Rediscovery of the Elements

Sir Humphry Davy and the Alkalis



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In a previous HEXAGON article on Joseph Black,^{1h} the three alkalis known in the 1700s were listed: "vegetable alkali" (potash), "mineral alkali" (soda), and "volatile alkali" (ammonia).1h All were known to react vigorously with acids and "to change the color of syrup of violets to green." Ammonia was apparently a compound of nitrogen and hydrogen,2d as shown by Claude Louis Berthollet (1748-1822) at his famous laboratory at Arcueil.1c It was natural, therefore, that Antoine-Laurent Lavoisier (1743-1794) himself, the "father of modern chemistry,"1b who first recognized the true elements and listed 31 that are now found in the Periodic Table,3 would exclude the "fixed alkalis"—potash and soda—from his list,3 because they might be compounds of nitrogen as well. Lavoisier was even unsure of whether potash, produced commercially by the incineration of plants, existed before possibly being created in the plants.2c He further speculated that "vegetable alkali" was synthesized from components in the atmosphere and "mineral alkali" was formed naturally in the sea.3 The true nature of potash and soda was not clarified until the next century, at the Royal Institution in London (Figures 1, 2).

The distinction between potassium and sodium. Henri-Louis Duhamel du Monceau (1700–1782) was the first to differentiate clear-



Figure 1. Royal Institution, 21 Albemarle St. (N51° 30.58 W00° 08.55), was founded in 1799 and has not changed its location since. The Institution was founded by Sir Benjamin Thompson, Count Rumford (1753–1814), an American born British scientist who through observing the boring of cannons realized

heat was created by friction. 10,11a His colorful history included his 1804 marriage to Marie-Anne Lavoisier, the widow of the famous Antoine Lavoisier. 11a

Figure 2. Royal Institution, appearance in 1838 (painting by Thomas H. Shepherd, 1793–1864). At this time Michael Faraday was prominent among its scientists, having succeeded Humphry Davy, who was the first to prepare elemental potassium and sodium here in 1807.10



ly between "vegetable alkali" and "mineral alkali." ^{2b} Duhamel was a botanist; he developed an agricultural/forestry farm at Denainvilliers, a suburb of Pithiviers (75 km south of Paris). Duhamel showed in 1736 that the salts of the two alkalis, as prepared from mineral acids, differ in crystalline form, solubility, and taste. (Today mineralogists describe how "sylvite" (KCl) at Death Valley, California, is the last to precipitate out and tends to form granular masses compared to the distinctive

cubic "halite" (NaCl) crystals; persons taking "low-sodium" salt in their diet are acquainted with the more bitter, astringent taste of KCl.) Duhamel further showed that the alkali component common salt (sodium chloride) is identical with the alkali of Egyptian natron (sodium carbonate), and of borax (sodium borate). Duhamel's estate still exists, complete with his chateau and the original ventilated silo, designed by him and reputed to be the first ever constructed (Figure 3).



France (N48° 9.02 E02° 14.47). Courtesy, Wikipedia Commons, public domain.



Figure 4. Upon entering the Royal Institution, in the hallway is this portrait of Davy by Sir Thomas Lawrence (1769–1830), dated 1821. Davy joined the Royal Institution in 1801. By the method of electrolysis he was the first to prepare metallic potassium and sodium, and went on to prepare strontium, barium, calcium, magnesium, lithium, and boron. He was the first to recognize the elemental nature of chlorine and iodine.

Two decades after Duhamel's work, Berlin chemist Andreas Sigismund Marggraf (1709–1782), reproduced Duhamel's work and further differentiated "vegetable alkali" and "mineral alkali." ¹⁸ He prepared the saltpetres (nitrates) of each with nitric acid and demonstrated (1758) that "cubic saltpetre" (sodium nitrate) flashed yellow with charcoal and "prismatic saltpetre" (potassium nitrate) flashed blue-violet. These colors are the same as those observed in introductory chemistry classes by dropping metallic sodium and potassium into water.

The derivation of the names sodium and potassium. On the coasts of the Mediterranean Basin and Western Europe, there exists a scrubby tidal plant named saltwort, with the generic

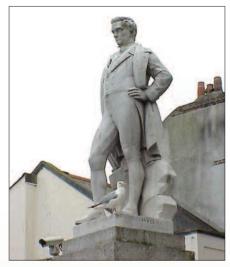


Figure 5. Statue of Humphry Davy at Market Jew Street, Penzance, Cornwall (N50° 07.14 W05° 32.18). Davy never forgot his roots in Cornwall and contributed scientific researches directed to the safety of the tin miners in the area.

name Salsola (meaning "salty"), given by Linneaus in 1753.4 This thistle-like plant was burned in trenches by the seashore to produce alkali economically. Of this genus, two species—S. soda and S. kali—were common sources of alkali. The "kali" was derived from Arabic "qily" meaning "ashes," and "soda" was derived from the Italian word for saltwort, ultimately derived from the Arabic "suwwad." Although incinerated plants generally produced "vegetable alkali," it was observed (e.g., by Duhamel) that Salsola could give either kind of alkali, and if Salsola was grown very close to the brackish water then "mineral alkali" was the main ash.26

The adoption of the names "soda" and "potash" for "mineral alkali" and "vegetable

alkali" occurred during the 17th and 18th centuries. Early references (1690) to "soda" include "soude" by Nicolas Lemery (1645–1715), the advocate of the corpuscular theory of "pointy particles" for acids and "spongy particles" for bases. From the ashes of burned wood came "pot-ash," prepared by boiling the ashes in metallic pots. The name "potash" originated from the German Pottasche, and was approved by the Académie francaise in 1762. Each of the control of the con

By the beginning of the 19th century the distinction between sodium and potassium compounds was clear, and each was now recognized as an element ^{2f} —in his lecture notes of 1806 John Dalton (1766–1844) recognized "soda" and "potash," and assigned each with its respective atomic weight⁵ (28 and 42; modern values 22.99 and 39.10). But no one had ever "seen" the elements in uncombined form.

Humphry Davy (1778–1829). The first person to prepare the alkalis in elemental form was Humphry Davy, at the Royal Institution in London, in 1807.6b,7 Humphry Davy (Figure 4) was born in Penzance in Cornwall (Figure 5). As a youth he was an alert and curious student; his first love was roaming about the countryside observing nature, the community, and the fishers and the tin miners. Drawing from the tales and ghost stories of his aunts and grandmother, he could tell stories that spellbound the common folks of Cornwall. This ability to captivate an audience was to prove beneficial later when he presented public lectures on science at the Royal Institution.7 Davy was a visionary; as he admitted himself, he preferred to "invent, rather than imitate."8 As he rose through the ranks of the scholars, he became the most widely known scientific figure in the British Isles, if not also on the Continent.7

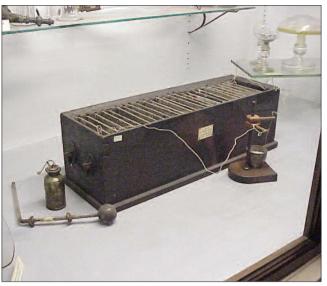


Figure 6. Exhibit in the Royal Institution: The slatted box is of the original design of the voltaic pile used by Davy. Typically, he would line up 100 or more 4- or 6-inch pairs of copper and zinc square plates, immersed in an alum/dilute sulfuric acid solution. This design was the same as that of Berzelius, who was conducting galvanic studies before Davy to show the differential migration of ionic species. The Berzelius museum was visited by the authors in 2000 and is now closed; it was located across the street from the Swedish Royal Academy of Sciences, Lilla Frescativägen 4A (N59° 22.02 E18° 03.09).

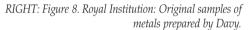




Figure 7. Royal Institution: The bladder to the left was used in Davy's laughing gas experiments. The item to the extreme right is an electrolysis bowl of 1806 design.



The preparation of elemental potassium and sodium. Alessandro Volta (1745-1827) in 1799 invented the voltaic pile or galvanic pile—the first electric battery (Figure 6). His announcement was communicated to the Royal Society of London in 1800, and the word of this new source of electricity spread rapidly, allowing research to develop in many new directions. It was quickly discovered that the voltaic pile could decompose substances; one of Davy's original findings was that water could be decomposed into hydrogen and oxygen in two separate vessels connected only by a conductor.7 Turning to the alkalis, he attempted decomposing potassium and sodium, but again could obtain only hydrogen and oxygen. Reasoning that the water was the source of these gases, he tried potash only slightly moistened; the result was molten metallic globules which he described as the "peculiar inflammable principle" which was "the basis of potash." (Figure 7) As he described the experiment, the globules resembled quicksilver, some of which "burned with explosion and bright flame... finally covered with a white film."6a (He had observed the ignition of evolving hydrogen and the formation of potassium oxide/hydroxide.) We have an eye-witness to the discovery,

Edmund Davy, his cousin, who was acting as assistant: "... [Humphry] could not contain his joy—he actually bounded about the room in ecstatic delight; and some little time was required for him to compose himself sufficient to continue the experiment." A few days later Davy repeated the experiment to obtain elemental sodium. Without a doubt, the elemental production of the "fixed" alkalis was the most famous of Davy's discoveries. (Figure 8)

Davy next turned to the alkaline earths. After some unsuccessful attempts, a suggestion by Berzelius (see Figure 6) to use an amalgam allowed the production in 1808 of elemental calcium, strontium, barium, and magnesium. In Davy's laboratory, elemental boron (Figures 9–11) was produced the same year by reaction of elemental potassium (simultaneously with Gay-Lussac, *vide infra*); and elemental lithium was prepared in Davy's laboratory in 1817 promptly after its discovery by Johan August Arfwedson (1792–1841) in Sweden.^{1d}

Joseph Louis Gay-Lussac (1778–1850). This French chemist, with Friedrich Wilhelm Heinrich Alexander von Humboldt (1769–1859), determined the composition of atmospheric air at the famous laboratory at Arcueil, 66 described

in a previous HEXAGON article.¹¹c Gay-Lussac moved on to l'École polytechnique in Paris, where he co-discovered boron.⁶ He and Louis Jacques Thénard (1777–1857) (the discoverer of hydrogen peroxide) at l'École polytechnique suggested that potassium and sodium were respective compounds of potash and soda with hydrogen.⁶ It remained for Davy to demonstrate the hydrogen was generated from residual water—pure potassium and sodium could not be forced to evolve hydrogen, no matter how savagely they were heated.⁶

The rivalry between Davy and Gay-Lussac was intense. Davy had been awarded a Prize by Napoleon for his electrochemical work,8,9 but Gay-Lussac was offended by the presumptive manner of Davy and was displeased by Davy's taking on the "iodine problem" which he had been studying for two years.8 As described in a previous HEXAGON article,1e this new substance, discovered by Bernard Courtois (1777-1838) in 1811, was a most confusing material—it looked like a metal, but dissolved in ether! When Davy visited Paris in 1813, he recognized the new substance as an element and named it "iodine" in analogy to the chlorine family to which he ascribed it-much to the consternation of the scooped Gay-Lussac, who



Figure 9. The famous California open-pit boron mine (N35° 2.94 W117° 40.98) is located in the Mojave Desert at Boron, 40 miles northeast of Los Angeles. This is the largest borate mine in the world. This deposit was formed 20 million years ago.

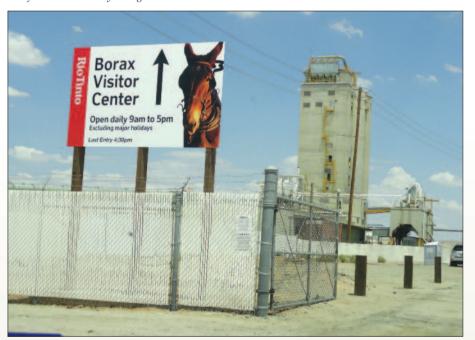


Figure 10. The Rio Tinto Borax Visitor Center, Suckow Road, Boron, California (35° 1.79 W117° 41.24), has a large variety of exhibits explaining the history and uses of borax and its derivatives, as well as many fascinating mineral specimens.

had named it "l'iode." ¹e The "romantic, qualitative" Davy and the "cautious, quantitative" Gay-Lussac ordinarily, in their dual roles, "served chemistry well;" however, Davy could easily overshadow Gay-Lussac, and the (London) Royal Society delighted in noting (20 January 1814) that Gay-Lussac had been trumped: [Iodine] was discovered about two years ago; but such is the deplorable state of scientific men

in France, that no account of it was published till the arrival of our English philosopher there."

Other contributions of Davy. The most important discovery of Davy was the alkali and alkaline earth metals, but the most important *invention* was the safety miner's lamp.⁸ (Figures 12,13) Davy was always mindful of the dangers associated with the tin mines of his Cornish



Figure 11. In the Borax Visitor Center, this impressive crystal of kernite ($Na_2B_4O_6(OH)_2 \bullet 3H_2O$) is displayed, with Jenny Marshall present, to show its enormous size. Ordinarily the only borate in a boron mine is borax ($Na_2B_4O_5(OH)_4 \bullet 8H_2O$), but this mine is unusual in that it has three additional minerals: kernite, colemanite ($CaB_3O_4(OH)_3 \bullet H_2O$), and ulexite ($NaCaB_5O_6(OH)_6 \bullet 5H_2O$).



Figure 12. Royal Institution: Davy's early designs of the safety lamp utilized small holes to cool the gases emanated from oil lamps so that pockets of firedamp would not be ignited.

homeland (Figure 14)—sometimes the flame of a lamp would ignite pockets of firedamp (methane) in the deep recesses of the tin mines, with disastrous consequences. Davy's final solution was a lamp surrounded by a wire gauze which would not allow the flame to come in contact with the explosive gases. Other notable discoveries of Davy included the effect of laughing gas (nitrous oxide, N₂O, discovered by Joseph Priestley in 1772), suggested by Davy as an anesthesia in surgical operations; and the cathodic protection of ships' hulls by plating with copper sheets.

Davy's fame as a riveting lecturer drew devoted audiences to the Royal Institution; his first lecture was given in 1801 on "The New Branch of Philosophy; Galvanism [chemically produced direct-current phenomena]." The preeminent *Philosophical Magazine* reported "Mr. Davy... acquitted himself admirably, from the sparkling intelligence of his eye, his animat-



Figure 13. This is a "Cambrian lamp," a modern replica of the "Clancy lamp," the final version of Davy's safety lamp. Davy never claimed a patent on the safety lamp, instead developing the design as a charitable gift to the miners of his home county. (From the collection of the authors)

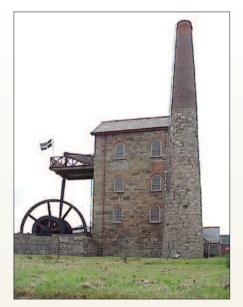


Figure 14. A historic tin mine in Cornwall, near the Camborne School of Mines, University of Exeter. This cultural heritage site is in Pool, near Redruth (N50° 13.90 W05° 15.74). Two millennia ago, nearby streams once enjoyed the visit of Romans, traveling in boats of shallow draft, who collected tin ore for the home base in Italy.

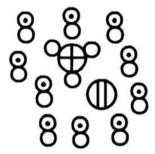
ed manner, and the *tout ensemble* we have no doubt of his attaining a distinguished eminence."⁸

Michael Faraday (1791-1867).6c Davy's devoted attendant was Michael Faraday, whom some people have described as Davy's greatest discovery. (Figure 15) Davy and Faraday were opposite in temperament and class; whereas the buoyant Davy concentrated on attaining "a gentleman's comprehensive education,"8 the serene Faraday, son of a blacksmith, came to the Royal Institution with minimal education. He heard his first lecture by Davy in 1812, and the next year became Davy's assistant—just in time for the two-year journey to the Continent. Because of Davy's fame, Napoleon had awarded him a special medal and invited him to visit France, even though the two countries were at war. Because Davy's valet was afraid to take the trip, the threesome, Davy, his wife, and Faraday, took the risky 1813-15 trip. Faraday actually doubled as a luggage-bearing attendant; Davy's wife treated him like a hireling, but Davy was kind. Faraday tolerated the overbearing treatment and rose to the occasion; he brushed shoulders with the most famous scientists in France—Gay-Lussac, Ampere, and Cuvier, as well as the visiting German scientist Humboldt-and learned much. He even met Count Rumford, the founder of the Royal Institution (see Figure 1), who had just separated from his wife, Marie-Anne neé Paulze Lavoisier, the widow of Antoine-Laurent Lavoisier who had been guillotined in 1794.8

From his lowly background, Faradaydescribed as "unmatched" as an example of "self-taught genius"8—rose to fame at the Royal Institution.8,10 With the barest of mathematical skills (he was trained only in algebra), he was the one to develop the concept of the electromagnetic field, later quantified by James Clerk Maxwell (1831-1879). He developed electrochemistry and introduced the terms electrode, anode, cathode, and ion.11b In chemistry he invented the precursor of the Bunsen burner, discovered benzene, and liquified chlorine. In 1825 Faraday instituted the Christmas lectures at the Royal Institution, which continue to this day. (Figure 16) The unit of capacitance (farad) was named in his honor.

Epilogue. Why Sodium and Potassium Chloride are not SoCl and PoCl. Dalton pioneered the concept of atoms to explain chemical reactions, postulating a one-for-one combination of atoms to demonstrate specific summations of weights of the elements to form compounds. Dalton was color-blind (hence, the term "daltonism")^{1c} and it was natural for him to visualize featureless spheres, like clumps of grapes, which were differentiated solely by their

weights, to explain his ideas. While this model proved essential for a descriptive model of the nano-world and its atomic weights, it proved to be unwieldly for shorthand descriptions. For example, consider Glauber's salt (modern formula Na_2SO_4 • $10H_2O$), which by Dalton's symbolism²¹ would be rendered as:



(The reader should not be confused by the incorrect stoichiometry; during the early 1800s a sulfate was considered to be SO_3 , water was believed to be HO, and sodium oxide was NaO_3 .)

Using equations, Thomas Thomson (1773–1852)^{2e} attempted letter symbols, such as w for oxygen, c for carbon, and h for hydrogen, so that oxalic acid = 4w + 3c + 2h and sugar = $5w +3c +4h [sic].^{2e,6d}$ Thomson, at the University of Edinburgh, was a most successful author, writing a famous textbook, A System of Chemistry, and the very informative and clearlywritten *History of Chemistry*. Thomson was very important in the early years of the 19th century by embracing the new ideas that became modern chemical theory; for example, he was virtually the first non-French antiphlogistinist. He championed the ideas of Dalton that promoted the concept of an atom-by-atom construction of the universe. Soon Thomson was using the initial letters of the names of elements, e.g., "Po" for potassium.

Meanwhile, Berzelius was refining accurate atomic masses, which proved to be indispensable a few decades later for the conceptualization by Mendeleev and Meyer for the periodicity of the elements. Berzelius, who discovered selenium, cerium, silicon, and thorium, dadopted the "initial letter" symbols of Thomson and used these abbreviated symbols to represent these compounds. With so many examples of "S,""P,""O,""So," and "Po," Berzelius toyed with the idea of symbolizing oxygens with dots and water with an "Aq." Glauber's salt would be represented by:

But this was visually misleading and made difficult the balancing of equations by inspection.

Latin names were used more commonly by Germanic nations than by the English or the French. Berzelius, for example, used the term



Figure 15. Faraday's statue. 2 Savoy Place, before the Institution of Electrical Engineers (N51° 30.58 W00° 07.12), on the Victoria Embankment of the Thames River (John Henry Foley, sculptor).

"Kalibasis" for the potassium analysis of a material. Berzelius substituted the Latinized symbols, "Na" (natrium) for "So" and "K" (kalium) for "Po," which removed the confusion of "So," "S," "Po," and "O."

Dalton called Berzelius' symbols "horrifying;"6d it was "unnatural" for scientists to use symbols other than in a mathematic sense. Even Berzelius himself could not make much use of his own invention at first. However, the symbolism gained greater acceptance after it was discovered that water contained two hydrogens and one oxygen^{1c} and thus that one-to-one atomic combinations were not the rule. By the mid-1800s, with more accurate relative atomic mass determinations, the Berzelius formulations were mandated. However, they originally employed superscripts rather than subscripts, although in the first part of the 20th century some texts, particularly those of the French, maintained the "superscript" conven-

Thus—we have Berzelius to thank when we write such formulas as Na_2SO_4 (instead of So_2SO_4) and K_3PO_4 (instead of Po_3PO_4). \bigcirc



Figure 16. The Royal Institution was famous for its lectures popularizing science, and soon evolved into an entertaining educational tool for the public, including the youth. The Christmas lectures were inaugurated by Faraday in 1825. This bronze replica by W. B. Fagan shows Michael Faraday lecturing. In the front row of the audience, from right to left, are Tyndal, Huxley, Wheatstone, Crookes, Darwin, Daniels, and Frankland.

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