cave floor.[1g] He was puzzled by malignant air, because when "all mephitic air had been removed by caustic lixivium [alkali], what remains does not become in any way more wholesome."[3] In another experiment, Rutherford noted that air "which has been blown through ignited coals, and then purified from all mephitic air, is nevertheless still found to be malignant and quite similar to that which is spoiled by respiration."[3] Hearing of Priestley's experiments, where plants became invigorated (and not "poisoned") by fixed air,[3] Rutherford realized that the "malignancy" induced by respiration, combustion, or calcining was a separate phenomenon from the "mephitic" nature of fixed air. Unfortunately, Rutherford never resolved the issue of "mephitic air" vs. "malignant" air.

It is not known where Daniel Rutherford conducted his research.[4a] Quite possibly it was in one of the buildings on the north side of the Physic Gardens (see map of previous *HEXAGON* publication[1g]) which included the original laboratories set up by John Rutherford's Medical group.[4b,5] These buildings were later

Figure 6. The Rutherford Building in the modern University of Edinburgh (N55° 55.33 W03° 10.25) is named after Daniel Rutherford, Professor of Botany and keeper of the Royal Gardens at Edinburgh. Rutherford is also known for inventing the maximum-minimum thermometer; he was also the uncle of Sir Walter Scott (1771–1832).

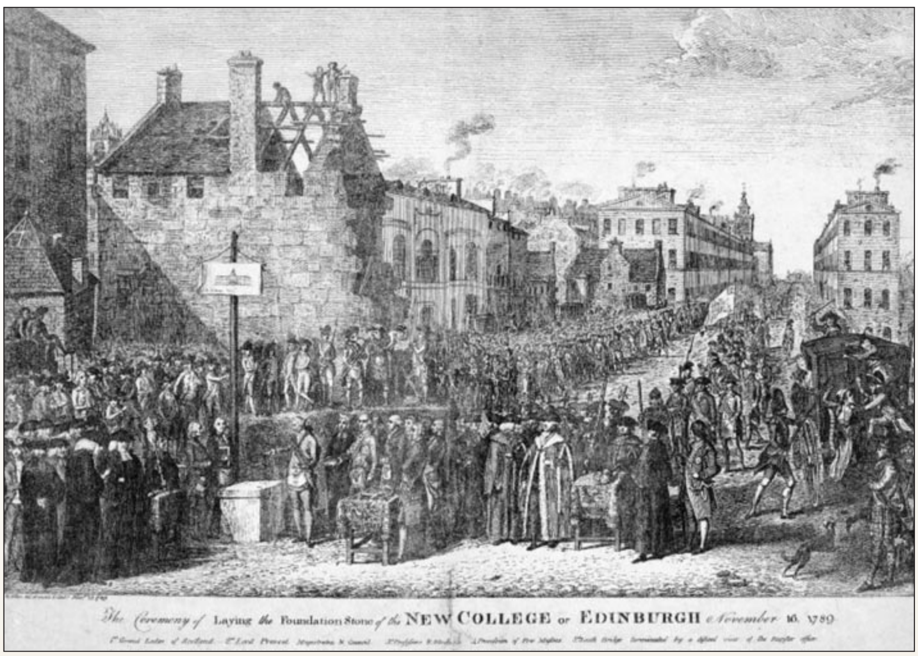

Figure 7. The cornerstone of the New College was laid on November 16, 1789, by George III. The view is northward on North Bridge. The observer's viewpoint is close to the original location of John Rutherford's Medical buildings on the north side of the Physic Gardens, i.e., where the son Daniel Rutherford probably performed his research on "malignant air." See the next figure for the modern appearance of this site. (Drawing 1789, David Allan.)

used by Joseph Black (starting in 1766) for his teaching and laboratory procedures, before he moved into the new chemistry building which was constructed in the Old University Quadrangle in 1781. This building was the one where Hope performed his research on strontium,[1a,4a] and was removed during the later construction of the New Campus at the same site (Figures 7,8).

Cavendish's parallel research. William Ramsay, the discoverer of the inert gases,[1f] believed that since Rutherford recognized that "malignant air" was a new substance, he "may well be credited" with the discovery of nitrogen.[6] However, Henry Cavendish (1731–1810; the discoverer of hydrogen)[1f] performed some work which anticipated Rutherford's research. Six months before Rutherford's thesis was published, Joseph Priestley (1733–1804)[1c] read a paper[7] to the Royal Society relaying private information furnished by Cavendish. In his research, Cavendish gave a more quantitative, but less general, description of Rutherford's gas. Cavendish passed ordinary air through a red-hot tube of charcoal, with subsequent removal of fixed air by caustic alkali. Cavendish repeated this procedure repeatedly, until no more diminution of the air was observed. Thus, he observed a reduction of 180 to 162 ounces,[8c] and he noticed that the density "differed little from ordinary air, perhaps somewhat lighter."[8c] It is not clear what interpretation he gave of these observations, but it appears that he, like Rutherford, considered the residual gas to be the consequence of the "destruction of common air." His work was never formally published, and he has not been generally viewed as a co-discoverer of the gas. (Cavendish later isolated a small quantity of inert gaseous residue from nitrogen by sparking, but he did not understand it was a new separate substance, later recognized as a new element—argon—by Ramsay and Raleigh.[1f])

Scheele's discovery of "spoiled air." Carl Wilhelm Scheele (1742–1786)[1b] may be considered to be a co-discoverer of nitrogen. He described two kinds of air, viz., "spoiled air" and "fire air" (German "verdorbene Luft" and "Feuerluft" or Swedish "skamd luft" and "elds luft," respectively.)[8a] His work was performed at the same time as Rutherford's, but it was not published until 5 years later.[9] (Similarly, oxygen was discovered by Scheele before Priestley, but the opportunistic Priestley published first.[1b,c])

Scheele's understanding of nitrogen was advanced beyond that of Rutherford. Instead of viewing the gas to be the product of some vague "destruction" of air, Scheele believed that "air must be composed of two different kinds of elastic fluids."[9] If had he had published promptly, there is no doubt he would be considered *the* discoverer of nitrogen. In fact, in the German Wikipedia, Scheele is considered the lone discoverer of nitrogen; Rutherford is not mentioned.[10]

What should the new gas be called? After Rutherford's announcement[3] of 1772, the designation "phlogisticated air" or "malignant air"

Figure 8. This is the Edinburgh "New College," South Bridge, built in 1827–1831, on the site of the Old College where Black and Rutherford worked, but is now actually the "Old College," because of the New Campus further south. It presently houses the library complex of the university (Playfair Library Hall).

was commonly used for the portion of the atmosphere remaining after ordinary air had been "destroyed" by combustion and fixed air had been removed.[8b] But it was not clear whether (a) the diminution of the atmosphere during combustion was a fundamental transformation of air, a "consequence of the atmosphere becoming overcharged with phlogiston,"[8b] or perhaps, (b) as Scheele suggested, the atmosphere was composed of two distinct parts that were separable. During the next two decades, various names were proposed for the "phlogisticated air," including:

(a) "mofette"—the gas escaping from a volcanic vent—used earlier by Lavoisier;[8d]

(b) "azote"—"without life"—proposed by Guyton de Morveau, 1737–1816, who introduced the New Chemical Nomenclature (Méthode de Nomenclature Chimique);[8d]

(c) "azotic gas"—used by Cavendish;[11]

(d) "nitrogène" or "nitrogen"—"niter generator," created by sparking the atmosphere—proposed in 1790 by Jean-Antoine Chaptal (1756–1832),[8g] a French industrialist and popular author science texts; and George Pearson (1751–1828), a student of Joseph Black who translated Méthode de Nomenclature Chimique[8e] into English[8i] in 1794.

In Lavoisier's 1789 *Traité*[12] nitrogen was recognized as an element for the first time; he listed it as "azote." The French chemical literature has retained "azote;" but with Pearson's translation of *Nomenclature Chimique*, "nitrogen" passed into the English vocabulary. The Germans use "Stickstoff" ("suffocating substance") and the Swedes "kväve" ("asphyxiate") since the 1790s. The Russians transliterated the French name and call the substance "азот."

Just what exactly is this new gas? Lavoisier's identification of *azote* as an element[12] did not immediately settle the issue of exactly what this substance was. William Higgins (1763–1825), an Irish chemist who in 1784 was one of the earliest antiphlogistonists and an early advocate of the atomic theory, proposed that the atmosphere was indeed a mixture of gases, but was unclear whether oxygen and nitrogen in the atmosphere were separate substances or were combined.[8j] John Dalton (1766–1844) proposed a clearer description of the atmosphere,[1d] which he declared consisted of discrete particles.[8k] In 1803 he hypothesized[8k] that each element consisted of atoms of a specific weight, and he gave each element its own special symbol (e.g., ⊙ for oxygen, ⦶ for nitrogen).[8k] Dalton was formalizing these ideas on the atmosphere and its constituent elements during Priestley's twilight years as Priestley continued to preach that phlogisiticated air (nitrogen) was an undefinable substance containing dephlogisticated air (oxygen), possibly even a compound of dephlogisticated air and inflammable air (hydrogen).[13] But Priestley was now virtually alone with his antiquated philosophy, and when he died (1804) there were no remaining significant adherents to the philosophy of phlogiston.[13] Nitrogen had joined the ranks of the true elements and was included as an authentic member of the elements in Dalton's grand philosophy of 1808.[14]

But the story is not yet finished. A major source of confusion was the large inventory of nitrogen oxides that had been described principally by Priestley and Cavendish. Jöns Jakob Berzelius (1779–1848), the Swedish chemical giant who seemed to be at the "center of nearly every significant scientific discovery in chemistry,"[15] thought nitrogen was a compound of oxygen with an "ammonium" radical, analogous to his idea that chlorine was a compound of oxygen with a muriatic radical.[16] However, by 1823 Berzelius had accepted chlorine[1e] and nitrogen as bona fide elements.[16] But it was not until the final acceptance of Avogadro's hypothesis and the application of Gay-Lussac's Law of Combining Volumes, when Stanislao Cannizzaro (1826–1910) prepared his famous pamphlet of 1858,[17] that the true nature of atmospheric nitrogen was understood. This pamphlet—which was distributed to members of the Karlsruhe Chemical Congress of 1960 and which inspired a German and a Russian (Lothar Meyer and Dmitri Mendeleev) to formulate the Periodic Table several years later[1d]—finally established the true nature of atmospheric nitrogen: a diatomic element, N_2.

The legacy of Joseph Black. The scientific thinking of Joseph Black was so advanced that often he is regarded as one of the first in Great Britain to accept Lavoisier's New Chemistry.[19] James R. Partington (1886–1965), the author of the comprehensive *A History of Chemistry*, implies[8f] that Black was endorsing Lavoisier's views in Edinburgh even before 1784. However, a closer study of Black's life shows a more conservative approach. It was actually one of his students, Richard Lubbock (1759–1808),[8h] who first vigorously advocated Lavoisier's ideas. Lubbock called the vital portion of the atmosphere *principium sorbile* (absorbable principle; called by Lavoisier *principe oxigène*) and he devoted his entire Dissertation in Edinburgh (1784) to this subject.[8h] (After graduation Lubbock became a practicing physician in Norwich, in Norfolk County, England). The first professor in Scotland to advocate exclusively Lavosier's chemistry[19] actually was Black's student, Thomas Charles Hope, who became professor at Glasgow in 1787, later at Edinburgh.

The cautious Black believed there were too many unanswered questions—with a "scheme so dependent upon a few key experiments. . ." he was worried that "should these experiments be overturned the entire structure was undermined."[19] With the backdrop of the Scottish Enlightenment, the role of Black was to create the cultural environment at Edinburgh which allowed free debate, tolerating all views.

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Student societies flourished that nurtured this intellectual freedom, giving rise to "one of the earliest sustained debates over the new chemistry outside Paris."[19] The conversion of Black was gradual. In the end, he was convinced not by the students' youthful exuberance which he fostered, but ultimately by the wealth of their data and cogent arguments. In 1790 he finally proclaimed his endorsement of the New Chemistry in a letter to Lavoisier,[19] which was published in the French journal Annales de chimie.[20]

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