

## From Triads to Catalysis: Johann Wolfgang Döbereiner (1780–1849) on the 150th Anniversary of His Death

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**Abstract:** The Time: May 7, 1999. The Place: The auditorium (Döbereiner-Hörsaal) (Figure 1) of the Chemical Institute of the Friedrich-Schiller-Universität Jena, the famous German university founded in 1558, which numbered among its faculty the illustrious philosophers Johann Gottlieb Fichte, Georg Wilhelm Friedrich Hegel, and Friedrich Wilhelm Joseph von Schelling; the writer and critic Friedrich von Schlegel; and the dramatist and poet (Johann Christoph) Friedrich Schiller, whose name the university now bears [1].

The Event: A Döbereiner Festkolloquium (Figure 2), attended by about 300 persons and organized by the university's Chemische-Geowissenschaftliche Fakultät, Institut für Anorganische und Analytische Chemie and sponsored by Degussa (originally **D**eutsche **G**old- und **S**ilber-**S**cheide-**A**nstalt, now Degussa-Hüls AG) and the Fonds der Chemischen Industrie, to commemorate the 150th anniversary of the death of the university's Professor of Chemistry and Technology, Johann Wolfgang Döbereiner (1780–1849).

The Program: Two scientific lectures by leading authorities in those fields of chemistry whose foundations were erected by Döbereiner—catalysis and the periodic system of the elements: “Heterocyclenecarbenes: New Controlling Ligands in Catalysis” by Professor Wolfgang Anton Herrmann, President of the Technische Universität München and “On the Nuclear Physical Limitation of the Number of Elements—The 100-Year Journey from Polonium to Element 112” by Professor Peter Armbruster of the Gesellschaft für Schwerionenforschung mbH Darmstadt, head of the team that discovered the last seven elements of the periodic table up to element 112. Two history of chemistry lectures: “Johann Wolfgang Döbereiner—a Pioneer for Modern Chemistry” by Professor Dietmar Linke of the Brandenburgische Technische Universität Cottbus and “Döbereiner's Contemporaries—Chemists, Natural Scientists, Philosophers” by Professor Egon Uhlig of the Universität Jena.

This was not the only celebration for Döbereiner in recent history. On the occasion of the bicentennial of his birth (1980) an International Döbereiner-Kolloquium was held on May 20–22 at Jena. In that year the Deutsche Demokratische Republik (East Germany) issued a commemorative postage stamp in his honor (Figure 3). Perhaps the latest colloquium will serve to renew interest in a creative and prolific chemist who, although renowned during his lifetime, is not as well known by today's chemists and chemical educators as he deserves to be.

### Döbereiner's Early Life

Döbereiner (Figure 4) was born on December 13, 1780 in Hof an der Saale in Bavaria in the Fichtelgebirge mountain range of Southern Germany [2–20]. A self-made man in the literal sense of the word, he was the son of a coachman,

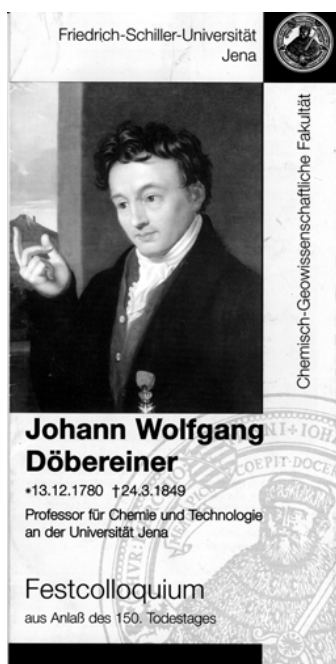
Johann Adam Döbereiner, who was first a servant and later a manager of an estate in Münchberg in Oberfranken (Upper Franconia) where the boy grew up in close proximity with nature and agriculture but received little schooling. Financially unable to provide his precocious offspring with any but the barest essentials of education, his father put him to farm work. His mother, Johanna Susanna Döbereiner (née Göring), however, valued learning and encouraged him by arranging for lessons with the pastor in a neighboring village.

After three years of an apprenticeship with an apothecary named Lotz in Münchberg, at the age of seventeen young Döbereiner began five precarious *Wanderjahre*, holding similar positions in Dillenburg, Karlsruhe, and eventually Strasbourg, where, unable to afford to enroll at the university, he attended lectures on chemistry, botany, and mineralogy, studied on his own, and learned French. In 1802 he returned to his parent's home. In the following year (1803), at the age of twenty-three, he married Clara Henriette Sophia Knab (1784–1861), a childhood friend and daughter of a distinguished Münchberg family. Their first child was born in 1804. One of his sons, Franz Karl Alexander Döbereiner (1809–1866), helped his father, especially with his research on platinum, revised several of his books, and later became Professor of Chemistry at the Universität Halle and the author of several semipopular and semitechnical books [8]. The couple eventually had eight children—five sons and three daughters.

Although now an apothecary, Döbereiner had neither the money nor license to buy a pharmacy. He opened an agricultural produce business (*Landesproduktenhandlung*) and small chemical factory in the small town of Gefree near Bayreuth, and he began to produce pharmaceutical-chemical preparations. By 1803 he was reporting his experiments with white lead ( $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ ), sugar of lead ( $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ ), epsom salt ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), and other commercially valuable products in the *Neues allgemeines Journal der Chemie*, edited by Adolph Ferdinand Gehlen (1775–1815), which brought him to the attention of chemists. After complaints of envious neighbors caused him to lose his license and his business, his relatives gave him a position in charge of bleaching and dyeing in their textile mill, where he investigated the bleaching of cotton goods with sodium hypochlorite ( $\text{NaClO}$ ), preparation of caustic soda ( $\text{NaOH}$ )



**Figure 1.** The Döbereiner-Hörsaal (auditorium) with the Döbereiner monument erected in 1958 (courtesy, Prof. Dr. Ernst-Gottfried Jäger).



**Figure 2.** The Döbereiner-Kolloquium announcement with oil painting of Johann Wolfgang Döbereiner (1780–1849) in 1825, two years after his discovery of the heterogeneous catalysis of platinum, by Georg Philipp Schmidt (Goethe-Gedenkstätte Jena; courtesy, Prof. Dr. Ernst-Gottfried Jäger).



**Figure 3.** 5-pfennig stamp issued on February 21, 1980 to commemorate the 200th anniversary of Döbereiner's birth, portrait from chalk and charcoal drawing by Johann J. Schmeller, 1825 (see Figure 4) with first published sketch of Döbereiner's Feuerzeug, 1824 (see Figure 16), Deutsche Demokratische Republik, Scott standard postage stamp catalogue no. 2088 (courtesy, Prof. Dr. Dietmar Linke).



**Figure 4.** Johann Wolfgang Döbereiner (1780–1849) in 1825, Chalk and Charcoal Drawing by Johann J. Schmeller, 1825 (courtesy, Prof. Dr. Dietmar Linke).

from  $\text{Na}_2\text{SO}_4$ , and other processes, which he reported in Gehlen's journal. The blockade of the Napoleonic war, however, forced the plant to close.

Döbereiner then began to supervise agricultural estates, where he modified brewing and distilling practices. At this time he began his lifetime friendship with Johann Salomo Christoph Schweigger (1779–1857), Professor of Mathematics and Physics at the high school (*Gymnasium*) in nearby Bayreuth, the future site (1876) of composer Richard Wagner's Festival Theater (*Festspielhaus*). In 1811 Schweigger was to become the editor of the *Journal für Chemie und Physik*, the successor of Gehlen's journal, which had ceased publication in 1809, and just as Döbereiner had published in Gehlen's journal, he now began to publish in Schweigger's journal.

### The Call to Jena

In 1810 Döbereiner's agricultural projects were discontinued, and once again the 29-year-old father of a family found himself unemployed and unable to pay his debts. Fortunately, at this lowest point in his life fate suddenly intervened. Döbereiner was surprised to learn from the Senate of the Universität Jena that he had been nominated to be Extraordinary (*ausserordentlicher*) Professor of Chemistry and Technology by Duke (*Herzog*) Carl August (1757–1828) (Figure 5) of the small state of Sachsen-Weimar-Eisenach (Figure 6), an enlightened and liberal ruler and a patron of the arts and sciences. The duke (he became Grand Duke (*Grossherzog*) in 1815) had asked Gehlen to recommend a successor to Professor Johann Friedrich August Götting (1753–1809), who had died in the previous year. Gehlen, knowing that Döbereiner was out of work, proposed his name with little hope of success, for he did not have a high school (*Gymnasium*) certificate let alone any higher education. Only after Döbereiner arrived in Jena did he learn that he needed a doctorate to occupy the position. He was granted this degree





Figure 5. Johann Wolfgang Von Goethe (1749–1832) and Grand Duke Carl August (1757–1828) in the courtyard of the Jena Castle (courtesy, Prof. Dr. Ernst-Gottfried Jäger).

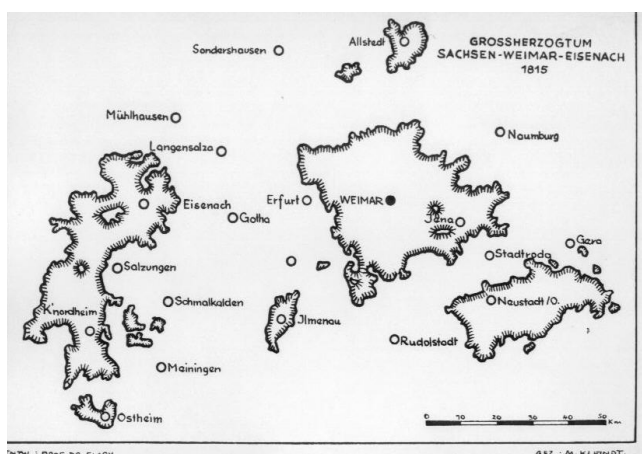


Figure 6. Grand Duchy of Sachsen-Weimar-Eisenach with Boundaries of 1815 (courtesy, Prof. Dr. Dietmar Linke).

(Figure 7) on November 10, 1810 at half the usual fee and was allowed to pay this debt in installments because of his poverty. In the winter semester of 1810/1811 he began to lecture on general experimental chemistry, chemical technology, and pharmacy.

Döbereiner was so grateful for the unexpected call (*Berufung*) to the Jena professorship, which he always regarded as the greatest event in his life, that, despite later, more remunerative offers from five other universities (Bonn, Dorpat (now Tartu, Estonia), Halle, Munich, and Würzburg), he retained his loyalty to Jena. He traveled little and remained in Jena for the remaining four decades of his life even though the tiny state could afford to pay him only a meager salary barely adequate to support his growing household and pay his professional expenses. Because he possessed no business acumen, he remained poor. For example, in 1828 he was unable to attend a meeting of natural scientists in Berlin. Although he traveled little, he was visited by numerous prominent persons, for example, Berzelius, Mitscherlich, and Heinrich Rose, and he carried out an extensive correspondence.

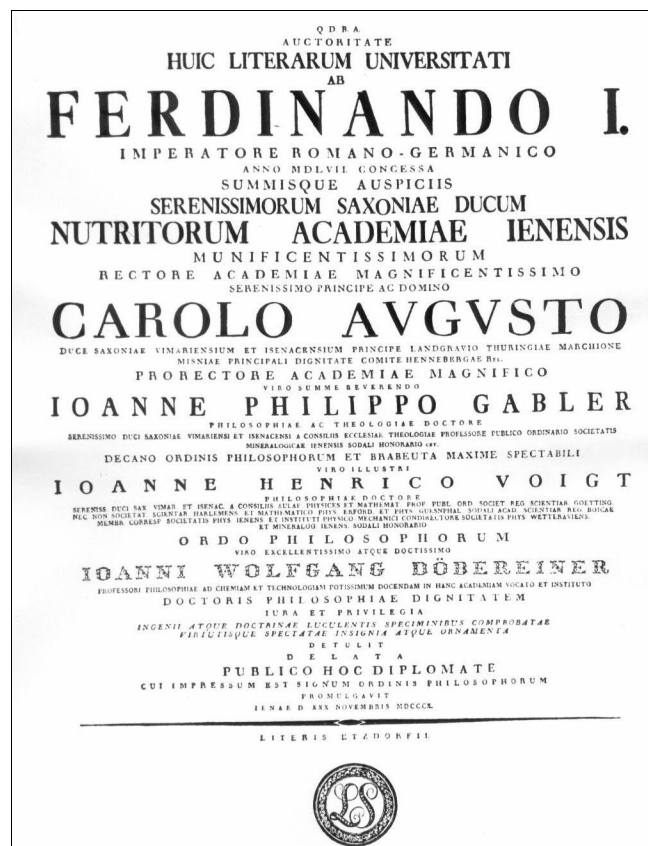


Figure 7. Döbereiner's Doctoral Diploma, Universität Jena, November 30, 1810 (courtesy, Prof. Dr. Dietmar Linke).

### The Two Johann Wolfgangs

At Weimar, only 12 miles from Jena, on September 8, 1810 Döbereiner met another Johann Wolfgang—Germany's most famous poet and dramatist Johann Wolfgang von Goethe (1749–1832) (Figures 5 and 8), the beginning of another close lifetime friendship and one of the reasons that Döbereiner chose to remain at Jena, close to Weimar. Goethe occupies a place in the German-speaking world that is similar to that of Shakespeare in the English-speaking world. He was not only a patron of the natural sciences but also made a number of his own scientific contributions, and he became Döbereiner's most famous student [21–23]. Alexander Gutbier (1876–1926), *Rektor* of the Universität Jena, paired the two in a lecture of 1926:

For the attainment of high goals in academic life at least two men in mutual trust must be found: the professor, willing to work like Döbereiner, and the minister or ministerial official ready to take responsibility like Goethe [18, 23].

Döbereiner's tombstone in Jena bears the inscription, "Goethe's advisor, creator of the rule of triads, discoverer of platinum catalysis" (Figure 9). Because Goethe was Döbereiner's immediate supervisor (he served in Carl August's court as Qualified State Minister (*zuständiger Staatsminister*) to the Universität Jena), the two spent two days discussing plans for equipping the chemical laboratory, which was then located in the upper floors of the former ducal palace in Jena and which contained old apparatus from Weimar,



**Figure 8.** Johann Wolfgang Von Goethe (1749–1832), portrait in oil by G. O. May, Oberhessisches Museum, Giessen [22b, P 9] (Reproduced with the permission of Callwey Verlag, Munich).



**Figure 9.** Döbereiner's tombstone in the old Jena cemetery on the Philosophenweg, destroyed by wartime bombing in March 1945 but later restored, photograph by Dietmar Linke (courtesy, Prof. Dr. Dietmar Linke).

material from Götting's tenure, and books from the ducal library.

Döbereiner is probably the only chemist to have a birthday poem written specifically for him by Goethe. By 1816 Döbereiner had become depressed and sick as a result of overwork, and Goethe asked Döbereiner's students to honor him on his 36th birthday (December 13, 1816) with a torchlight parade (*Fackelzug*) at which one of the students recited the following poem:

“Dem Professor Döbereiner im Namen seiner Kinder, zum Geburtstag”

Wenn wir dich, o Vater sehen  
In der Werkstatt der Natur  
Stoffe sammeln, lösen, binden,

Als seist du der Schöpfer nur,  
Denken wir: Der solche Sachen  
Hat so weislich ausgedacht,  
Sollte der nicht Mittel finden  
Und die Kunst, die fröhlich macht?

Und dann, schauen auf nach oben,

Wünschen, bester Vater, wir,  
Was die Menschen alle loben,  
Glück und Lebensfreuden dir...

(To Professor Döbereiner, in the Name of His Children for His Birthday)

Whenever we see you, oh Father,  
In Nature's laboratory  
Collecting, dissolving,  
combining substances,

As if you alone are the Creator,  
We think: Should whoever has  
So wisely invented such things,  
Not find the means  
And the art that makes us joyful?

And then, we behold on high,

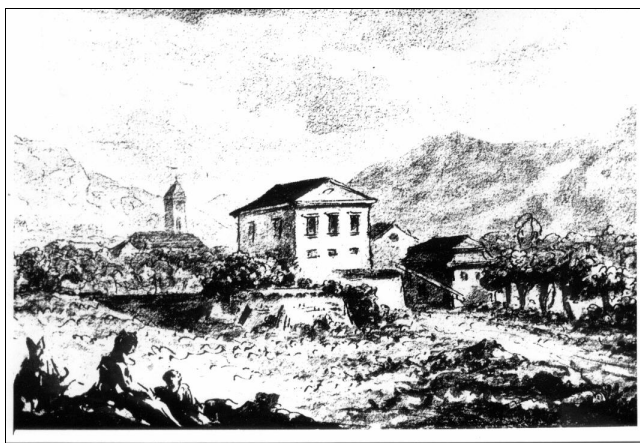
Best father, wishes,  
Which all people praise,  
Good luck and joy in living to you...

This poem (Goethe, J. W., in *Extrablatt zu den Priviligierten Jenaischen Wochenblättern*, No. 38, 1.9.1849), sung to the melody of Ludwig van Beethoven's musical setting of Schiller's "An die Freude" (Ode to Joy) from his Symphony No. 9, in D Minor, Op. 125, with which it fits remarkably well, was used as a musical prelude to open the Döbereiner-Kolloquium in Jena mentioned at the beginning of this article.

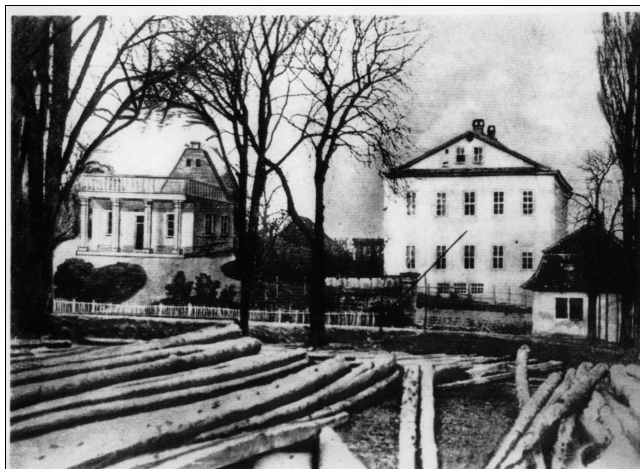
Because the palace laboratory was too small, in 1816 the university purchased a house (Figure 10), called the Hellfeld House (*Hellfeldsche Haus*) after its former owner, located near the Neutor (New Gate) as a residence for Döbereiner, and Goethe had it also equipped as a laboratory. In 1819 Döbereiner was promoted to Full (*ordentlicher*) Professor, and in the winter 1820/1821 semester he began to present a public laboratory course in a large room on the ground floor of the house that also served as his dwelling. In 1833 a new laboratory with auditorium, designed by Goethe, was built in the large garden near Döbereiner's house (Figure 11). With money borrowed from his daughters' savings Döbereiner completed the necessary equipment. In 1843 his mother, who lived with him, died. After a short but painful "cancer-like illness that caused destruction of the throat and the upper part of the esophagus" [11, 16], Döbereiner died in Jena on March 24, 1849 (Figure 9).

### Inorganic Research

Among his inorganic research Döbereiner reported that air is a mixture rather than a compound, mentioning John Dalton's similar results [24]. He devised a quantitative separation of calcium from magnesium by means of ammonium carbonate ( $(\text{NH}_4)_2\text{CO}_3$ ) or ammonium oxalate ( $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ) in the presence of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) [25]. By the reaction of barium chromate ( $\text{BaCrO}_4$ ) with sulfuric acid ( $\text{H}_2\text{SO}_4$ ) he established the identity of chromic acid (chromium(VI) oxide,  $\text{CrO}_3$ ) [26], which had earlier been questioned by Brandenburg [27]. He prepared carbon monoxide by thermal dehydration of formic acid ( $\text{HCOOH}$ ) with sulfuric acid [28]. Similarly, he prepared a mixture of carbon monoxide and carbon dioxide by heating oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) with sulfuric acid [29]. Although he thought that the gas from formic acid also contained carbon



**Figure 10.** Hellfeld House, Neugasse 23, Döbereiner's home and workplace from 1816 (drawing by Goethe, 1810, courtesy, Prof. Dr. Dietmar Linke).



**Figure 11.** Hellfeld House, Neugasse 23, in 1883, Döbereiner's home and workplace from 1816; left, in the garden is the laboratory with auditorium built in 1833 (courtesy, Prof. Dr. Dietmar Linke).

dioxide, Berzelius (1825) pointed out that the formula of formic acid shows that only carbon monoxide is evolved, whereas that of oxalic acid shows that carbon monoxide and carbon dioxide should be formed in equal volumes.

Döbereiner also discovered the catalytic action of manganese dioxide (pyrolusite, *Braunstein*) on the thermal decomposition of potassium chlorate, explaining it as the action of a porous body [30]. The reaction is the basis for the familiar preparation of oxygen known to every introductory chemistry student. His discovery that hydrogen escaped from a cracked flask [31] led Thomas Graham (1805–1869) to his law of diffusion [32]. In Graham's words, "The original observation of Döbereiner...will always hold its place in scientific history as the starting-point of the experimental study of gaseous diffusion" [33].

### Organic Research

Döbereiner's earliest research, carried out during the early beginnings of organic chemistry, dealt with the nature of carbon and its compounds. Because of its behavior toward metals, he mistakenly considered carbon to be a metal. He prepared pure carbon (graphite) by heating a mixture of pine

soot (amorphous carbon), powdered iron, and manganese dioxide in a closed crucible to a high temperature and dissolving the iron-manganese alloy in acids. He called the residue of shiny, black-gray, shiny leaflets, which conducted electricity and volatilized on heating in air, "carbon metal" (*Kohlenmetall*) or "carbonium" [6, 7].

Following Gay-Lussac and Chevreul's example [34], Döbereiner used copper(II) oxide in organic combustion analysis [35]. He determined the compositions of sucrose ( $C_{12}H_{22}O_{11}$ ) and ethanol ( $C_2H_5OH$ ) [36], he was one of the first to observe the fermentative conversion of starch paste into fermentable sugar, and he gave a correct explanation of alcoholic fermentation [37]. He obtained acetic acid by the catalytic oxidation of alcohol with platinum black [38]. Saussure believed that in the oxidation of wine (ethanol) to vinegar (acetic acid) a volume of carbon dioxide equal to that of the oxygen absorbed is evolved [39]. Döbereiner, however, found that in this reaction, taking place in the presence of platinum black, only acetic acid and water but no carbon dioxide are formed [40]. He also used the catalytic oxidation of ethanol vapor to prepare impure aldehyde [41], and he prepared crystalline aldehyde ammonia [42]. He synthesized formic acid by distilling tartaric acid ( $HOOCCHOHCHOHCOOH$ ) with manganese dioxide ( $MnO_2$ ) and dilute sulfuric acid [43], and he synthesized furfural ( $C_4H_3OCHO$ ) from sucrose by the same method [44]. Regarding indigo as a "vegetable metal" (*Pflanzenmetall*), he thought that he had prepared an indigo amalgam [45].

### Döbereiner's Triads

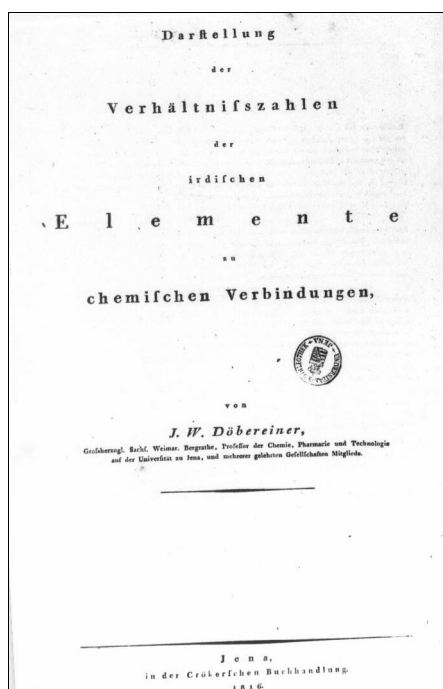
Döbereiner's recognition of the relation between atomic weights (equivalent weights) and chemical properties is his contribution best known to chemical educators and students alike. It is invariably mentioned in introductory chemistry texts as the first of the many predecessors of Dmitrii Ivanovich Mendeleev (1834–1907) and his periodic classification of the elements.

Döbereiner was quick to recognize the fundamental significance of what Jeremias Benjamin Richter (1762–1807) called stoichiometry—"the art of measuring chemical elements"—and from early in his career he carried out "stoichiometric studies" and determined the combining weights (atomic or equivalent weights) of many elements, which he compiled in a book published in 1816 (Figure 12) [46]. In a letter of September 30, 1816 to Goethe, he first mentioned what was to evolve into his *Dreiheit* (rule of triads),

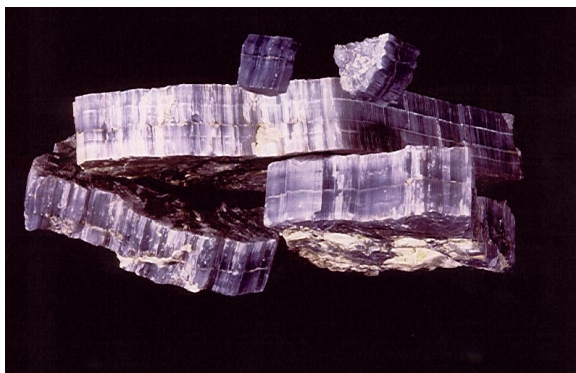
The [mineral] coelestine [celestite, strontium sulfate,  $SrSO_4$ ] found at Dornburg [Figure 13] shows remarkable relationships: its specific weight is the mean of that of anhydrite [calcium sulfate,  $CaSO_4$ ] and heavy spar [barite, barium sulfate,  $BaSO_4$ ], namely  $(2.95 + 4.47:2 = )$  3.71 and the equivalent number of

its base, strontia [strontium oxide,  $SrO$ ], is likewise the mean of the base of anhydrite, lime [calcium oxide,  $CaO$ ], and that of heavy spar, baria [barium oxide,  $BaO$ ], namely  $(27.5 + 72.5:2 = )$  50. It could almost be believed that coelestin [ $SrSO_4$ ] is a chemical compound of 1 stoichiometric portion of anhydrous gypsum [ $CaSO_4 \cdot 2H_2O$ , i.e.,  $CaSO_4$ ] with 1 such portion of heavy spar [ $BaSO_4$ ] and [that] strontia [ $SrO$ ] is the result of a combination of lime [ $CaO$ ] and baria [ $BaO$ ]. However, 1





**Figure 12.** Title page to a folding table with equivalent weights, based on H = 1, O = 7.5, and S = 15, Jena, 1816 (courtesy, Prof. Dr. Dietmar Linke).



**Figure 13.** Samples of the mineral coelestine (celestite,  $\text{SrSO}_4$ ) From Dornburg Near Jena (courtesy, Prof. Dr. Ernst-Gottfried Jäger).



**Figure 14.** Grand Duchess Maria Pavlovna (1786–1859) [20, P 244] (Reproduced with the permission of Johnson, Matthey, London).

have not succeeded in obtaining this result (artificially) in a synthetic manner [21].

As early as 1817 Döbereiner demonstrated that the equivalent of strontium (42.5) is the arithmetic mean of those of calcium (20) and barium (65) [47]. In 1829, in an article titled “An Attempt to Group Elementary Substances according to Their Analogies,” he extended this type of numerical relationship to other groups of chemically similar elements (which Leopold Gmelin (1788–1853) later called “triads” in his *Handbuch der Chemie*) to many other families of elements such as sulfur-selenium-tellurium, lithium-sodium-potassium, chlorine-bromine-iodine, and osmium-iridium-platinum [48, 49]. These relationships can also be observed with atomic numbers as well as atomic weights [50].

Döbereiner’s idea of triads attracted little attention for many years, but it was the first of the many attempts to produce a rational and systematic arrangement of the chemical elements by Pettenkofer, Dumas, Kremers, Gladstone, Cooke, Lenssen, Béguyer de Chancourtois, Newlands, Mercer, Carey Lea, Odling, and Hinrichs, among others, that culminated in the definitive work of Lothar Meyer, Mendeleev, and Moseley.

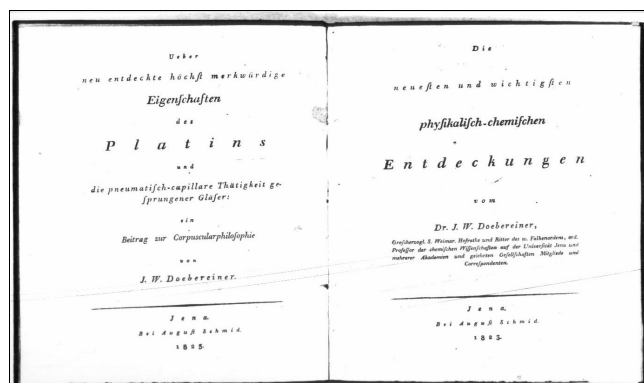
### Research on Platinum

Döbereiner’s next most significant discovery was an outgrowth of his interest in platinum needed for laboratory vessels that would be resistant to chemical reagents. In 1812 he started extracting and isolating platinum metals from two pounds of American platinum ore [6, 7]. Two years later platinum ores were discovered in Russia’s Ural Mountains, and this new source greatly facilitated his work.

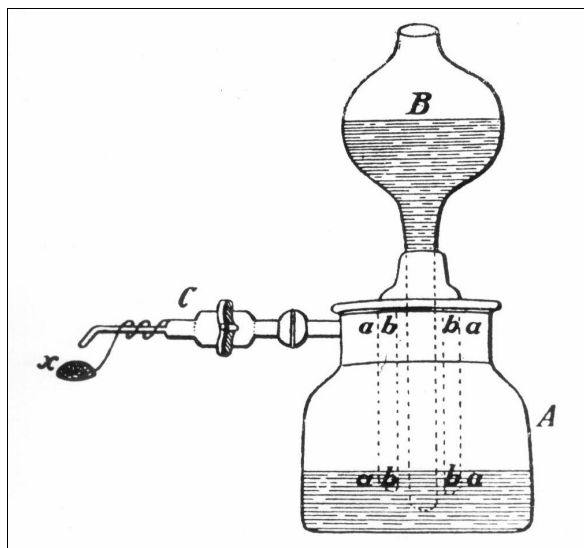
Carl August’s court in Weimar had close family connections with the Czar’s court, and the Grand Duke’s daughter-in-law, wealthy Russian Grand Duchess Maria Pavlovna (1786–1859) (Figure 14), daughter of Czar Paul I and a sister of his successors Nicholas I and Alexander I, was a patroness of Döbereiner’s who made generous donations of platinum ore and metal for his laboratory [20, 23]. In addition to being

interested in chemistry, she was in close contact with Nicholas I’s Minister of Finance, Count Egor Frantsevich Kankrin (1775–1845), who was also Head of the Mining Department in St. Petersburg. He adopted the grand duchess’ suggestion that Döbereiner’s expertise with platinum would be useful in improving Russia’s refining processes. Döbereiner was unwilling to leave Jena, but his son Franz went to Russia, where he worked in the laboratory of his father’s former student Gottfried Wilhelm Osann at the University of Dorpat (now, Tartu, Estonia), with his father acting as consultant. Together with Friedrich Weiss, the younger Döbereiner published an article on the isolation and purification of platinum (Weiss, F.; Döbereiner, F. *Ann. Chem.* **1835**, *14*, 15).

In 1816 Humphry Davy (1779–1829) found that flammable gases like “fire damp” (methane,  $\text{CH}_4$ ) when mixed with air burned without producing a flame in the presence of platinum. This discovery formed the basis for his invention of the miner’s safety lamp, which, in 1817, brought him the Royal Society’s coveted Rumford Medal for work in the applications of modern science [51]. In 1820 Sir Humphry’s younger cousin, Edmund Davy (1785–1857), found that finely divided platinum (later called *Platinschwarz* by Justus von Liebig and *Platinmohr* by Döbereiner—both meaning platinum black), prepared by reducing platinum sulfate with boiling ethanol,



**Figure 15.** Title page of Döbereiner's book, *Ueber Neu Entdeckte Höchst Merkwürdige Eigenschaften Des Platins...*, Jena, 1823 (courtesy, Prof. Dr. Dietmar Linke).



**Figure 16.** First published version (1824) of Döbereiner's *Feuerzeug*, from a model of November 9, 1823 (courtesy, Prof. Dr. Dietmar Linke).

reacted with ethanol vapor and remained white hot until all the ethanol was consumed [52].

Immediately after reading Edmund Davy's article in a German translation that appeared in 1821, Döbereiner repeated the experiment and found that the ethanol was oxidized to acetic acid. He correctly considered this important phenomenon as due to the activity of the platinum instead of the action of the ethanol on the platinum, as the Davys had mistakenly assumed. Thinking at the time that Edmund Davy's product was a suboxide of platinum, he stated,

The platinum sub-oxide, moreover, does not undergo any change during this transformation of the alcohol and can be immediately used again to acidify fresh, perhaps limitless, quantities of alcohol...a circumstance that permits its use for the large-scale preparation of acetic acid (*Essigsäure*) [53].

He even designed a vinegar lamp (*Essiglampe*), in which ethanol was supplied by a cotton wick to a small funnel containing platinum black.

Döbereiner spent the Christmas vacation of 1822 in Weimar with Goethe and demonstrated these experiments to him. He continued to work with platinum black and the finely divided

powdered metal prepared by ignition of ammonium hexachloroplatinate(IV) ( $(\text{NH}_4)_2\text{PtCl}_6$ ) and extended his work to include other vapors and gases, including hydrogen [13, 17, 54]. He first suggested that the reaction was "an electrical one, whereby hydrogen forms an electrical chain with the platinum," but in a small book devoted to the phenomenon (1823) (Figure 15) he considered it to be "probably of a quite special nature, that is, neither mechanical nor electrical nor magnetic" [55].

On July 27, 1823 Döbereiner exposed hydrogen to powdered platinum prepared as above and observed that on admission of air or oxygen at room temperature or even at  $-10^\circ\text{C}$ : "There now followed in a few moments that strange reaction; the volume of the gases diminished and after ten minutes all the admitted air had condensed with the hydrogen to form water" [56].

He also considered the most suitable form to use for the powdered platinum—small molded pellets of potter's clay impregnated with platinum, the first example of a supported catalyst. When he substituted pure oxygen for air, the reaction intensified to the extent that the filter paper holding the platinum charred. Two days later he wrote about his discovery, which he had repeated "at least thirty times that day and always with the same result," in a letter to Goethe: "Permit me, your Excellency, to give you news of a discovery that seems to be important in the highest degree from the points of view of both physics and electrochemistry" [ref. 21, letter 94 (July 29, 1823)]. He also reported his discovery to the editors of several scientific journals, including Lorenz Oken (1779–1851) (*Isis*, published in Jena), his friend Johann Salomo Christoph Schweigger (1779–1857) in Bayreuth [56], and Ludwig Wilhelm Gilbert (1769–1824) in Leipzig [54].

On August 3 Döbereiner made an even more remarkable observation. On directing a jet of hydrogen at the platinum from a distance of 4 cm so that it was premixed with air, the platinum became red-hot, then white-hot, and the jet ignited spontaneously, the basis for what was to be called his pneumatic lighter (*Döbereinersches Feuerzeug*) (Figure 16) [6, 7, 23, 57–59]. He immediately reported this discovery to the editors mentioned in the last paragraph, who published it as appendices to his first announcements [54, 56].

### The Transmission and Replication of Döbereiner's Discovery

Because of close relations between chemists across national boundaries as well as multiple publication of articles and abstracts in different languages, as early as the 1820s scientific information could be transferred with a speed and efficiency astonishing even to us in our Internet era. Bill Brock cites Döbereiner's discovery as an example *par excellence* of this speed [60]. This discovery, which produced fire without flint and tinder, quickly created an international sensation and was immediately tested and confirmed by many chemists and physicists.

One of Döbereiner's friends in Paris wrote to him that the reports of his discovery had caused "a great sensation here and excited the liveliest interest," while Grand Duke Carl August wrote to him, "I am delighted that your splendid discovery excites the attention of foreign countries. I return to you the letter from Paris and thank you for the published paper" [61]. By the end of August Döbereiner's report had appeared in the



Jöns Jacob Berzelius  
1779–1848

**Figure 17.** Jöns Jacob Berzelius (1779–1848) at the age of 47, portrait in oil by Johan Way, 1826, Library of The Royal Swedish Academy of Sciences [20, P 252] (Reproduced with the permission of the Royal Swedish Academy of Sciences, Stockholm).

*Annalen der Physik* [54], *Journal für Chemie und Physik* [56], *Annales de Chimie* [57], *Neues Journal der Pharmacie*, *Isis*, and *Bibliothèque Universelle* [62]. That month Karl Wilhelm Gottlieb Kastner (1783–1857), Professor of Chemistry and Physics at the Universität Erlangen, reported it to his former student Justus von Liebig (1803–1873), who was then in Paris [63]. At the suggestion of the German explorer and naturalist Alexander von Humboldt (1769–1859), Liebig showed Kastner's letter to Louis Jacques Thénard (1777–1857), Professor of Chemistry at the École Polytechnique, who had also seen a brief report of Döbereiner's work in the Parisian daily newspaper *Journal des Débats*, which predicted: "This beautiful discovery is going to open up a new field of research in physics and chemistry" [64].

On August 26 Thénard reported it to the Académie des Sciences in Paris, and on September 18, in his lecture opening the second annual meeting of the Gesellschaft Deutscher Naturforscher und Ärzte at Halle, Döbereiner demonstrated his discovery, stating, "Most likely a new natural principle is operative here that will become apparent through further investigation" [65]. Further experiments on the effect of heated samples of the solid metals platinum, palladium, rhodium, cobalt, nickel, gold, and silver on inflammable mixtures of gases such as hydrogen and oxygen by Thénard and his younger co-worker Pierre Louis Dulong (1785–1838), who reported them to the Académie des Sciences on September 15 [66], prompted Jean Nicolas Pierre Hachette (1769–1834) of the École Polytechnique to write to Michael Faraday (1791–1867) in London:

I saw demonstrated yesterday the beautiful experiment of Döbereiner, a German scientist (of Stuttgart, I think [*sic*]). You are no doubt familiar with it. It consisted in directing a current of hydrogen on to platinum powder obtained from

the solution of this metal in *aqua regia* [3HCl:1HNO<sub>3</sub>] by precipitation of the ammonium salt [(NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub>]. The hydrogen gas inflames, by simple contact. In your hands this fact will not be the last of its kind [67].

Faraday now began his own experiments. By September 27 he had repeated Döbereiner's work [68] and had written a short note for the Royal Institution's *Quarterly Journal of Science and the Arts* in October [69], the same month in which Döbereiner published his own monograph on the subject [55], and English translations of Döbereiner's and Dulong and Thénard's articles appeared in the *Philosophical Magazine* [70]. According to Faraday, "A most extraordinary experiment has been made by M. Döbereiner. It was communicated to me by M. Hachette; and having verified it I think every chemist will be glad to hear its nature" [69]. Thus, within a short period of only three months Döbereiner's discovery had been reported in a monograph and in about a dozen European scientific journals. But the most influential *imprimatur* came from the great Swedish chemist Jöns Jacob Berzelius (1779–1848) (Figure 17), then the supreme authority on matters chemical, in his *Jahres-Bericht*, a series of annual reports that he had begun in 1821 to review advances in physical science during the previous year: "From any point of view the most important and, if I may use the expression, the most brilliant discovery of last year (1823) is, without doubt, that fine platinum powder has the ability to unite oxygen and hydrogen even at low temperatures...made by Döbereiner" [71].

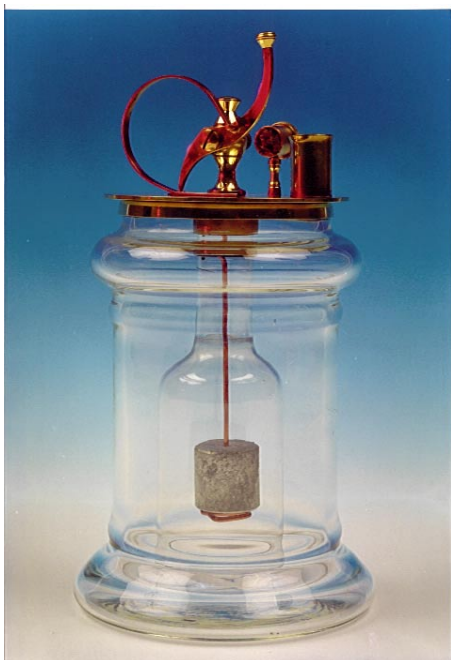
This assessment is even more remarkable in view of the fact that Berzelius had previously held Döbereiner in the lowest esteem: "I do not know whether...[Thomas Thomson] or Döbereiner...is the worst chemist in existence at the moment" [72].

### Döbereiner's Pneumatic Lighter

Döbereiner quickly applied his discovery to the construction of the pneumatic gas lighter (*Döbereinersches Feuerzeug*) that bears his name [73]. In this ingenious device (Figure 18) hydrogen gas, generated from zinc and sulfuric acid, streams through a narrow opening toward a holder in which platinum sponge is suspended on a thin platinum wire, whereupon it ignites. The resulting flame can then be used to light a candle. If the platinum becomes inactive, it can be activated by heating. About 20,000 of these lighters, some elaborately ornamented by decorative artists, were in use in Germany and England by 1828, and they soon became typical objects in many Biedermeier-style households. Döbereiner, however, refused to patent his invention, declining an offer from England to sell the rights to his invention for 80,000 talers, a sum that would have solved all his monetary problems (His annual salary as *ordentlicher Professor* amounted to only 500 talers [15]). He maintained, "I love science more than money, and the knowledge that with it I have been useful to many mechanical artists makes me happy" [7, 17].

During the 1820s many types of phosphorus matches were sold. For example, matches with tips composed of a "percussion powder" of potassium chlorate and antimony sulfide and called "friction lights" by their inventor John Walker (1781–1857) were marketed in England beginning on April 7, 1827. By the middle of the nineteenth century these and so-called "safety matches" (*Sicherheits- or schwedische Zündhölzer*), invented in 1848 by Rudolph Christian Böttger





**Figure 18.** Döbereiner's *Feuerzeug*, Deutsches Museum Fotoarchiv, Munich [22b, P 148] (Reproduced with the permission of Callwey Verlag, Munich).

(1806–1881), one of Döbereiner's students, began to replace Döbereiner's lighter. Yet, Döbereiner's lighters were still in use as late as the advent of World War I [17].

Böttger was originally a candidate of theology, who became so enthusiastic about Döbereiner's lighter that he turned to chemistry, dedicating himself to the lighter's improvement and eventually becoming Professor of Chemistry and Physics at the Physikalischer Verein at Frankfurt am Main (1835–1875) [6, 7]. In 1831 Böttger found that the ignition power of platinum sponge is destroyed by ammonia or ammonium sulfide vapors but that it can be restored by heating. Döbereiner called this property of ammonia "depotentiating action" (*depotenzierende Wirkung*).

### The Concept of Catalysis

In his annual report to the Royal Swedish Academy of Sciences for the year 1835, in the section on vegetable chemistry, titled "On a previously little noticed force which is probably active in the formation of organic compounds" and dated March 31, 1835 [74], Berzelius cited a number of phenomena of "action by contact," including Döbereiner's discovery, and filled a much needed gap in the nomenclature of chemistry by ascribing to them a common cause, which he called "catalysis." This term had been used much earlier by Andreas Libavius (ca. 1540–1616) in the sense of "breaking down, decomposition" (Greek, *κατά*, down; *λύσις*, [75]). Also, on March 15, 1655 the English author and diarist John Evelyn (1620–1706) used the word in the same sense: "this sad catalysis and declension of piety to which we are reduced" [76] and in a letter of 1658 to Sir Thomas Browne: "so generall a catalysis of integrity" [77].

### According to Berzelius:

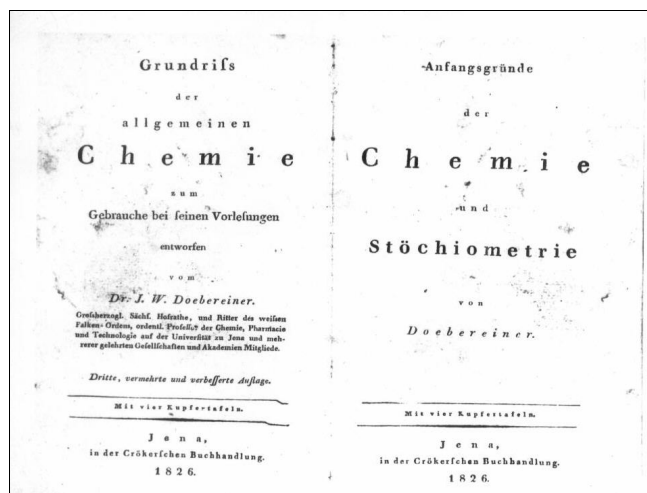
It is demonstrated that many simple and compound bodies, both in the solid and dissolved form, have the property of exerting an influence quite different from ordinary chemical affinity, whereby they bring about in a body a reaction of the components in different proportions, without themselves taking part with their components, although this can sometimes be the case. This is a new force in inorganic and organic nature, bringing into being chemical activity, and more widely distributed than has hitherto been thought, the nature of which is completely concealed. If I call it a new force it is not my meaning that it is independent of the electrochemical relations of matter, but on the contrary I can only assume that it is a special kind of manifestation of these. So long as its nature and relations are unknown it will be convenient to consider it a new force, and to give it a name. I will, using a derivation well known in chemistry, call it the *catalytic force* (*katalyska kraft*, *katalytische Kraft*) of the bodies, and the decomposition it produces *catalysis*, just as the separation by ordinary chemical affinity is called analysis. The nature of the catalytic force seems to consist essentially in the circumstance that substances are able to bring into activity affinities which are dormant at this particular temperature, and this not by their own affinity but by their presence alone.... It is a question whether an unequal degree of catalytic force with various bodies can produce the same variety of products as heat or various temperatures; and if different catalyzing bodies (*katalysirende Körper*) can produce different catalytic products from a given compound body. It is also in question whether a given catalyzing body can act on a large number of different compound bodies, or whether (as at present seems likely) only on some and not on others. These are questions for future investigation [74].

### Teaching and Books

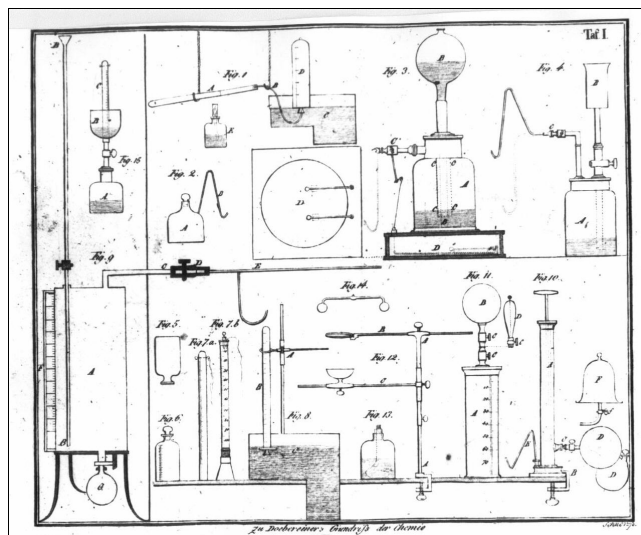
Despite the fact that Döbereiner had never had any normal formal education, this *Autodidakt* was an outstanding teacher who could not only arouse and maintain the interest of his students but also give them the opportunity of profiting from his knowledge and practical expertise by laboratory exercises. As we have seen, beginning with the winter 1820/1821 semester his *chemisch-praktisches Kollegium* made the Universität Jena a leader in practical laboratory instruction before Justus von Liebig performed a similar but better known service for the Universität Giessen [6, 7].

Among Döbereiner's students are numbered Rudolph Christian Böttger, the inventor of the safety match mentioned above; Friedlieb Ferdinand Runge (1794–1867), a founder of the coal-tar industry and a pioneer in paper chromatography; university pharmacist Karl Christoph Traugott Friedemann Göbel (1794–1851), who took over Döbereiner's lectures on pharmacy and pharmaceutical chemistry after 1819; and Gottfried Wilhelm Osann (1797–1866), the authority on the platinum metals who mistakenly believed in 1827 that he had discovered three new metallic elements, which he named pluran, ruthen, and polin. However, as we have pointed out, Döbereiner's most famous student was, of course, Goethe [5, 6].

Goethe not only studied Döbereiner's chemistry textbook, but, as he stated in his *Tag- und Jahresheften*, he studied stoichiometry with Döbereiner in 1815 and 1817. Whenever he came to Jena, he visited Döbereiner in his laboratory and



**Figure 19.** Title Page Of Döbereiner's Book, *Grundriss Der Allgemeinen Chemie Zum Gebrauche Bei Seinen Vorlesungen*, 3rd Edition, Jena, 1826 (courtesy, Prof. Dr. Dietmar Linke).



**Figure 20.** Laboratory and analytical apparatus from Döbereiner's time, from *Grundriss Der Allgemeinen Chemie Zum Gebrauche Bei Seinen Vorlesungen*, 3rd Edition, Jena, 1826 (courtesy, Prof. Dr. Dietmar Linke).

discussed and observed his latest experiments. Likewise, he often invited Döbereiner to visit him in Weimar. In October 1820 he asked him to demonstrate the deflection of a magnetic needle by an electric current, which Danish physicist and chemist Hans Christian Ørsted (1777–1851) had discovered that spring, and on December 16, 1822 Döbereiner met Ørsted at Goethe's house. While Goethe was writing his *Zur Farbenlehre* (On the Theory of Color) (1810), he asked Döbereiner to carry out "chromatic" experiments in support of his theory [5, 6].

As complements and guides to his lectures Döbereiner wrote a number of textbooks and monographs that were widely used in his time. Several books dealt with applied chemistry for factories such as those dealing with vinegar, wine, and beer (Through his efforts the brewing of Bavarian-type lager beers became known in middle and northern Germany). Thus, in addition to his already cited monographs [46, 55, 73], we may list the following among his most important books, many of

which are rare today (Because of the variation in titles of the different editions, the list is somewhat confusing and may involve duplication):

- *Lehrbuch der allgemeinen Chemie, zum Gebrauche seiner Vorlesungen*, 3 vols.; Jena, 1811–1812.
- *Anfangsgründe der Chemie und Stöchiometrie*; Cröker: Jena, 1811, 1819, 1826.
- *Grundriss der allgemeinen Chemie zum Gebrauche bei seinen Vorlesungen*; Jena, 1811, 1819, 1826 (Figures 19 and 20); Döbereiner, F. *Supplement zu J. W. Döbereiner's Grundriss der Chemie. Tabellarische Darstellung der organischen Stoffe in alphabetischer Ordnung für Aerzte, Chemiker und Pharmaceuten*; Stuttgart, 1837.
- *Anleitung zur kunstmässigen Bereitung verschiedener Arten Essige im Auftrage der höchsten Landes-polizey-Stelle*; Cröker: Jena, 1814, 1816, 1819, 1832.
- *Elemente der pharmazeutischen Chemie, zu Vorlesungen und zum Gebrauche für Aerzte und Apotheker*; Jena, 1814, 1819.
- *Handbuch der pharmazeutischen Chemie*; Jena, 1816, 1831.
- *Anleitung zur Darstellung und Anwendung aller Arten der kräftigsten Bäder und Heilwässer welche von Gesunden und Kranken gebraucht werden*; Cröker: Jena, 1816.
- (Beträge) *Zur Gärungschemie und Anleitung zur Darstellung verschiedener Arten künstlicher Weine, Biere usw.*; Jena, 1822, 1844.
- *Deutsches Apotekerbuch zum Gebrauche bei Vorlesungen und zum Selbstunterrichte für Apoteker, Droguisten, Aerzte und Medizin-Studierende*; Jena, 1816, 1836; with Döbereiner, F., Balz: Stuttgart, 1840.
- *Anleitung zur Darstellung und zum Gebrauch aller Arten der kräftigsten Bäder und zur künstlichen Bereitung der wirksamsten Heilwasser, welche von Gesunden und Kranken getrunken und als Bäder gebraucht werden*; Jena, 1816.
- *Neueste stöchiometrische Untersuchungen und chemische Entdeckungen*; Jena, 1816.
- (*Beiträge zur pneumatischen Chemie*); Cröker: Jena, 1821–1825 (Figure 21).
- *Beiträge zur Gärungschemie*; Jena, 1822, 1844.
- *Beiträge zur physikalischen Chemie*; 3 parts; Cröker: Jena, 1824, 1825, 1835.
- *Chemie für das praktische Leben*; Jena, 1836.

### Applied Research

Döbereiner was a technologist as well as a chemist, and for him the main attraction of science was the benefit that it could provide for humanity. As expert consultant on technical-chemical matters for Duke Carl August and Goethe, the duke's minister, he was able to give free rein to his altruistic, practical concerns with the full approval and support of his patrons. He was appointed superintendent of all brewing, distilling, and dyeing factories and was consulted on every conceivable subject requiring his scientific expertise such as the use of gas from Ilmenau coal for street illumination, water gas (a mixture of carbon monoxide and hydrogen) as an industrial fuel, the manufacturing of steel, the analysis of spa and mineral waters,



**Figure 21.** Title page of Döbereiner's book, *Zur Pneumatischen Chemie, 4th Part*, in which (as in the 5th Part) his works on platinum catalysis are reported, Jena, 1824 (courtesy, Prof. Dr. Dietmar Linke).

and the preparation of celestine and baryta optical glass (Through the work of industrialist Carl Zeiss (1816–1888) and chemists Ernst Abbe (1840–1905) and Otto Friedrich Schott (1851–1935) Jena was later to earn a worldwide reputation for the manufacture of fine optical instruments).

In order to strengthen the economic condition of the duchy he devised methods for replacing foreign dyestuffs with home-grown products such as the extraction of indigo from woad (*Isatis tinctoria*), madder from madder root (*Rubia tinctorum*), and safflower, the coloring matter of *Carthamus tinctoria*, and he served as an expert witness in the law courts [5, 6, 13]. Inasmuch as Carl August's small duchy lacked financial resources, most of Döbereiner's industrial plans and contributions were never put into large-scale practice.

### Honors

In 1813 Duke Carl August promoted Döbereiner to the rank of Mining Counselor (*Bergrat*), and in 1818 Döbereiner was appointed Privy Counselor (*Hofrat*) when he declined the call (*Berufung*) to the Universität Halle. After he invented the pneumatic lighter he was awarded the Knight's Cross of the Weimar House Order of Watchfulness or of the White Falcon. In 1851 the city of Jena erected a monument in his memory on what is today the Goetheallee, thus beginning the tradition of honoring in this place leading personalities of the university [6, 11, 15]. In 1958 a statue of Döbereiner by H. Steiger was erected in front of the Döbereiner-Hörsaal (named after him in 1974 (Figure 1). Since 1965 the Pharmazeutische Gesellschaft der Deutschen Demokratischen Republik has awarded a Döbereiner-Medaille "for service in the field of pharmacy" [18]. Döbereiner's name is also honored by a street and a pharmacy in Jena, a school in Rudolstadt-Schwarza, and a work collective in the district of Gera in southeastern Germany [15, 18]. And we have already mentioned the postage stamp (Figure 3).

### Döbereiner's Legacy

Lack of space has prevented us from exploring the full gamut of Döbereiner's multifaceted activities in pure and applied chemistry. Although renowned both as a researcher and educator in his own day (his work was cited about twenty

different times by Hermann Kopp (1817–1892) in his classic book on the history of chemistry [78]) and in his native land today, with the exception of his contributions to the classification of the elements and heterogeneous catalysis by platinum, time has not been kind to Döbereiner's memory. A born but largely self-educated scientist who had been closely linked to nature from his earliest youth, he was "an idealist, poor in worldly possessions, but rich in knowledge, who, without thought to his own advantage, unselfishly gave of this wealth so that others might aid humanity" [6].

**Acknowledgment.** I am indebted to Professor Ernst-Gottfried Jäger, Chairman of the Döbereiner Festkolloquium Preparation Committee, Friedrich-Schiller-Universität Jena, and Professor Dietmar Linke, Brandenburgische Technische Universität Cottbus, for useful source materials and colorful illustrations. I also wish to thank Diane Majors and Randy Vaughn-Dotta of California State University, Fresno for assistance in the preparation of this article.

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