

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: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$. 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 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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