

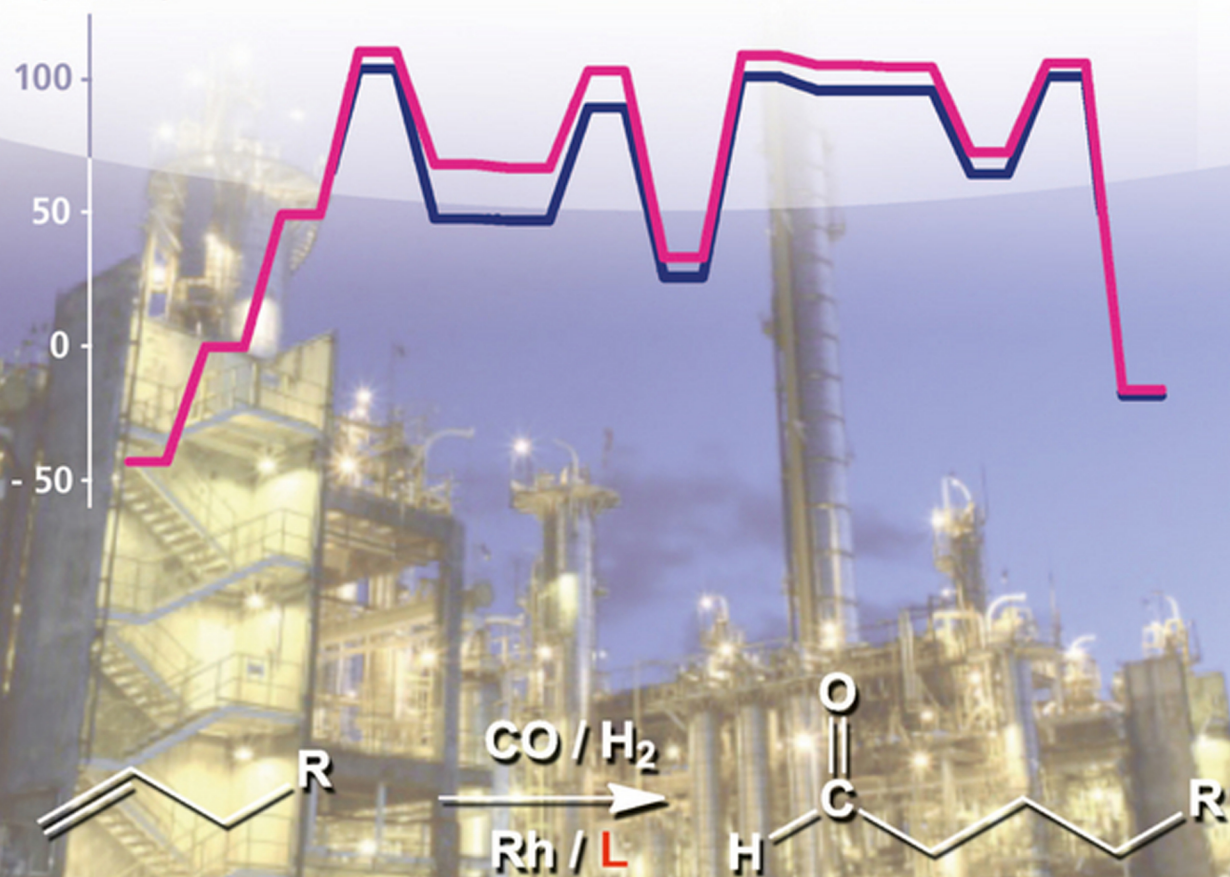
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Lutz H. Gade and Peter Hofmann

Molecular Catalysts

Structure and Functional Design

With a Foreword by Nobel Laureate Roald Hoffmann

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Molecular Catalysts

Structure and Functional Design

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Foreword

1

The Magic Force That Became a Science

In Heidelberg Castle, among many wonders, one finds the German Pharmacy Museum (*Deutsches Apotheken-Museum*). As one wanders through it, one comes to the object illustrated below (Figure 1). This is Döbereiner's lighter or igniter, *Döbereinersches Feuerzeug*. For about 40 years in the nineteenth century, it was an object of industrial and middle class utility. Chemical light years behind the wonders of catalysis described in this book, it was, nevertheless, in its time the first example of a practical designed application of catalysis. I would like to tell you its story; as I do I will call it the Feuerzeug, because the German word is more poetic than its English equivalent.

The story I will tell you is of a catalyst for one of the simplest chemical reactions, the combustion of hydrogen: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$. It is also a story of chemistry in culture, of a Russian–German geopolitical tie that, in the 1820s, helped a Jena professor to invent a new way of lighting fires using, of all metals, platinum. So, this is a story of fire too. And one of modern surface chemistry.

2

It Should Go Off, Shouldn't It?

Is there a problem with the above reaction, hydrogen burning? The hydrogen-filled balloon set off by a taper is the chemistry lecturer's favorite demonstration. You can vary the effect by adjusting the mixture of hydrogen and oxygen in the balloon – pure hydrogen gas (H_2) will give you a respectable pop and a neat flame, just a little H_2 will simply not go off. The most bang for the buck comes from a mixture of hydrogen and oxygen gas (O_2). I remember waking up sleeping dogs in my class, not to mention students, with this demonstration.

The reaction is highly exothermic: the change in free energy for all gaseous components under standard conditions is a very respectable 242 kJ per mole of H_2 . And all it takes is a lighted taper or match to set it off.



Figure 1 Döbereiner's Feuerzeug, from the German Pharmacy Museum in Heidelberg. This one is from around 1840. (Reproduced with permission of the Deutschen Apotheken-Museum Heidelberg.)

“... a match to set it off.” That’s just the point: the radicals in the flame and the heat of the match initiate the reaction, after which it indeed proceeds, posthaste. The mixture of hydrogen and oxygen, in the absence of that match or of a catalyst, would just sit there—the activation energy for the uncatalyzed reaction is very high.

Hydrogen was first well identified by Cavendish in 1766. Its burning to water and the parallel and more difficult decomposition of water to H_2 and O_2 were cornerstones of Lavoisier’s chemical revolution. The reaction was just as reluctant to go in the 1780s as it is today. There were no safety matches until 1855. So Lavoisier set it off with an electric spark. And within 50 years, a German chemist, Johann Wolfgang Döbereiner, used the same H_2 and O_2 reaction, now catalyzed, as a ready source of fire, replacing other sources of fire in home and laboratory.

3

Incendiary Acts

How were fires lit before? To begin with, from other fires, of course. Two further techniques evolved around the world – the first generated heat by rubbing wood rapidly against wood, the second created sparks by striking hard stones against

stone or metal. In both cases, the heat or spark had to be “caught” by a flammable material nearby. Tinder could be mostly anything organic, but certain dried mushrooms were particularly valued. The ingenuity in the construction of bows for rubbing wood sticks or the compact steel-silex-tinder kits of seventeenth-century soldiers is remarkable.

In the seventeenth and eighteenth centuries, as optics evolved, the burning glass or mirror became an important fire source, albeit a fair weather one. Ehrenfried Walther von Tschirnhaus (1651–1708), a natural philosopher and polymath with a practical bent, built the best of these, capable of reaching the highest temperatures then possible on earth. Sparks also came from the newly discovered electricity. Still another source was invented in 1770 and has a fascinating connection to chemistry and physics. This is the pneumatic lighter, in which the heat generated in a rapidly compressed gas is sufficient to inflame tinder.

4

Döbereiner's Feuerzeug

Johann Wolfgang Döbereiner was born in Hof an der Saale in 1780. His beginnings were simple. He was largely self-educated, the son of a coachman. But Döbereiner's talents were recognized, and in 1810 he was appointed to a professorship in Jena. This town was in the Grand Duchy of Saxe-Weimar-Eisenach, a princely state under the administration at just that time of another Johann Wolfgang, namely Goethe. Goethe and Döbereiner had an extensive correspondence, *inter alia* dealing with the tarnishing of silver spoons in red cabbage and the composition of Madame de Pompadour's toothpaste. Goethe went to Jena to study analytical chemistry with Döbereiner [1]¹⁾. A contemporary analog would be if the present French Prime Minister Manuel Valls took off a few weeks to learn about supramolecular chemistry with Jean-Marie Lehn at the University of Strasbourg. It would be good for Valls, but ...

Döbereiner did much interesting chemistry. For instance, he was responsible for noting an important regularity in the chemistry of the elements, that of triads, one of the forerunners of Mendeleev's periodic table. And Döbereiner observed in 1823 that when platinum metal (in a finely dispersed form called platinum (Pt) sponge) was exposed to hydrogen, much heat was generated. The platinum in fact glowed red hot to white hot, and if more hydrogen were supplied, the hydrogen burst into a hot but nearly colorless flame.

Döbereiner writes to his Prime Minister Goethe, as follows:

Ich erlaube mir, Eurer Exzellenz von einer Entdeckung Nachricht zu geben, welche [...] im hohen Maße wichtig erscheint. Ich finde [...], dass das rein metallische staubfeine Platin die höchst merkwürdige Eigenschaft hat, das Wasserstoffgas durch bloße Berührung [...] zu bestimmen, dass es sich mit

1) I thank Dr. Linke for introducing me to the Döbereiner story.

Sauerstoffgas zu Wasser verbindet, wobei eine bis zum Entglühen des Platins gesteigerte Summe von Wärme erregt wird. [2, 3]

[I allow myself, your Excellency, to give you news of a discovery which appears to most important. I found that finely divided metallic platinum has the most remarkable property, to induce hydrogen to combine with oxygen to give water, on simple contact. In the process heat is released, sufficient to make the platinum glow.]

And Berzelius, in his Annual Reports on the Progress of Chemistry, writes the year after:

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 fine platinum powder has the ability to unite oxygen and hydrogen even at low temperatures.

Within days, Döbereiner turned this beautiful observation into a practical igniter. Figure 2 shows the design. One has a bottle that can be tightly sealed. Inside a glass cylinder in that bottle hangs a piece of zinc (*d*). the bottle is filled with sulfuric acid (typically 25% sulfuric acid (H₂SO₄)). There is a controlled outlet from the glass bottle, the stopcock (*e*). The zinc (Zn) reacts with sulfuric acid, generating hydrogen gas *in situ*:



When the stopcock is opened, the H₂ is directed through a thin tube (*f*) onto a bit of platinum sponge (*g*). A flame lights, essentially instantaneously. When the stopcock is closed, the flame goes out. More H₂ is generated, but comes to a stop as gas pressure build.

5

Geopolitics and Science

Döbereiner continued his research with the catalytic properties of platinum. Actually Humphry Davy had discovered the phenomenon 6 years ago, heating a fine platinum wire above a coal gas flame. Davy compared copper, silver, gold, palladium, and iron in this effect, and found that only Pt and Pd initiated exothermic burning; he was thus the first to focus on selectivity, a matter of some importance in this book. Döbereiner actually made a supported catalyst (a mainstay of industrial catalysis and automotive catalytic converters today) by shaping small balls of potter's clay impregnated with platinum.

The word catalysis came from further north, from the authoritative pen of Jöns Jacob Berzelius in 1835. In his highly influential Annual Reports (translated into German and many other languages; but it is good to see a language besides English and German in chemistry ...), he wrote the following:

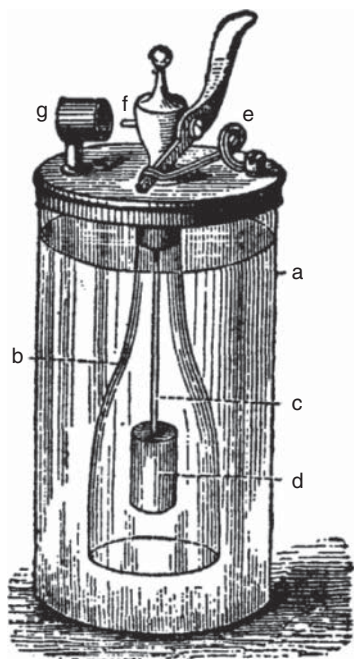


Figure 2 Schematic of an early Döbereiner lighter. (Adapted from *Nordisk familjebok/ Ugglepplagan*. Vol. 7. Egyptologi - Feinschmecker, p. 163–164, 1907. From Wikipedia.)

Jag skall derföre ... kalla den kroppars katalytiska kraft, sönderdelning genom denna kraft katalys, likasom vi med ordet analys beteckna åtskiljandet af kroppars beståndsdelar medelst den vanliga kemiska frändskapen. [emphasis in original] [4]

[I shall, therefore ... call it that body's catalytic force, the decomposition of other bodies by this force catalysis, just as we signify by the word analysis the separation of the constituents of bodies by the usual chemical affinities.]

Berzelius viewed catalysis as a special force, to some not that different from the heritage of the Philosopher's Stone [3]; it took 60 years and the great science and intuition of Wilhelm Ostwald to point us in another direction.

For his work, Döbereiner needed great supplies of the precious metal, and a geopolitical note is in order here: platinum originally came from Spanish colonial mines in the New World, and that is presumably Döbereiner's original source. Around 1824, major deposits were discovered in the Urals. How could Döbereiner, who was struggling desperately in his laboratory finances, get the precious white metal? Well, the Empress of Russia, Catherine the Great (1729–1796), was a German princess from the Duchy of Anhalt-Zerbst. There were close Russian–German ties throughout this period, and they continued until the World War I. In Döbereiner's principality, the wife of Carl Friedrich, the then heir

to the Grand Duke, was Maria Pavlovna, the daughter of Czar Paul I of Russia. Platinum from the Urals came easily to Jena; he may have had a kilogram of it.

6

Chemistry in Culture

Döbereiner's lamp became a common way to light fires in industrial settings in the first half of the nineteenth century. Within 5 years of its discovery, 20,000 lamps were in use in Germany and England. It entered the middle-class home as well. (Nothing like this could happen today; imagine the horror of today's risk-avoiding society at the thought of filling a lamp with sulfuric acid!) And if a utilitarian technology is to be accepted into society, it must be culturally processed. What I mean is that it is clothed according to the prevalent esthetics of the time. In 1829, a Berlin manufacturer could offer "... as a pleasant and useful Christmas present a lighting machine, outfitted with platinum, elegant, clean, and sturdily constructed, with Chinese and other decoration, insensitive to wetness and cold ..."

In time the safety match, the cerium frictional spark source (see Primo Levi's Ce chapter in his *Periodic Table*), the cigarette lighter and the gas stove electronic lighter put Döbereiner's Feuerzeug into the museum.

Look at the Pharmacy Museum Feuerzeug again. The image on the housing is more than a genre painting. Two young women appear to be playing a game: one watching and the other active. There is a basin with water (see the jug in front to replenish the water). And in the basin are two floating "boats," perhaps made of wood or paper. In each is a candle. The boats look circular, but their action will be more pronounced if they were not, or if a piece of the rim of one is cut out a bit. Try it yourself, please. The young women are doing a scientific experiment. And one which is fun too.

7

How Does Hydrogen Burn?

One hundred and seventy-two years after Döbereiner's discovery, in 1995, Laurens K. Verheij and Markus B. Hugenschmidt write:

In recent years many studies on the reaction between hydrogen and oxygen on metal surfaces have been reported. Although this reaction is expected to be one of the simplest oxidation reactions, rather complex phenomena are observed which make a determination of the reaction mechanism difficult. Even for the water formation reaction on Pt(111), the system which has been most widely studied, an understanding of the reaction process seems only just emerging [5].

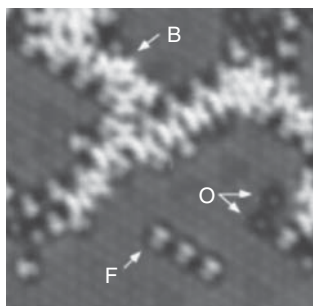


Figure 3 Schematic of O_2 molecules and O atoms (gray) adsorbed on a platinum surface (left). The image generated by the scanning tunneling microscope reveals two shapes of oxygen molecules on the platinum surface (right). Molecules can

appear to form “clover-leaf” (B) or “pear-like” (F) shapes. In some places, one sees the molecules dissociated to adsorbed oxygen atoms (dark circles, marked “O”). (Photograph courtesy of Wilson Ho.)

In the next 20 years, understanding did emerge, as incomplete as it is. It came through the beautiful work of Gerhard Ertl [6] and of others [7]. The sequence of events is not simple, not easily revealed, despite the availability of tools unimaginable to either Döbereiner or Ostwald, such as scanning tunneling microscopy. I show a teaser, an image relevant to the very first steps of the reaction, when oxygen molecules impinge, as they must, on a platinum surface (Figure 3).

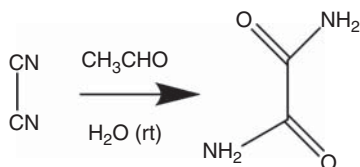
At low temperatures, way below room temperature, O_2 bonds to the surface first as a molecule and in several different ways. The clover-leaf pattern is for an O_2 lying across two Pt atoms. Do you know why one “sees” clover-leaves and not dumbbells? The pear-like features are likely O_2 molecules bound at an angle to the surface, one atom further up than the other. As one heats up the surface, the diatomic (O_2) ruptures into individual oxygen atoms, which sit bonded to triangles of platinum. At ambient temperatures, it is not likely that an O_2 coming onto the surface survives very long before it breaks apart. The hydrogen molecules break apart even more readily on the same surface.

And what happens after that? How do the chemisorbed H and O atoms find each other, form water? Good questions, the subject of current research. Something as simple as a burning hydrogen is ... not simple.

8

Knowing without Seeing

The stories of the book before you are different from Döbereiner’s, for they are, for the most part, tales of catalysis in solution, so-called homogeneous catalysis. This type of seeming magic is also old, even if we do not consider the many instances of catalysis that nature has wrought, and limit ourselves to human-crafted interventions. So, in 1860, the aging Liebig found an aldehyde-catalyzed transformation of some utility from cyanogen to oxamide, shown below [8]:



On surfaces or in solution (and the distinction is being undermined everyday now by the catalysis on nanoparticles), modern catalysis operates within the framework of Wilhelm Ostwald's transformation of catalysis from magic to rate change (as often slowing down as enhancing, but that is another story). Here is how Ostwald put it:

Ein Katalysator ist jeder Stoff, der, ohne im Endprodukt einer chemischen Reaktion zu erscheinen, ihre Geschwindigkeit verändert [9]

A catalyst is a substance that changes the rate of a chemical reaction without appearing as a product of it.

It took the next hundred years after Ostwald to shift the emphasis from the observation of a changed rate to the search for the partial establishment of the underlying mechanism of chemical reactions, both organic and inorganic. These mechanisms, incredibly rich in their variety, are a *Leitmotif* of the book before you. The tools for “seeing” in solution are not yet developed. And I like it so, for it leaves room for what has always been in my mind the strength of chemistry, its great intellectual achievement – the marshaling of chemical and physical fragmentary evidence into a knowing *without* seeing. People do know, putting together pieces from kinetics, and from signals from within. The latter detected by the lovely tools we have invented of spectroscopic attention to those signals, and in turn elicited by small electromagnetic perturbations. And now theory too. It is absolutely amazing how much we may know, without seeing *per se*. That we do that – understand without direct sight – I think should make sometimes arrogant scientists more tolerant of the ways of knowing that artists and writers and social scientists have. They also listen, create, and understand.

Roald Hoffmann

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