

Phlogiston theory

A grand prequel

BY **DAVE SAMMUT**

A long-since discounted theory remains a significant backdrop for some great science of its time.

I read recently that during the long, weary march back from his failed Russian campaign in 1812, Napoleon claimed to have discovered the 'fifth element' ... mud. This may have been apocryphal, but it put me in mind of another story.

I have to preface the story with my ignorance. I'm an industrial chemist. As a rule of thumb, if you give me two pure chemicals and a large enough vat, I could probably manufacture for you a third, slightly impure, chemical. So I'm writing here from that spirit of wonder about the world that I would hope drives us all in our scientific vocation, as opposed to claiming any specific expertise on my own part.

Years ago as a neophyte chemist, I was delighted with phlogiston theory, as put forward in concept by Johan Joachim Becher in 1667 and later named and elaborated by Georg Ernst Stahl in 1703. The basic concept was that materials that burned in air must contain a substance, termed phlogiston, which was released during combustion.

According to the theory, the roasting of a metal (such as tin) gave a 'calx' of metal (metal oxide) plus phlogiston. During combustion, that phlogiston was released into the atmosphere. Experiments at the time then demonstrated that the addition of phlogiston to the calx of a metal brought about the reverse reaction. So when charcoal or sulfur, considered to be rich in phlogiston, were heated with the calx of tin, the phlogiston was transferred to the calx and the tin was restored to its metallic state.

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phlogiston before it became 'phlogisticated', and a burning candle in a closed vessel would therefore go out. Conversely, 'dephlogisticated air' had the potential to support combustion. At a point in history prior to the discovery of oxygen, or of air as a mixture of gases, this is internally consistent. Indeed, it is basically a mirror image of the truth. 'Phlogisticated' air is denuded of oxygen; 'dephlogisticated' air has its full 21% complement.

The 18th century was an inspirational period in chemistry. Emerging from the four-element theory of the universe, the chemistry enlightenment had begun and a great era of discovery was imminent. At the beginning of that century, only a handful of actual elements was known – the ancient metals and non-metals copper, silver, tin, gold, mercury, lead and sulfur – and these were not widely recognised as elements in themselves. Bismuth and phosphorus were 'modern' discoveries, and carbon hadn't been isolated until the late 17th

century. This was an era ripe for revelation.

Yet the experimental scientists of the era were working under extraordinary limitations. There was no reliable source of heat for their experiments. Control was often as simple as the number of candles that were applied to a vessel. Daniel Gabriel Fahrenheit didn't invent his alcohol thermometer until 1709, nor the mercury thermometer until 1714, nor the measurement scale bearing his name until 1724. And there was a significant disconnect between theoretical and experimental scientists, with the former – somewhat surprisingly to our modern eyes – holding sway.

Phlogiston theory was dominant for much of the 18th century, and continued to be taught at Harvard until at least 1788. Regardless that it was wrong, I admire the self-consistency of the theory. And notwithstanding that there are now-obvious problems with the theory, notably including that a metal combusted in air will gain weight rather than losing it (a fact that was available to but ignored by phlogiston theorists), I readily acknowledge the limitations of the era. This is particularly so when experimental science as we know it was still being developed.

Phlogiston theory provided the context for some of the greatest science of the era, for names that we now laud as the founders of our modern understanding.

Joseph Black's groundbreaking thesis, first published in 1754, showed for the first time that air is a mixture of gases and not a single substance. Among his experiments, Black used the 'air' released from mild alkalis (carbon dioxide) to extinguish a candle, showing that this was different from ordinary air, but that it must be present and dispersed in the atmosphere. However, his work was not widely accepted for several decades, and so even approaching a decade before Antoine Lavoisier's English-

Breathing room

I couldn't help but include some of the science that led to the discovery of the role of oxygen in life. Starting with studies of mice, Priestly found that the ability of air to sustain life could be used up in respiration, but that this property of air could be restored using plants.

In 1774, Priestly isolated oxygen from the decomposition of a 'red calx' of mercury (HgO), using a lens to focus the sun's rays. He went on to discover that this new form of 'air' was better than ordinary air for both respiration and combustion. He placed a mouse in a vessel in which it would normally survive for about 15 minutes with ordinary air. This mouse ran about for fully 30 minutes, and then having been removed apparently dead, was revived when warmed (perhaps by one of the particularly energetically burning candles in his new 'air').

Further experiments showed that this new air was between four and five times better than ordinary air ... and that Joseph Priestly wasn't particularly fond of mice.



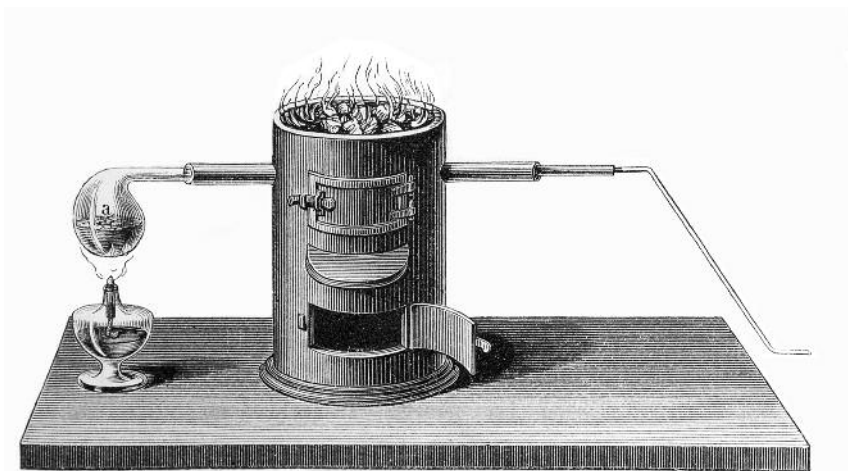
language publication of *Elements of chemistry* in 1790, the prevailing view was that there were only three gases: 'air' (not yet widely recognised as a mixture of gases), 'fixed air' (carbon dioxide), and 'inflammable air' (hydrogen, discovered by Henry Cavendish in 1776).

Although only a part-time chemist, Joseph Priestly discovered 10 gases, including ammonia, sulfur dioxide and nitrous oxide. Having the good fortune to live close to a brewery (arguably every chemist's dream), Priestly had a

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ready source of deep beds of 'fixed air' from the vats that he used for experimentation. Sloshing water back and forth between vessels with 'fixed air', he found that he could produce a sparkling drink, and with further experimentation using chalk and sulfuric acid, then dissolving the gas in water under pressure, he produced soda water. And as a Scot in a time of a very healthy whisky industry, so was born a drink that has graced gentlemen's clubs for more than two centuries to follow.

Priestly's most important gaseous discovery was of course oxygen. Yet Priestly described his experiments in terms of phlogiston theory. And as late as 1796, in his *Experiments and observations relating to the analysis of atmospherical air*, Priestly wrote that 'In all other cases of the calcination of metals in air, which I have called the phlogistication of air, it is not only evident that they gain something, which adds to their weight, but that they likewise part with something.'



The discovery that water is a compound of hydrogen and oxygen was made in the early 1780s. Lavoisier demonstrated that iron reacts with water, releasing hydrogen. Engraving from 'Schule der Chemie' by Dr J. A. Stöckhardt, Braunschweig, Vieweg und Sohn, 1857. Unidentified Author.

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A contemporary of Priestly, Carl Wilhelm Scheele, was actually the first to discover oxygen, but it was Priestly who published first. However, in his 1780 *Treatise on air and fire*, Scheele presented his reasoning within a phlogistic framework. Primarily a mineral chemist, Scheele went on to be the first to identify a range of elements and compounds, including molybdenum, tungsten, barium and tartaric, citric, hydrofluoric and a range of other organic and inorganic acids.

Similarly, Henry Cavendish's discovery of hydrogen as 'inflammable air' was made through the reaction of metals with acids. He believed that the hydrogen was released by the metals

involved in the reaction, and that in capturing the gas released he had isolated phlogiston itself.

What I find fascinating about all of this is not that the scientists of the era were wrong on the subject of phlogiston, but how they reasoned their way through a series of observations, and how, most importantly, the scientific process of careful experimentation, publication and peer review ultimately guided the collective footsteps of the scientific community onto the 'right' path.

I believe that there is a valuable lesson in this for today's young chemists. As scientists, we learn as much from our mistakes as from our successes, often more.

However laudable Antoine Lavoisier's achievements in chemistry, it is worth noting that his *Elements of chemistry*, which arguably augured the death of phlogiston theory, introduced its own erroneous 'caloric' theory. Lavoisier, following careful measurement of mass and heat, reasoned that heat was a type of fluid made of indestructible particles called 'caloric' that flowed from a hotter body to a cooler body via pores. As a precursor to kinetic theory and the conservation of energy, caloric theory held sway for another 50 years and more.

This process of error and correction has been repeated over and over. Even in living memory, the geologic science of tectonic plates has made the transition from wild surmise, bucking the prevailing theory, through to established science. The theory of anthropogenic climate change is struggling with that same transition.

One of the truly great aspects of science is that it is, at its best, empirical, testable and repeatable. It is honed in the fires of repeated scrutiny and adjustment, hammered on the anvil of peer review. Even the greatest scientists in our memory were wrong about something. As a scientist, I take great pleasure in being wrong from time to time. It's part of a grand tradition.

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