Döbereiner's Lighter

Roald Hoffmann

The dry statement that a catalyst allows an equilibrium to be established more rapidly hardly captures the double magic of that chemical phenomenon. In the course of a reaction, the catalyst gets involved, consumed and then regenerated, touching the deep myths of resurrection, a phoenix arising from its ashes, Persephone returning to earth. And the catalyst that makes a thermodynamically feasible, yet absolutely unwilling reaction go, after oh, so many futile attempts to coax it to do what it must, inevitably evokes the mystery of mountains moved, of shut doors suddenly opening.

This is a story of a catalyst for one of the simplest chemical reactions, the combustion of hydrogen: $2H_2 + O_2 \rightarrow 2H_2O$. 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 platinum, normally thought of as the most chemically resistant of metals. So, this is a story of fire too. And one of modern surface chemistry.

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 229 kilojoules per mole of H_2. And all it takes is a lighted taper or match to set it off. So who needs the catalyst?

"... a match to set it off." That's just the point: The flame and 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 equilibrium is on the side of water, so much so that at room temperature, at equilibrium in a liter of the mixture, there would be on the average less than one molecule remaining (out of $\approx 10^{22}$ to start with) of unburnt H_2. But the reaction is darned slow. At room temperature the collisions of H_2 and O_2 do not impart (on the average) nearly enough energy to the molecules to stretch their bonds as they approach some transition state for the reaction. To put it another way, the H_2 and O_2 molecules must be disrupted to react; resisting this, they do not sense the joy that is waiting for them at the end. They need a matchmaker!

We use that molecular torpidity of the uncatalyzed reaction, of course. Otherwise, how could I fill the balloon with H_2 and O_2 from their tanks, tie a knot sealing the balloon, attach a string to it, carry it to my lecture room and let it dangle for half a lecture, as the students wait for the inevitable explosion?

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, such as the lens that served Lavoisier. For some 40 years Döbereiner's lighter served as an important source for household and industrial fire lighting.

Incendiary Acts

How were fires lit before? From other fires, of course, to begin with. Two further techniques evolved around the world—the first generated heat by rubbing hard wood rapidly against soft, 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 most 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 17th-century soldiers is remarkable.

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In the 17th and 18th century, as optics evolved, the convex burning glass became an important fire source, albeit a fair-weather one. 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.

Döbereiner's Feuerzeug

Johann Wolfgang Döbereiner was born in Hof an der Saale in Germany 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 Mme. Pompadour's toothpaste. Goethe went to Jena to study analytical chemistry with Döbereiner. (A contemporary analogue would be if the present French Prime Minister Jospin took off a few weeks to learn about supramolecular chemistry with Jean-Marie Lehn at the University of Strasbourg. It would be good for Jospin, 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 Mendeleyev's periodic table. And Döbereiner observed in 1823 that when platinum metal (in a finely dispersed form called platinum sponge), was exposed to hydrogen, much heat was generated. The platinum (Pt) in fact glowed red- to white-hot, and if more hydrogen were supplied, the hydrogen burst into a hot but nearly colorless flame.

Within days Döbereiner turned this beautiful observation (which Davy had also made six years before on platinum wires) into a practical lamp. Figure 1 shows the design. One has a bottle that can be tightly sealed. In an open glass cylinder in that bottle hangs a piece of zinc *(d)*. The bottle is filled with sulfuric acid (typically 25 percent sulfuric acid (H_2SO_4)). There is a controlled outlet from the glass bottle, the stopcock *(e)*. The zinc (Zn) reacts with sulfuric acid, generating hydrogen gas *in situ*:

$$Zn + H_2SO_4 \rightarrow Zn^{2+} + SO_4^{2-} + H_2$$

When the stopcock is opened, the H_2 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 H_2 is generated, but comes to a stop as gas pressure builds.

Döbereiner continued his research with the catalytic properties of platinum (the word "catalysis" was coined by Berzelius in 1836); he actually was the first to make a supported catalyst (a mainstay of industrial catalysis and automotive catalytic converters today) by shaping small balls of potter's clay impregnated with platinum. For his work Döbereiner needed great supplies of the precious metal, and a geopolitical footnote 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 first World War. 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.

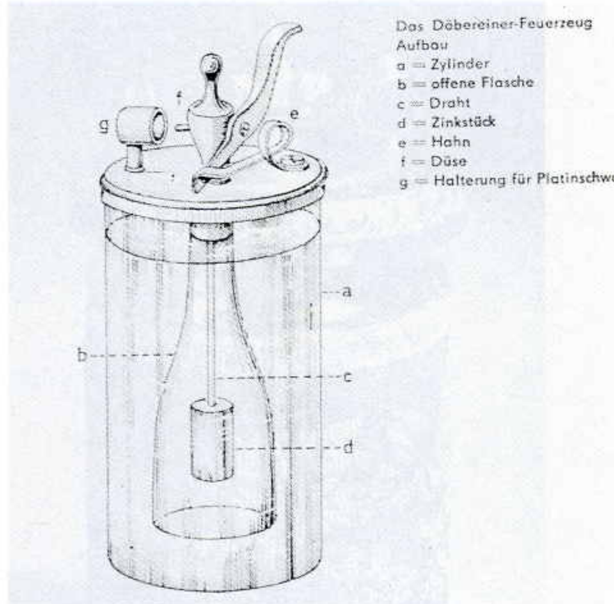

Figure 1. Schematic of an early Döbereiner lighter.

Döbereiner's lamp became a common way to light fires in industrial settings in the first half of the 19th century. Within five 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 when a utilitarian technology is accepted into society, it is culturally processed. What I mean is that it is clothed according to the prevalent aesthetics 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 deco-

Figure 2. Döbereiner lighter, from the collection of the Kirms-Krackow House in Weimar, Germany.

ration, insensitive to wetness and cold...." Figure 2 shows a household Döbereiner lamp of the 19th century.

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 lamp into the museum.

How Does Hydrogen Burn?

One hundred seventy-two years later, 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.

Here is a sketchy summary of what modern surface chemistry, with its expensive arsenal of ingenious spectroscopies, has taught us about the water-forming reaction on clean single-crystal surfaces of platinum under high vacuum: Both O_2 and H_2 undergo "dissociative chemisorption" on a platinum surface (under the conditions of Döbereiner's lighter the H_2 would impinge on a platinum surface already exposed to the oxygen of the air). The following reactions summarize what happens:

$$O_2 + Pt \text{->} Pt\text{-}O_2 \text{->} Pt\text{-}O\ (a)$$
$$H_2 + Pt \text{->} Pt\text{-}H\ (a)$$

Here the (a) stands for an atomic or molecular species adsorbed on the surface. And the notation hides much interesting detail: For instance, is there a "precursor state" in which H_2 molecules bond to the surface before the H–H bond is broken? Where exactly, and in what geometry, does the H atom sit on the surface—is it above a single platinum atom, or bonded to two or three platinum atoms? The same questions may be asked for O_2.

We know some, only some, of the answers. At low temperatures, way below room temperature, the O_2 is bonded to the surface first as a molecule, and in no less than three different ways. As one heats up the surface, the diatomic (O_2) ruptures into individual oxygen atoms, which sit bonded to triangles of platinums. 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 surface. A consensus is emerging that on the surface, the Pt-bonded oxygen atoms and hydrogen atoms cluster, or form islands of Pt-O(a) and Pt-H(a).

Recently, there appeared two beautiful papers illustrating the immense complexity of a step as seemingly simple as the breakdown of an oxygen molecule into individual oxygen atoms on a platinum surface. One paper comes from the group of Gerhard Ertl at the Fritz Haber Institute of the Max Planck Society in Berlin, the other from my colleague at Cornell, Wilson Ho, and his coworkers. Figure 3 shows an image from the latter group's paper of oxygen molecules and atoms adsorbed onto a platinum surface, made at atomic resolution with a scanning tunneling microscope (STM). The molecules are the light spots, and they come in two types— "pear like" (labeled F in the figure) and "clover-leaf" (labeled B) shapes. Please don't worry that the shapes don't look like the O_2 dumbbell you expect. The STM technique does not really "see," for instead of sensing the position of the nuclei, it measures the flow of electrons from the STM instrument tip into available orbitals in the oxygen atoms or molecules. The orbitals (calculating them is my stock-in-trade) describe quantum mechanically where the electrons are. A clover-leaf pattern turns out to be exactly what one would expect—it confirms that these are O_2 molecules. The darker individual circles (marked o) are oxygen atoms formed by molecules falling