Johann Wolfgang Döbereiner's *Feuerzeug*

ON THE SESQUICENTENNIAL ANNIVERSARY OF HIS DEATH

By Professor George B. Kauffman

Department of Chemistry, California State University, Fresno

Johann Wolfgang Döbereiner, born in 1780, was the Professor of Chemistry and Technology at the University of Jena, from 1810 to 1849. During this time he observed the action of platinum black on hydrogen, which led to his invention of the pneumatic gas lighter (Feuerzeug) and to Berzelius' concept of catalysis, besides making other contributions to pure and applied chemistry. On the one hundred and fiftieth anniversary of his death in 1849 a Festkolloquium was held to commemorate his work at the Friedrich-Schiller-University of Jena. Here we describe some aspects of his life and work.

On 7th May 1999, a *Festkolloquium*, in honour of Johann Wolfgang Döbereiner, was held at the Friedrich-Schiller-University Jena (Friedrich-Schiller-Universität Jena). The event was organised by the Chemisch-Geowissenschaftliche Fakultät, Institut für Anorganische und Analytische Chemie of the University, which was founded in 1558 and which has 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. The colloquium commemorated the 150th anniversary of the death, on 24th March 1849, of Johann Wolfgang Döbereiner, Professor of Chemistry and Technology at Universität Jena.

About 300 persons gathered in the Döbereiner-Hörsaal of the Chemistry Institute, where "*Das Vokalkomitee*" presented a musical prelude beginning with a poem written specially for Döbereiner's 36th birthday (13th December 1816) by his friend, the poet and dramatist, Johann Wolfgang von Goethe. The poem, "*Dem Professor Döbereiner im Namen seiner Kinder, zum Geburtstag*" (To Professor Döbereiner, in the Name of His Children for His Birthday), 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, is as follows:

Wenn wir dich, o Vater sehen	Whenever we see you, oh father,
In der Werkstatt der Natur	In Nature's laboratory
Stoffe sammeln, lösen, binden,	Collecting, dissolving, combining substances,
Als seist du der Schöpfer nur,	As if you alone are the Creator,
Denken wir: Der solche Sachen	We think: Should whoever has
Hat so weislich ausgedacht,	So wisely invented such things,
Sollte der nicht Mittel finden	Not find the means
Und die Kunst, die fröhlich macht?	And the art that makes us joyful?
Und dann, schauen auf nach oben,	And then, we behold on high,
Wünschen, bester Vater, wir,	Best father, wishes,
Was die Menschen alle loben,	Which all people praise,
Glück und Lebensfreuden dir...	Good luck and joy in living to you...

Johann Wolfgang Döbereiner
1780–1849

After early struggles with solvency, Döbereiner was appointed in 1810 to be the Extraordinary (*ausserordentlich*) Professor of Chemistry and Technology at the University of Jena. In 1823, he observed the ignition, by finely divided platinum powder, of a stream of hydrogen directed at it, the platinum becoming white-hot. News of this work, later to be called catalysis, was quickly published and led to other scientists repeating his work

The participants were greeted by Professor Christian Robl, Dean of the Chemisch-Geowissenschaftliche Fakultät, and Professor Klaus Manger, Speaker of the special research programme "Ereignis Weimar-Jena, Kultur um 1800".

The scientific part of the programme consisted of two lectures by leading authorities in those fields of chemistry whose foundations were laid by Döbereiner – catalysis and the periodic system of the elements – "Heterocyclencarbenes: 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. Armbruster headed the team that discovered the last seven elements of the Periodic Table up to element 112. The history of chemistry part of the programme consisted of the 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 Friedrich-Schiller-Universität Jena.

"The Most Brilliant Discovery"

As early as the 1820s, because of close relations between chemists across national boundaries and multiple publication of articles and abstracts in different languages, scientific information could be transferred with a speed and efficiency that is astonishing even to us in our Internet era. As an example par excellence of this phenomenon, Bill Brock cites Döbereiner's discovery in 1823, which the great Swedish chemist, Jöns Jacob Berzelius, later called

"catalysis" (1). On 27th July 1823, Döbereiner exposed hydrogen to powdered platinum prepared by igniting ammonium hexachloroplatinate(IV), $(NH_4)_2PtCl_6$, and observed that on admission of air, at room temperature or even at –10°C, "after ten minutes all the admitted air had condensed with the hydrogen to form water" (2–4).

When Döbereiner substituted pure oxygen for air, the reaction intensified to the extent that the filter paper holding the platinum charred. That same week he reported his discovery to his patron, close friend and most famous student, Germany's greatest poet and playwright Johann Wolfgang von Goethe (1749–1832), who also served in Grand Duke Carl August's court as Qualified Minister (*zuständige Minister*) for the Universität Jena. At the same time, he also reported it to the editors of several scientific journals.

On 3rd August, Döbereiner observed that if a jet of hydrogen was directed at the spongy 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. This was the basis for what was to be called the *Döbereinersche Feuerzeug* (lighter) (5–10). This discovery, in which fire was produced without flint and tinder, quickly created an international sensation and was immediately tested and confirmed by many chemists and physicists.

Rapid Publication of his Results

By August, Döbereiner's account had appeared in the *Journal für Chemie und Physik* (2), *Annalen der Physik* (3), *Annales de Chimie* (9), *Neues Journal der Pharmacie*, *Isis*, and *Bibliothèque Universelle* (11). That same month Karl Wilhelm Gottlieb Kastner (1783–1857), Professor of Chemistry and Physics at the Universität Erlangen, wrote about it to Justus von Liebig (1803–1873), who was then in Paris (12).

At the suggestion of the German naturalist and explorer Alexander von Humboldt (1769–1859), Liebig showed Kastner's letter to Louis Jacques Thénard (1777–1857), who had also seen a brief report of Döbereiner's work in the *Journal des Débats* of 24th August. Thénard reported it on 26th August to the Académie des Sciences in Paris. On 13th September, Döbereiner demonstrated his discovery at the meeting of the Gesellschaft Deutscher Naturforscher und Ärzte at Halle. Additional experiments by Thénard and Pierre Louis Dulong (1785–1838), who described them to the Académie on 15th September (13), prompted Jean Nicolas Pierre Hachette (1769–1834) of the École Polytechnique to write on 16th September 1823 to Michael Faraday (1791–1867) in London. Faraday began experiments of his own and related them in the Royal Institution's *Journal of Science and Arts* in October, the month in which Döbereiner published his own monograph on the subject (14). That same month English translations of Döbereiner's and Dulong and Thénard's articles appeared in the *Philosophical Magazine*.

Thus, within three short months Döbereiner's discovery had been reported in a monograph and in about a dozen European scientific journals. Berzelius, then the supreme authority on matters chemical, in his *Jahres-Bericht*, a series of annual reports that he had begun in 1821 in order to review advances in physical science during the previous year, wrote for 1823: "From any point of view the most important and, if I may use the expression, the most brilliant discovery of last year is, without doubt, that...made by Döbereiner" (15). This appraisal 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" (16).

Döbereiner's Life and Career

Who was this man who was suddenly thrust into the limelight by his unexpected discovery? Born on 13th December 1780 in Hof an der Saale in Bavaria, Döbereiner – a self-made man in every sense of the word – was the son of a coachman who was not financially able to provide the bright boy with any but the barest essentials of schooling (17–24). However, his mother encouraged him, and, after three years of an apprenticeship with an apothecary, he began,

The great German poet, Johann Wolfgang von Goethe, who was a Minister for Grand Duke Carl August of Sachse-Weimar-Eisenach, and the Duke in the courtyard of the castle at Jena. Goethe was a friend of Döbereiner. The Grand Duke appointed Döbereiner to be Professor of Chemistry and Technology at the University of Jena

at the age of seventeen, five precarious *Wanderjahre*, eventually reaching Karlsruhe and Strasbourg, where he attended lectures on the sciences. He returned home and at the age of twenty-three married Clara Knab, a childhood friend.

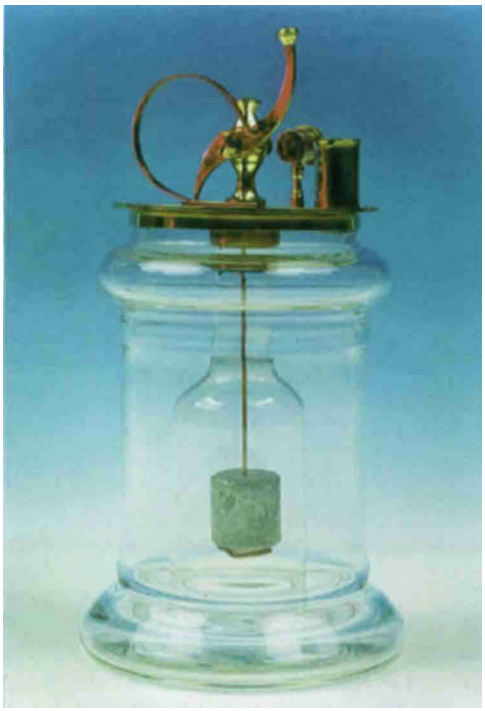
Although he was now an apothecary, Döbereiner had neither the money nor licence to buy a pharmacy. He opened an agricultural produce business and began to produce pharmaceutical-chemical preparations. By 1803 he was reporting his experiments with white lead, sugar of lead, magnesium sulfate and other commercially valuable products in the *Neues allgemeines Journal der Chemie*, edited by Adolph Ferdinand Gehlen (1775–1815), which brought him to the attention of other chemists.

When Döbereiner lost his licence and his business, his relatives gave him a position in charge of bleaching and dyeing in their textile mill, but the Napoleonic war forced the plant to close. He then began to supervise agricultural estates, but these were discontinued in 1810, and once again, the twenty-nine year old father of a family found himself unemployed and unable to pay his debts.

At this lowest point in his life, Döbereiner was surprised to learn from the Senate of the Universität Jena that he had been nominated to be Extraordinary (*ausserordentlich*) Professor of Chemistry and Technology. Grand Duke (*Grossherzog*) Carl August (1757–1828) of Sachse-Weimar-Eisenach, an enlightened and liberal ruler and patron of the arts and sciences, had asked Gehlen to recommend a successor to Professor Johann Friedrich August Göttling (1753–1809) who had died the previous year. Gehlen, who knew that Döbereiner was out of work, proposed his name with little hope of success for he did not have a high school (*Gymnasium*) certificate, nor any higher education. Only after Döbereiner arrived in Jena did he learn that he needed a doctorate to occupy the position. He was granted a doctorate on 10th November 1810 at half the usual fee and because of his poverty was allowed to pay this debt in installments. Döbereiner was so grateful for the position that, despite more remunerative offers from five other universities, he remained at Jena until his death on 24th March 1849.

Research on Platinum

Döbereiner's most significant discovery was an extension of his interest in platinum, which was necessary for laboratory vessels resistant to chemical reagents. As early as 1812 he began to extract and isolate platinum metals from two pounds of American platinum ore (5, 6).



Döbereiner's *Feuerzeug*, the gas lighter in which hydrogen gas, produced by the action of sulfuric acid on zinc, ignites after passing over platinum sponge hanging from a platinum wire. The Feuerzeug was used to light candles

In 1823 platinum ores were discovered in the Ural Mountains of Russia, 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), was a patroness of Döbereiner and made generous donations of ore to his laboratory (7).

In 1816 Humphry Davy (1779–1829) observed that flammable gases, such as methane ("fire damp"), burned without producing a flame in the presence of platinum, when mixed with air. This was the basis for his invention of the miners' safety lamp, which brought him in 1817 the Royal Society's coveted Rumford Medal for work in the applications of modern science (25). 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, reacted with ethanol vapour and remained white-hot until all the ethanol was consumed (26).

In 1821, after reading Edmund Davy's article in a German translation which appeared in that year, Döbereiner repeated this experiment and found that the ethanol was oxidised to acetic acid. Because the platinum was not consumed, he suggested that the reaction could be used "for the large-scale preparation of acetic acid" (*Essigsäure*) (27), and he even designed a vinegar lamp (*Essiglampe*), in which ethanol was supplied by a cotton wick to a small funnel containing platinum black. He spent the Christmas vacation of 1822 in Weimar with Goethe, who was not only a patron of the natural sciences but also made a number of original scientific contributions (28), and demonstrated these experiments to him. Döbereiner continued to work with platinum black and the finely divided metal prepared by ignition of ammonium hexachloroplatinate(IV) and extended this work to include other vapours and gases, particularly hydrogen, which led him to "the most brilliant discovery" discussed above (2–4).

Döbereiner first suggested that the reaction was "an electrical one, whereby hydrogen forms an electrical chain with the platinum", but he later considered it to be "probably of a quite special nature, i.e., neither mechanical nor electrical nor magnetic" (14). In 1835 Berzelius named the phenomenon "catalysis" (29).

Döbereiner's Platinfeuerzeug

Following this discovery, Döbereiner quickly applied it to construct the pneumatic gas lighter (*Döbereinersche Feuerzeug*) that bears his name (30). In this ingenious device 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 flame can then be used to light a candle. If the platinum becomes inactive, it can be activated by heating. By 1828 about 20,000 of these lighters,

some elaborately ornamented by decorative artists, were in use in Germany and England, and they soon became typical objects in many Biedermeier-style households. However, Döbereiner refused to patent his invention, declaring "I love science more than money, and the knowledge that with it I have been useful to many mechanical artists makes me happy" (4, 6).

Various types of phosphorus matches were sold during the 1820s. Those with tips composed of a "percussion powder" of potassium chlorate and antimony sulfide and called "friction lights" by their inventor John Walker (1781–1857) had been marketed in England since 7th April 1827. By the middle of the nineteenth century these, and so-called "safety matches" (*Sicherheits-* or *schwedische Zündhölzer*), which were invented in 1848 by Rudolph Christian Böttger (1806–1881), one of Döbereiner's students, began to replace Döbereiner's lighter. Böttger was originally a candidate of theology, who became so enthusiastic about Döbereiner's lighter that he turned to chemistry, dedicating himself to the improvement of the lighter. He eventually became Professor of Chemistry and Physics at the Physikalische Verein at Frankfurt am Main (1835–1875) (5, 6). In 1831 he found that the ignition power of platinum sponge is destroyed by ammonia or ammonium sulfide vapours but that it can be restored by heating. Döbereiner called this property of ammonia "depotentiating action" (*depotenzierende Wirkung*). Döbereiner's lighter was still in use at the beginning of World War I (4).

Other Research

Almost equal in importance to his work on the catalytic action of platinum was Döbereiner's recognition of the relationship between atomic weights and chemical properties, making him the first of the many predecessors of Dmitrii Ivanovich Mendeleev and his periodic classification of the elements. As early as 1817 he demonstrated that the equivalent of strontium (42.5) is the arithmetic mean of those of calcium (20) and barium (65) (31). In 1829 he extended this so-called "law of triads" to many other families of elements such as sulfur-selenium-tellurium, lithium-sodium-potassium and chlorine-bromine-iodine (32, 33). These relationships can also be observed with atomic numbers as well as atomic weights (34).

Döbereiner also discovered the catalytic action of manganese dioxide (pyrolusite, *Braunstein*) on the thermal decomposition of potassium chlorate, the basis for the preparation of oxygen known to every introductory chemistry student (35). His discovery that hydrogen escaped from a cracked flask (36) led Thomas Graham (1805–1869) to his law of diffusion (37). 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" (38).

Among his numerous organic experiments, Döbereiner prepared carbon monoxide by heating formic acid with sulfuric acid (39) and a mixture of carbon monoxide and carbon dioxide by heating oxalic acid with sulfuric acid (40). He also used copper(II) oxide in organic combustion analysis (41). 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 (42). These are only a few of the numerous contributions that Döbereiner made to the pure and applied science that he loved so much.

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Noble and Rare Metals: NRM-2000

THIRD INTERNATIONAL CONFERENCE

The third in these broad ranging conferences, which take place every three years, is being held from 19th-22nd September, 2000, at the Donetsk State Technical University, Ukraine. The conference, which is entitled "Current Status and Strategy of Development in the XXI-st Century" is aiming to cover such topics as the geology and refining of the noble and rare earth metals; metal recovery, assaying and analysis; the science and technology of the platinum group metals and their alloys and a broad spectrum of their industrial uses and engineering applications.

The First Circular and further details on the conference may be obtained from the organising committee, Chairman: Professor Victor A. Goltsov, Donetsk State Technical University, 58 Artem Street, Donetsk 340000, Ukraine; e-mail: goltsov@physics.dgtu.donetsk.ua; tel: +380-(0)622-910-314; fax: +380-(0)622-921-278.