Joseph Priestley's Evolving Understanding of Carbon Monoxide

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What constituted the discovery of a gas in the 18th century?

As we know all too well, carbon monoxide is produced rather easily by heating carbon or carbon-containing compounds to high temperatures in the presence of an insufficient source of oxygen; excess oxygen would produce carbon dioxide. Priestley like his fellow chemists must have unwittingly produced carbon monoxide fairly often.

The discovery process really began with the isolation of the gas. Then various chemical and physical characteristics were observed and published to the world, although often not in the orderly fashion we expect in today's scientific writings. In the 18th century gases, or "airs" as Priestley called them, could be characterized in a number of ways, including: the reagents, not necessarily with weights recorded, and conditions used to produce them; the appearance and weight of the reagents at the end of the reaction; the color and odor of the gases; their specific gravities compared with like volumes of a familiar gas such as "common air"; whether or not they were flammable or supported combustion; whether they could support life; and how they reacted with several common reagents. A further important step was the chemist's understanding of what series of reactions had led to the product in question, what we might call the "reaction pathway," and how that explanation fit into a larger chemical system. Priestley and his chief rival in the matter of carbon monoxide (CO), William Cruickshank, did not feel constrained to cover all bases.

How to distinguish among the inflammable gases?

"When I first produced this air I was far from imagining that I had discovered any new species of air, essentially different from any other, so as to be entitled to a new appellation, but only another variety in the heavy inflammable air, which is known to be exceedingly various in different processes, and even in the different stages in the same process." Priestley, "Remarks on Mr. Cruikshank's Experiments upon Finery Cinder and Charcoal," Medical Repository 6 (1803).

In the late 18th century chemists were sorting out a confusing array of inflammable gases, amongst them what we would call hydrocarbons and carbon monoxide. Carbon monoxide, to Priestley, "heavy inflammable air," was one of the most interesting "airs" that he produced in his lengthy experimental program of producing airs from various solids heated to high temperatures in glass or earthenware retorts or tubes made from iron or earthenware. As early as 1774 he produced carbon dioxide ("fixed air") and carbon monoxide by using a burning glass to convert dry wood to charcoal in a glass vessel, but he only characterized carbon monoxide as being inflammable. In 1785, having made "finery cinder" (Fe3O4, the gray byproduct of iron foundries) by passing steam over iron filings in a red hot tube, he decided to make the reaction reverse. To drive off any moisture or other volatile substance, he first separately heated the finery cinder and charcoal, which was and is commonly used in refining metals (Priestley saw it as a source of the metalizing principle, phlogiston). Then he heated up a mixture of the finery cinder and charcoal in an earthen retort. Instead of the steam or water that he expected, he obtained a remarkable air, that is, after he had removed a small quantity of carbon dioxide by reaction with lime water. The following observations may have constituted his first real focus on CO. This inflammable air burned with a low blue flame, and he determined that it was about as heavy as common air. By 1790 he could distinguish between pure inflammable air (H2), which was ten times lighter than common air and burns explosively, and a number of other inflammable airs that were no more than half the weight of common air and burned with low flames in several colors. CO, then, was different. Priestley's attention soon turned to a use for CO in his ongoing arguments with Lavoisier's followers. Priestley liked nothing so much as an argument, and here he was egged on by his fellow phlogistonist James Watt.

Could controversy illuminate the identity of CO?

Lavoisier and his followers seemed to say that the gas they named hydrogen (water maker) could only be produced by decomposing water. But in the experiment with finery cinder and charcoal an inflammable air was produced, but there was no uncombined water among the reagents. Priestley repeated this point in 1796 and 1800 in monographs in defense of phlogiston published respectively in Philadelphia and Northumberland, and which he distributed widely. These works evoked responses from several Lavoisian chemists who repeated Priestley's finery cinder experiment and directed the attention of the chemical world to this inflammable gas that many had probably produced before. Among these were Princeton's John Maclean, the University of Pennsylvania's James Woodhouse, and William Cruickshank, professor of chemistry at the Royal Military Academy in Woolwich, England. In the course of these arguments, Priestley became more and more clear in expressing the distinction between the light inflammable air from his heavy inflammable air as did his opponents, but their explanations differed appreciably. Cruickshank called this heavy inflammable air "gaseous oxyd of carbon." Is a rose the same by any other name?

The arguments soon turned to the reactions leading to this gas. Priestley thought that the finery cinder contained water very tightly bound and that charcoal gave up its phlogiston to the metal and united with the oxygen of this bound water to form both the fixed air and the heavy inflammable air. (Curiously, water had re-entered the explanation.) As a Lavoisian Cruickshank thought that the finery cinder contained oxygen (not water), which reacted with carbon in the charcoal without resort to phlogiston. He also thought that fixed air was first created and later decomposed into this new air by the self-same iron or its oxide. Priestley tried to disprove this last idea by spending the noon hours several days in a row in his yard in Northumberland focusing his burning glass on fixed air in a bell jar. Even at this high temperature and even when he used iron filings, the fixed air did not convert into heavy inflammable air. (Why this reaction did not work remains a puzzle.) And Priestley seems to have forgotten that he had in the past (1790 and 1799) succeeded in making an inflammable air from fixed air by passing the latter back and forth through a red hot tube containing iron filings. Back then, though, he did nothing to test the other properties of this inflammable air, which would have been carbon monoxide. Priestley also argued with Cruickshank on semantic grounds that Cruickshank's calling this gas an "oxide" was very strange, since in the Lavoisian system the oxides were supposed to be non-flammable.

Priestley never understood that poking a few holes in the Lavoisian system would not serve to bring the whole system down.

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