

Rediscovery of the Elements

Johann Wolfgang Döbereiner

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In the two previous "Rediscovery of the Elements" articles^{1,2} we followed the development of the Periodic classification of the elements, where there has been an amazing consilience of scientific law and theory, including specific heat data, gas laws, valence theory, chemical behavior trends, electrochemical data, atomic theory, homologous crystalline forms, quantum theory, etc., resulting in our modern Periodic Table.

In this story^{1,2} we have glossed over the initial attempts to organize the elements. When Lavoisier first recognized the true elements,³ he recognized four major groups: "Elements of the body," "Nonmetallic substances," "Metals," and "Earths." The Scottish chemist Thomas Thomson, some four decades later, organized the 53 known elements into three classes:⁴ "Supporters," whose voltaic composition result in their "attach[ing] themselves to the positive pole"; "acidifiable bases," which are electropositive elements combining with the supporters to form acids; and "alkalifiable bases," which are electropositive elements uniting with supporters to form alkaline compounds. (Note 1).

Lavoisier and Thomson had recognized categories, but more sophisticated systematic trends were needed before conception of the Periodic Table was possible. The first person to perceive these was Johann Wolfgang Döbereiner (1780–1849) at the University of Jena, Germany, who was able to identify correlations between chemical behavior and atomic weights.

Döbereiner was interested in stoichiometry and determining accurate atomic weights, particularly of new elements. He analyzed a new sulfate mineral called "celestine" from a mine in Dornburg, 10 kilometers north of Jena, which supposedly contained the new element strontium. (Note 2). Döbereiner was intrigued that

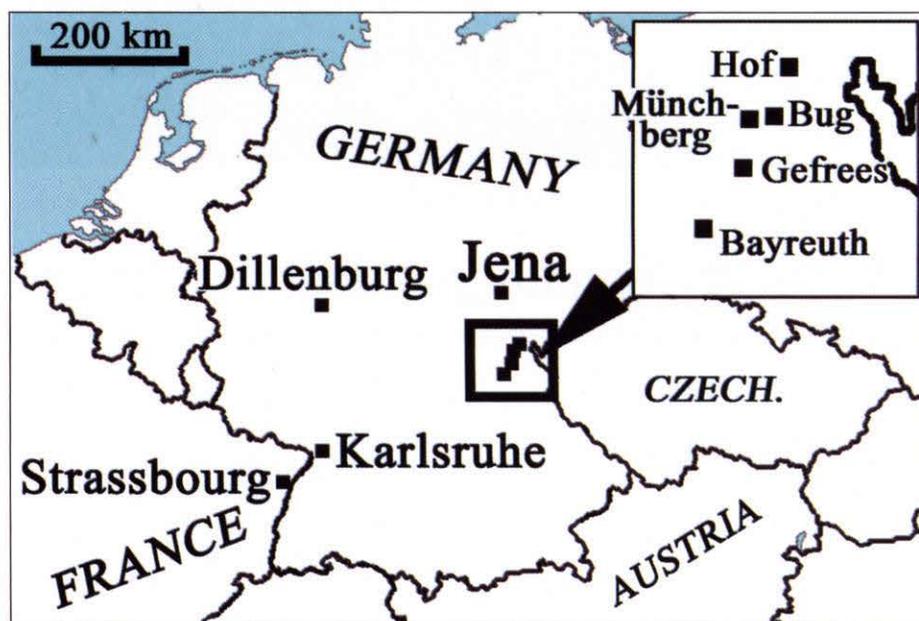


Figure 1. Döbereiner never traveled outside Germany. His earlier years were spent in the Münchberg area, his educational travels in Dillenburg, Karlsruhe, and Strassbourg (then part of Germany), and his mature years in Jena.

the atomic weight for the alkaline earth in the mineral was an arithmetic mean of the previously known atomic weights for calcium and barium; additionally, he determined specific gravity for celestine was also an average of the specific gravities for the calcium and barium sulfates.⁵ He thought "für einen Augenblick" ["just for a moment"]⁵ that the identity of the mineral was in error and that in fact it was a mixed sulfate, 1:1 $\text{CaSO}_4:\text{BaSO}_4$.⁵ When it later became clear that the identity was indeed a sulfate exclusively of strontium, Döbereiner was alert to additional coincidences, and over the next decade recognized other "analogies"⁶ and formulated his "Law of Triades." (Note 3). In total he observed four main triads: (Note 4)

(a) Halogens. The average of chlorine (35.45) and iodine (126.90) is 81.18; bromine is 79.90.

(b) Alkaline earths. The average of calcium (40.08) and barium (137.33) is 88.70; strontium is 87.62.

(c) Alkalis. The average of lithium (6.94) and potassium (39.10) is 23.02; sodium is 22.99.

(d) Elements "which combine with hydrogen to form characteristic hydrogen acids." The average of sulfur (32.06) and tellurium (127.60) is 79.83; selenium is 78.96.

Döbereiner could not distinguish more universal correlations among many elements because the true atomic weights (as opposed to integral multiples) could not be determined until valence was understood—but he was the first to recognize that a mathematical connection might be operating within a selected chemical group. This idea of repeated behavior allowed Mendeleev and Meyer² to conceptualize the first true Periodic Table some 40 years later.

Life of Döbereiner. J.W. Döbereiner was born in Hof in Eastern Germany (Figure 1). Soon after his birth, his family moved to a near-



Figure 2. Right: Rittergut am Bug lies 1 km north of Weißdorf (not shown in Figure 1), which is 4 km east of Münchberg. The location of this prosperous estate is 17 Bugbergstrasse, N 50° 11.73 E 11° 50.86. The plaque on the wall is expanded in upper left: "To the memory/of the pioneer of experimental chemistry/Johann Wolfgang Döbereiner/Professor of Chemistry in Jena/13.12.1780/24.3.1849/He spent his childhood here/and youth/as the son of the manor superintendent." Lower left: The road sign announcing the village of Bug.



Figure 3. Döbereiner was an apprentice at an apothecary once located at this site in Münchberg, 14 Ludwigstrasse, N 50° 11.55 E 11° 47.33.

by village called Bug am Weißdorf, near the village of Münchberg. His father, Johann Adam Döbereiner,⁷ a coachman, had procured a job at an estate at Bug and gradually worked his way up to manager of the property (Figure 2). The father needed young Johann Wolfgang for farm labor, but the youth still had time to enjoy the fresh countryside and study nature, and his mother ensured that he received proper schooling with a pastor in Weißdorf.⁷

At the age of 14, Döbereiner became an apprentice at the Lotz apothecary in Münchberg (Figure 3), where he learned the fundamentals of chemistry. Between the ages of

17–22 he devoted his time to "Wanderjahre" in Dillenburg, Karlsruhe, and particularly Strassbourg, where he studied and learned science, mostly through informal attendance at university classes and independent study. In 1803, at the age of 23, Döbereiner returned to Münchberg and married Clara Henriette Sophie Knab. The young bridegroom began a seven-year period of various chemical enterprises, first undertaking a manufactory and distribution center for pharmaceutical preparations in Gefrees (near Bayreuth), an agricultural business, then (1806) a textile business (bleaching and dyeing) in Münchberg, later



Figure 4. Statue of Goethe in Strassbourg. He obtained his education in law at this university.⁹ The location is Place de l'Université, N 48° 35.12 E 07° 45.67.

moving to Hofgut St. Johannis (Bayreuth) to start a brewery and distillery business. Döbereiner's businesses were always financially shaky, and he moved about often as his businesses failed.⁷

It would appear that Döbereiner was destined for a mediocre career, but then a most improbable combination of events brought him to the University in Jena. The chemistry professor at the University of Jena died (Johann Friedrich August Götting, 1753–1809),⁸ creating a vacancy. Another Johann Wolfgang—the famous Goethe, now Privy Councillor and Minister of State ("Qualified Minister")⁹ at Weimar, 19 kilometers to the west, was asked to recommend someone for the post, and he in turn asked Adolph Ferdinand Gehlen (1775–1815), editor of *Neues allgemeines Journal der Chemie*. In spite of Döbereiner's economic difficulties, he had always conducted careful chemical experiments and published them in Gehlen's journal. The editor, most impressed with the quality contributions of Döbereiner, recommended him for the Jena post, although he felt there was little hope because Döbereiner did not even possess a Gymnasium certificate, let alone a graduate degree. But Döbereiner was accepted, and thus he moved to Jena in 1810. (Once he joined the faculty of the university, he was promptly awarded his advanced degree.)⁹

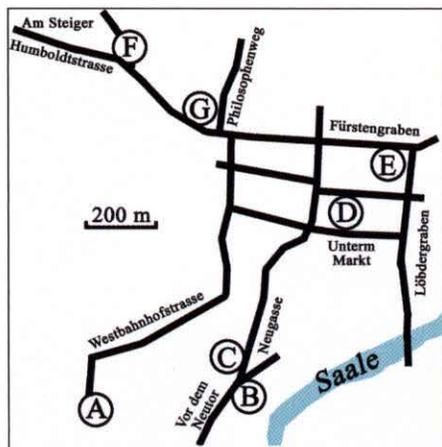


Figure 6. Map of Jena, Germany. (A) Bahnhof Jena-West, the train station accessing points west. (B) Bahnhof Jena-Paradies, the train station accessing points north and south. (C) Hellfeld Haus. (D) Statue of Johann Friedrich I. (E) Main university building on Fürstengrabe. (F) Döbereiner Hörssaal (lecture hall). (G) Friedenhof, the cemetery where Döbereiner is buried.

Goethe, who was responsible for Döbereiner's fortune at Jena, was the famous poet so revered by the German-speaking world—the "Shakespeare of the German Language."¹⁰ Although educated as a lawyer (Figure 4), Goethe became active in philosophy, poetry, and science. He was keenly interested in chemistry; his familiarity with alchemy is clear from his detailed description of the alchemical laboratory¹¹ in *Faust*.¹² Goethe wrote *Farbenlehre*,¹³ a popular guide to the study of color phenomena, in which he issued his famous aphorism, "[The] history of science is science itself."¹⁴

Döbereiner, immersed in poverty for so long, was so grateful for this opportunity at the University of Jena that he devoted the remainder of his life there, even though he was offered several positions elsewhere—Bonn, Dorpat (Tartu), Halle, München, and Würzburg.¹⁰ He vigorously plunged into developing the chemistry program at Jena. Planning with Goethe, a building was purchased in 1816 (Hellfeld Haus) and equipped with a laboratory.¹⁰ Döbereiner engaged in a number of discoveries, including the identity of chromic acid, the composition of sugar, the catalytic action of manganese dioxide on potassium chloride (still used today as a laboratory procedure for producing oxygen), the correct interpretation of alcoholic fermentation, and the loss of hydrogen from a cracked flask (which guided Thomas Graham [1805–1869] to his law of diffusion of gases).¹⁵

Often Goethe would visit and witness, if not participate, in some of the chemical experiments. The two had active discussions, dealing with, among other things, "the tarnishing of silver spoons in red cabbage and the composition

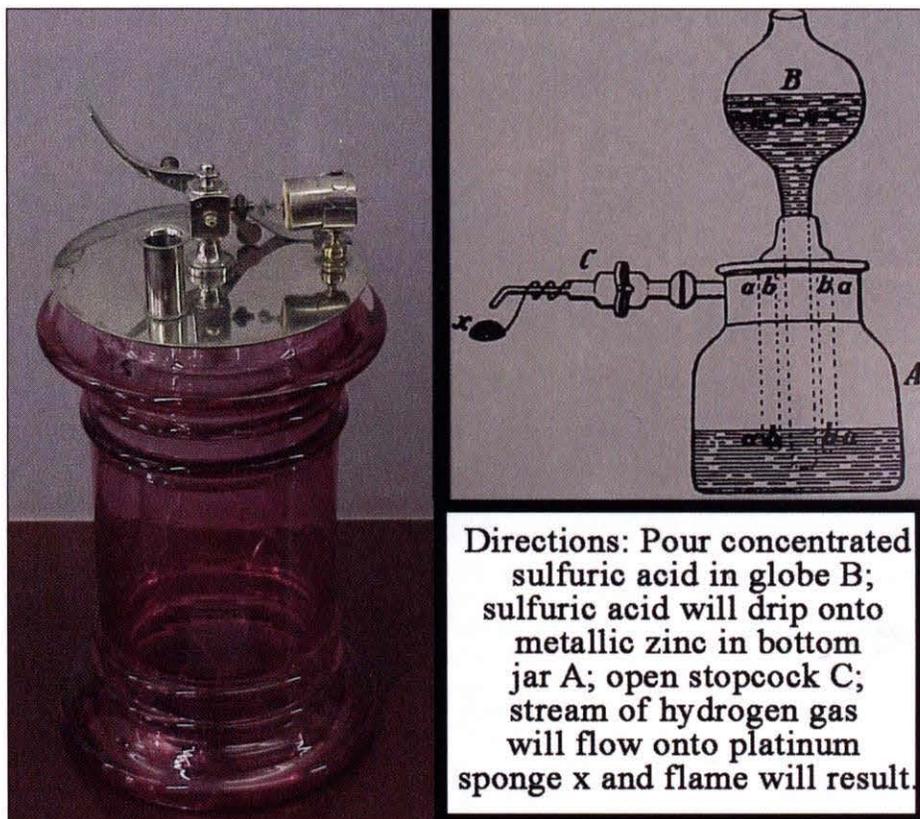


Figure 5. Döbereiner's Feuerzeug. Left: A model from the 1820s, on exhibit at the Deutsches Museum in München. Right: Drawing from exhibit in the Döbereiner Hörssaal. The generated flame could be used to light a candle.

of Mme. Pompadour's toothpaste."¹⁶ The close friendship between Goethe and Döbereiner meant both financial and emotional support for Döbereiner. Legendary is the birthday poem that Goethe wrote for Döbereiner in 1816 during one of the chemist's episodes of depression, to be recited by students during a torchlight parade.⁷

Other than Döbereiner's famous "Law of Triads," the most important work was his discovery of the action of platinum on hydrogen. Döbereiner discovered in 1823 that in the presence of finely divided platinum (platinum black), hydrogen would spontaneously combust and burst into flame.¹⁷ This discovery led to the design of the "Döbereinersche Feuerzeug" (Döbereiner lighter),¹⁸ which was all the rage across Western Europe, particularly England and Germany (Figure 5). Döbereiner's lighter lamp was quickly adapted for use in thousands of households throughout Western Europe, used even until World War I, until it was gradually replaced by safety matches (invented in 1848 by one of Döbereiner's students, Rudolph Christian Böttger, 1806–1881).⁸ During Döbereiner's lifetime, his platinum "metallic action" discovery was his most celebrated research; his "Law of Triads" was far ahead of its time and was not yet appreciated.

This remarkable property of platinum captured the imagination of the best minds in

Directions: Pour concentrated sulfuric acid in globe B; sulfuric acid will drip onto metallic zinc in bottom jar A; open stopcock C; stream of hydrogen gas will flow onto platinum sponge x and flame will result.

Europe. While others thought the spontaneous combustion of hydrogen and other compounds on platinum was a reaction of the platinum (i.e., the platinum underwent a permanent chemical change), Döbereiner perceived a phenomenon induced by the platinum (the platinum could be continuously used, again and again). Döbereiner even conceived atomic models to explain the mechanism of the reaction of hydrogen with the platinum surface,⁸ visualizing "chains of hydrogen atoms" on the platinum surface. This chemical action—whereby bodies can "exert an influence . . . without themselves taking part with their components"¹⁰ was deemed so important by Jöns Jakob Berzelius (1779–1848)—then "the supreme authority on matters chemical"¹⁰—that he proclaimed Döbereiner's discovery the "most important and . . . brilliant of the past year."¹⁹ Berzelius later gave this new force a name—"catalytic force" (*katalytische Kraft*), from Greek "cata" (down) and "lysis" (loosening).²⁰ (Note 5).

Rediscovering Döbereiner in Jena. (See Figure 6 for map of Jena.) Today Jena is a romantic little village nestled in the Saale Valley, flanked by chalk hills, quiet and full of history. Wandering about Jena, we saw hundreds of plaques, reminding us of famous philosophers and scientists who graced the university since its creation in 1548: Schiller, Hegel, Humboldt,



Figure 7. Hellfeld Haus, 23 Neugasse, N 50° 55.46 E 11° 35.04. Many plaques can be seen on the wall (Note 6), including Döbereiner's. Inset: Döbereiner's plaque: "Here lived and worked /Joh. Wolfgang Döbereiner/Professor of Chemistry/ born 1780, lived here 1816-1849, died 1849."



Figure 9. Statue of Johann Friedrich I, "der Grossmüthige" ("the Magnanimous"), the founder of the Jena University. Location: In the historical market place, N 50° 55.69 E 11° 35.29.

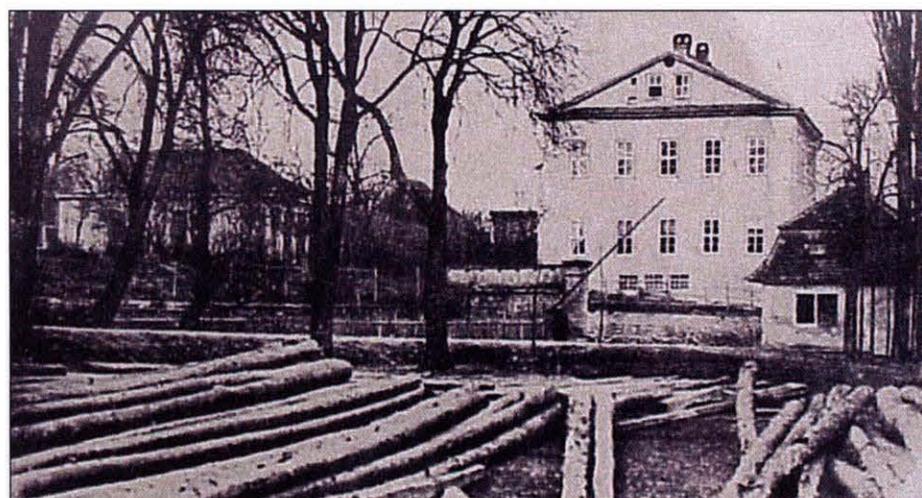


Figure 8. Old picture of Hellfeld Haus, dating from 1883. Photo taken from approximate present site of Paradies railway station.

Haeckel, Zeiss, Goethe, etc. Walking north from the railway station on "Vor dem Neutor," Döbereiner's plaque is spotted on the walls of Hellfeld Haus (Figure 7), now a biology building. This used to be the outskirts of town, literally at the south gate ("Neutor" means "New Gate"). An old picture of Hellfeld Haus (Figure 8) reminds us how much congestion and construction occurred since the early part of the 1800s.

Strolling northward on Neugasse, one reaches Market Square, which has existed for half a century. In the center of the square is a statue of Johann Friedrich I "the

Magnanimous" (1503-1554) (Figure 9), founder of the university. Further north is the main university building (Figure 10), built in 1907. Today the university's official designation is "Friedrich-Schiller-Jena Universität," named not only for its founder Johann Friedrich I, but also for the famous German romantic writer Johann Christoph Friedrich von Schiller (1759-1805), professor of history and philosophy at Jena, and a close friend of Goethe. On the second floor of the main building hangs a large wall painting, reminding one of the importance of Goethe's continuing guidance in developing the university (Figure 11).

Walking another kilometer further west from the main university building, one arrives at the Döbereiner Hörsaal (Figure 12). Inside is a 600-seat lecture hall, a wall painting of Döbereiner (Figure 13), and an exhibit describing his life and works.

Döbereiner's Legacy. Between Döbereiner Hall and the main university building is the Johannisfriedhof (Johannis cemetery), where one can find Döbereiner's grave (Figure 14). Its inscription reads:

JOH WOLFGANG DOEBEREINER
 PROFESSOR D CHEMIE A DER UNIVERS
 JENA 810-1849
 13.12.1780 24.3.1849
 BERATER GOETHES ["Advisor to Goethe"]
 SCHOEPFER DER TRIADENLEHRE
 ["Creator of the Law of Triads"]
 ENTDECKER DER PLATINKATALYSE
 ["Discoverer of the platinum catalyst"]

Of these three contributions, modern students are most familiar with the "Law of Triads," although during his time, his platinum research was deemed the most important. It continues today in the legacy of catalysis, extending into industrial manufacturing, enzyme chemistry, and chemical synthesis. Döbereiner worked tirelessly, never taking financial advantage of his discoveries and tak-



Figure 11. In the Hauptgebäude hangs this painting by Hans W. Schmidt (1907), which shows Goethe (left) and Grand Duke Karl August (1757–1828) meeting on the courtyard of the castle at Jena, on the site of the present Hauptgebäude, and the approximate location of Döbereiner's laboratory before his move to Fellfeld Haus in 1816. The Grand Duke appointed Döbereiner as professor of chemistry at Jena.

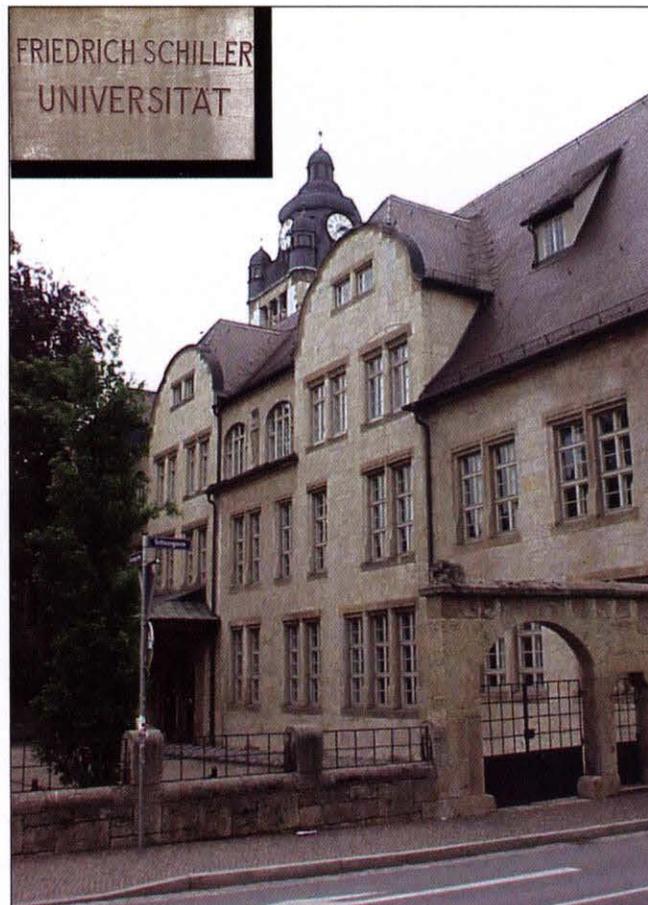


Figure 10. Main university building (Universität Hauptgebäude) on Fürstengrabe (N 50° 55.78 E 11° 35.40), built in 1905. Reminding us that this was once part of Deutsche Demokratische Republik (Communist East Germany), a plaque inside boasts that Karl Marx (1818–1883) received his doctorate in philosophy in 1841 at this university. Inset: Plaque on the building.

ing out patents for his creations (including the very popular Feuerzeug), instead devoting his time to the service of others.

"Döbereiner was a born scientist who, closely linked with nature from his youth on, observed passionately, gathered experiences, evaluated them with clear understanding, and put them into their proper scientific setting. At the same time he was an idealist, poor in worldly possessions, but rich in knowledge, who, without thought of his own advantage, unselfishly gave of this wealth so that others might aid humanity."⁷ ○

Notes.

1. Lavoisier's four groups included:³ (a) "Substances from the three kingdoms, which may be regarded as elements of the body": O, N, H, heat(!), and light(!); (b) "Substances non-metallic oxidizable and acidifiable": S, P, C, Cl, F, B; (c) "Substances metallic oxidizable and acidifiable": Sb, Ag, As, Bi, Co, Cu, Sn, Fe, Mn, Hg, Mo, Ni, Au, Pt, Pb, W, Zn; (d) "Substances salifiable earths": Ca, Mg, Ba, Al, Si. Thomson's three groups included: 4 (a) "Supporters: O, Cl, Br, I, F;" (b) Acidifiable bases: H, N, C, B, Si, S, Se, Te, P, As, Sb, Cr, U, Mo, W, Ti, Nb; (c) Alkalifiable bases: K, Na, Li, Ba, Sr, Ca, Mg, Al, Be, Y, Ce, Zr, Th, Fe, Mn, Ni, Co, Zn, Cd, Pb, Sn, Bi, Cu, Hg, Ag, Au, Pt, Pd, Rh, Ir, Os.

2. In 1790 strontium earth was discovered in its carbonate (SrCO_3 , strontianite) in Scotland, and was characterized in 1792 by Charles Hope in Edinburgh.²¹ Celestine (SrSO_4), named for its faint blue color, was first collected by A.G. Schütz in the wilds of Pennsylvania (present Blair County near Bellwood) in 1791 during Washington's presidency, taken back to Europe, analyzed by Heinrich Klaproth in 1797, and found to contain "strontium and sulfuric acid."²²

3. Döbereiner called his trends "Analogies";⁵ Leopold Gmelin (1788–1853) in his *Handbuch der Chemie* renamed them "Triads."¹⁵ Döbereiner's 1829 paper³ included not only the four classic triads [see text], but also cruder correlations for Zn, Fe, Cu, Ni, and the platinum group metals. Interestingly, he lamented the absence of a third element completing the series (P, As, . . .), not realizing that Sb (known for centuries) was the missing member!

4. A reader of Döbereiner's original papers is easily confused by the atomic weights he used; before valence was understood, the "atomic weight" of elements in different groups depended upon whatever convention a scientist chose.¹ For example, for the first triad he investigated, he used 27.5 for calcium, 50 for strontium, and 72.5 for barium; sometimes he adapted Berzelius' values based on oxygen = 100; and sometimes the values he used were

coincidentally the same as today's (e.g., the halogens). To avoid confusion here, the atomic weights used in this paper are the modern atomic masses.

5. Berzelius first proposed "catalytic force" when he began to appreciate that there was a special force working in plants²⁰—which today we recognize as the action of enzymes. In this treatise ("Einigen Ideen über eine bei der Bildung organischer Verbindungen in der lebenden Natur wirksame, aber bisher nicht bemerkte Kraft," in the section of "Planzenchemie,"²⁰ Berzelius mainly discussed the action in plants, but refers to inorganic examples, including Davy's oxidation of alcohols by platinum, Döbereiner's action of platinum sponge on hydrogen gas, and Thénard's hydrogen peroxide and its decomposition by silver or fibrin.

6. The Heldfeld Haus wall displays these plaques, among others: Paul Luther (1533–1593), son of Martin Luther and professor of medicine at Jena; Otto von Guericke (1602–1686), who proved the power of a vacuum with the evacuated hemispheres demonstration, a student at Jena; and Ernst Abbe (1840–1905), who lived there, a professor of physics at Jena and an expert in optics who invented the Abbe refractometer (1869) in conjunction with the thriving local Zeiss optical enterprise; etc.

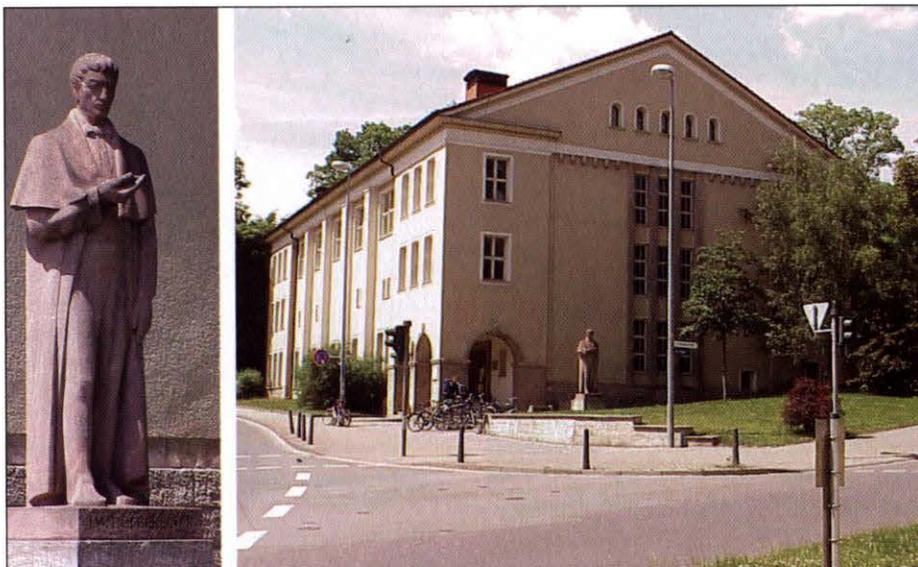


Figure 12. Döbereiner Hörsaal, 3 Am Steiger (N 50° 55.93 E 11° 34.78), named after Döbereiner in 1974. A statue of Döbereiner, created by H. Steiger in 1958, stands in front (left).



Figure 14. Gravestone of Döbereiner in the Johannisfriedhof (N 50° 55.84 E 11° 34.92). The cemetery can be entered on Philosophenweg. The gravestone is eroded and difficult to read (inscription detailed in text).

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Figure 13. Painting of Döbereiner in the lecture hall, by Georg Philipp Schmidt, 1825. At the back of the Hörsaal is a poster exhibit on Döbereiner's life and works.