

9. The complete program, including a list of attendees, is given in R. B. Warder, "Proceedings of the Congress on Chemistry Held in Chicago, Illinois, August 21 to 26, 1893", *J. Am. Chem. Soc.*, **1893**, *15*, 305 (June number, issued 6 October.)

10. These papers are scattered throughout *J. Am. Chem. Soc.* for 1893 and 1894 but are poorly identified as having originated at the Congress.

11. F. W. Clarke, et al., "International Chemical Congresses", *J. Am. Chem. Soc.*, **1894**, *16*, 880.

12. The only mention of the Brussels meeting by the Society occurred in the preliminary announcement for the 2nd International Congress of Applied Chemistry held in Paris in 1896; see Anon., *J. Am. Chem. Soc.*, **1896**, *17*, 307.

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TRANSLATIONS

The following experiment is taken from Tiberius Cavallo's "A Treatise on the Nature and Properties of Air," London, 1781. Readers wishing to submit their interpretations of the chemistry involved, complete with balanced equations, should send their answers to the editor by the copy due date listed inside the front cover. Answers will appear in the next issue along with a fresh puzzle.

Dr. Higgins' Experiment of Detonating Cupreous Nitre by Contact with Tin. This salt [i.e., cupreous nitre] taken moist, but not very wet, and beaten to the fineness of basket sea-salt in a mortar, is to be strewed to the thickness of a shilling on a piece of tin, twelve inches in length, and three in breadth.

Then the foil is to be instantly rolled up, so as to include the salt as it lay between the coils. The ends are to be shut by pinching them together, and the whole is to be pressed flat and close.

All this being done as quick as possible, the first part of the phenomena is, a part of the salt deliquesces. 2. The part, impregnated with tin changed in colour, and of a thicker consistence, begins to froth forth from the ends of the coil. 3. A strong frothing, accompanied with moderate warmth. 4. The emission of copious nitrous fumes. 5. Heat intolerable to the fingers. 6. Explosion and fire, which burst and fuse the tin-foil in several places, if it be very thin.

The Answer to Last Issue's Puzzle

No reader responses were received and, indeed, it took the

editor nearly a week of library research to unravel the mystery. The result, which is quite interesting, appears as this issue's *Whatever Happened To ... ?* column.

WHATEVER HAPPENED TO HOMBERG'S PYROPHORUS?

William B. Jensen, University of Cincinnati

"Homberg's Pyrophorus" was accidentally discovered by Wilhelm Homberg (1652-1715) sometime around 1680 while attempting to extract an "odorless white oil" from human excrement for the purpose of transmuting mercury into silver (1). In the course of these experiments, Homberg distilled the excrement with a wide variety of other materials, one of which happened to be common potash or potassium alum [$K_2(SO_4)Al_2(SO_4)_3 \cdot 24H_2O$], and noticed that, after cooling the apparatus and breaking open the luting, the dry residue in the retort spontaneously burst into flame.

This result quite naturally caught Homberg's attention, as one of his abiding fascinations, like that of many of his contemporaries, was with the preparation and study of materials which were either spontaneously inflammable or phosphorescent or both. Indeed, during his student travels in Italy, he had investigated the preparation and properties of the so-called Bologna Stone, a form of phosphorescent barium sulfide, and he later perfected a recipe for a phosphorescent variety of calcium dichloride (known as "Homberg's Phosphorus") made by heating a mixture of slaked lime [$Ca(OH)_2$] and sal ammoniac [$(NH_4)Cl$]. Homberg is also credited with having obtained the original recipe for the preparation of elemental phosphorus from Johann Kunckel, supposedly in exchange for a toy barometer invented by Otto Guericke in which the humidity of the air was indicated by "a little man who came out of his house and stood at the door in dry weather but retired under cover in moist weather"(2). Apparently in the 17th century trinkets could buy more than just prime New York real estate!

Incredibly, given his persistent interest in both pyrophoric and phosphorescent substances, Homberg failed to follow up on his alum-excrement observations until 1711, or nearly 30 years after the original experiments, when he again returned to the subject and finally published a paper describing the preparation and offering a rationale for its properties (3). Assuming the product to be a mixture of a water-free salt (obtained from the alum) and an easily inflammable oil (obtained from the excrement), he postulated that its spontaneous ignition was due to the reaction of the salt with the moisture in the air. Like the reaction of quick lime [CaO] and water, this reaction supposedly generated sufficient heat to ignite the inflammable oil.

Homberg initially described his mixture as yet another kind of "phosphorus", but later adopted the more appropriate term of "pyrophorus" - a word which eventually came to signify all spontaneously inflammable solids. The curious properties of



Scheele noted the necessity of moisture and oxygen for the ignition process

the material intrigued Homberg's contemporaries and the attempts to unravel its chemistry would eventually command the talents of some of the 18th century's most celebrated chemists (4).

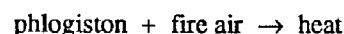
The first advance was made by Homberg's associate, Louis Lemery (1677-1743), who demonstrated in 1714 that the excrement could be replaced by a variety of other combustible animal and plant substances, including wood, blood, flesh and Spanish fly (5). He further postulated that the function of the combustible was to reduce the vitriolic acid in the alum to sulfur and that the resulting intimate mixture of sulfur and the unused organic combustible accounted for the mixture's inflammability.

An even more significant observation was made by Le Jay de Suvigny in 1760, when he discovered that alum was also not an essential ingredient, but rather an indirect source of alkali sulfate, and that, consequently, suitable pyrophors could be made by directly using pure potassium or sodium sulfate (6). He further postulated that the product contained a mixture of sulfur and sulfuric acid and that the heat generated by the latter on reacting with the moisture of the air was sufficient to inflame the sulfur and so account for the ignition.

In 1777 the Swedish apothecary and chemist, Carl Wilhelm Scheele (1742-1786), devoted a section in his famous book on *Air and Fire*, in which he first described his discovery of fire air or oxygen, to the now infamous pyrophorus (7). After first observing that "the kindling of this strange chemical product has already caused vain efforts to many in the endeavor to explain it clearly", Scheele suggested that the net result of heating the alum and combustible was to produce an intimate mixture of charcoal and liver of sulfur [K_2S]. He then proceeded to test this hypothesis by successfully synthesizing a

pyrophorus by heating together a mixture of charcoal and potassium sulfate. He further showed that both moisture and fire air were essential for ignition.

His explanation of the ignition process was based on his personal version of the phlogiston theory in which the charcoal saturated the liver of sulfur with phlogiston. In the presence of moist air, the attraction for water of the alkali in the liver of sulfur forced out this excess phlogiston, which was then seized by the oxygen of the air to produce heat in accord with Scheele's hypothesis that:



and the resulting increase in temperature kindled the remaining charcoal.

The same year Lavoisier (1743-1794) did a quantitative study of both the formation and ignition of the pyrophorus (8). In the first of these processes he showed that, in addition to elemental sulfur and liver of sulfur in the pyrophorus itself, a mixture of fixed air [CO_2] and heavy inflammable air [CO] was also produced, and he further showed that the pyrophorus could be synthesized by directly heating a mixture of charcoal, sulfur and fixed alkali (potassium or sodium carbonate). During ignition, Lavoisier found that the pyrophorus gained weight while simultaneously absorbing oxygen from the air - a process corresponding to the reoxidation of the sulfur and liver of sulfur to sulfuric acid and its eventual combination with the fixed alkali to produce an alkali sulfate.

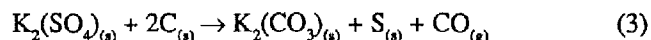
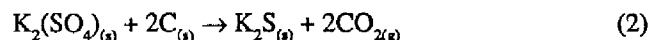
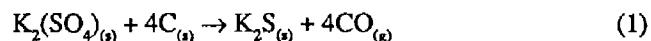
Though Lavoisier's rationale is essentially the one accepted today, his contemporaries continued to debate both



Lavoisier first recognized the existence of a second oxide of carbon as a result of his quantitative study of the pyrophorus

the nature of the pyrophorus and the mechanism of its ignition well into the first decade of the 19th century. Thus Louis Proust (1754-1826) challenged Suigney's ignition hypothesis in 1778, and Scheele and the German chemist, Johann Götting (1755-1809), carried out a polemic in 1786 on the necessity of fixed alkali in its preparation. In 1780 Pilatre de Rozier (1756-1785) insisted that somehow elemental phosphorus had to be present in order to account for the spontaneous inflammability, whereas in 1786 the Englishman, Bewin, postulated combination with a nitre-like acid in the air, and after Davy's isolation of the alkali metals, assorted suggestions involving the presence of metallic potassium and sodium began to appear (9).

The final consensus reached by the 1830's was little more than a minor elaboration of Lavoisier's original work (10). In modern terms, it involves the reduction of the alkali sulfate with carbon via at least three competing routes, with the finely dispersed alkali sulfide from reactions 1 and 2 and the unreacted carbon, preferably prepared by simultaneous pyrolysis of an organic compound, being the most important active products. The variable amount of free sulfur produced, which was also noted by Lavoisier, is probably generated by the third reaction:



As indicated by the thermodynamic data in Table 1, all of these processes become thermodynamically feasible at high temperatures and indeed probably proceed well below these temperatures due to the escape of the product gases into the surrounding atmosphere.

Ignition is due to the highly exothermic (Table 2) oxidation of the finely dispersed alkali sulfide:



which, in turn, ignites the carbon:

Table 1. The Thermodynamics of the Preparation Reactions

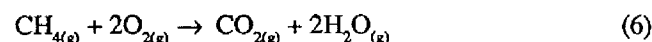
Reaction	$\Delta H/\text{kcal}$	$\Delta S/\text{cal K}^{-1}$	T/C at $\Delta G = 0$
1	137.00	168.36	541
2	140.00	84.00	1400
3	42.31	44.00	689

Table 2. The Thermodynamics of the Ignition Reactions

Reaction	$\Delta H/\text{kcal}$	$\Delta S/\text{cal K}^{-1}$	$\Delta G/\text{kcal at 293 K}$
4	-246.66	-82.61	-222.04
5	-94.05	2.06	-94.66
6	-191.76	47.77	-206.00



and the entire process is initiated by the moisture attracted by the anhydrous sulfide, much as the popular solid state reactions between zinc metal and solid iodine or ammonium nitrate, commonly used as lecture demonstrations, are initiated by adding a drop of water. Note that reaction 4 is more than twice as exothermic as the combustion of carbon in reaction 5 and is also more exothermic than the combustion of methane:



Interestingly, reactions related to equations 1-3 have also been studied as possible stages in the ignition of black powder (11) and, in the case of sodium salts, as possible stages in the Leblanc process for the manufacture of sodium carbonate (12).

Though Homberg's pyrophorus continued to be mentioned in some of the more comprehensive textbooks in the first half of the 19th century, its unique status was challenged by the discovery of a variety of other pyrophors in the 1830's and 1840's. In 1831 the American chemist, Robert Hare (1781-1858), reported the discovery of a pyrophorus made via the thermal decomposition of Prussian blue (13) and in the period between 1837 and 1840 the German chemist, Rudolph Böttger (1806-1881), showed how to make a large number of pyrophors via pyrolysis of lead carboxylate salts (14). These were much simpler to prepare than Homberg's pyrophorus and are still used as lecture demonstrations.

The chemical basis of these new pyrophors was clearly different from that of Homberg's preparation and eliminated the hope of a common chemical rationale. An understanding of the thermodynamic versus the kinetic aspects of these materials is naturally missing from the literature of this period, though the role of surface area and intimate mixing was appreciated and explicitly discussed by Murray as early as 1807 (10).

References and Notes

1. For biographical data on Homberg see J. R. Partington, *A History of Chemistry*, Vol. 3, Macmillan, London, 1962, pp. 42-48.
2. T. Thomson, *The History of Chemistry*, Colburn and Bentley, London, 1830, p. 240.

3. W. Homburg, *Mem. Acad. Royal. Sci.*, 1711, 39, 234 and *Ibid.*, 1711, 49, 307. Extensive English extracts can be found in the English translation of Pierre Macquer's *Elements of the Theory and Practice of Chemistry*, which was reprinted in part as the article on chemistry in the first edition of the *Encyclopaedia Britannica*, Vol. 2, Bell and Macfarquhar, Edinburgh, 1771, pp. 175-177.

4. Summarized in H. Kopp, *Geschichte der Chemie*, Bd. 4, Vieweg, Braunschweig, 1847, pp. 64-67.

5. See reference 4.

6. L. J. Suvigny, *Acad. Royal. Sci. Mem. div. Sav.*, 1760, 3, 180.

7. C. W. Scheele, *Chemische Abhandlung von der Luft und dem Feuer*, Swederus, Uppsala, 1777. English translation by L. Dobbin in *The Collected Works of Carl Wilhelm Scheele*, Bell, London, 1931, pp. 148-152.

8. A. Lavoisier, "Experiences sur la combinaison de l'alum avec les matières charbonneuses et sur les alterations", *Mem. Acad. Royal. Sci.*, 1777, 363. Reprinted in *Oeuvres de Lavoisier*, Tome II, Imprimerie Imperiale, 1862, pp. 199-208.

9. For the Scheele debate see Dobbin (7), pp. 304-306 and for the others Kopp (4).

10. See J. Murray, *A System of Chemistry*, Vol. 3, Longman, Hurst, Rees and Orme, London, 1807, pp. 583-584 and T. Graham, *Elements of Chemistry*, Lea and Blanchard, Philadelphia, PA, 1843, p. 362.

11. H. Debus, *Trans. Roy. Soc. (London)*, 1882, 173, 557, 559, 567, 570.

12. J. Mactear, "On the Part Played by Carbon in Reducing the Sulfates of the Alkalis", *J. Chem. Soc.*, 1878, 33, 475.

13. R. Hare, "New Pyrophorus", *Am. J. Sci. Art.*, 1831, 19, 173. The abstractor for *Chemische Central-Blatt* (1832, 3, 432) claimed that this preparation had been known long before Hare's report.

14. R. Böttger, "Über Darstellungen mehrerer Pyrophore", *J. Prak. Chem.*, 1837, 8, 477 (*Chem. Cent.*, 1837, 8, 51) and "Über das Verhalten mehrerer organische Stoffe zu Bleihyperoxyd in der Hitze und einige neue Pyrophore", *Ann. Pharm.*, 1840, 34, 87 (*Chem. Cent.*, 1840, 11, 472.) For additional examples see *Chem. Cent.*, 1844, 15, 223, *ibid.*, 1844, 15, 677., and *ibid.*, 1845, 16, 863.

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BONES AND STONES

What Do Chemists Learn from the Past?

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Chemists who are involved in the investigation of archeological materials are often asked, "Why study the past?" For most of us, archeological chemistry was not originally a part of our



John W. Mallet (1832-1912)

research program. As research chemists, we had developed some expertise in the study of materials (either of the material itself or the analytical techniques that could be used to characterize the material). Whether through our own readings and interest in history or through the contact with archeologists, we have become aware of the fact that our chemical expertise can be used to study those artifacts which are the reminders of mankind's past. As new techniques are developed and applied to the study of archeological materials, we continue to learn more about the way early man utilized a wide range of resources.

While the application of chemical techniques to the study of archeology continues to bring about new knowledge, the idea of studying the past using chemical methods is almost as old as the formal study of chemistry itself. I was most surprised to learn this fact when I heard John Sharkey's address on John W. Mallet, the seventh president of the ACS (presented to the HIST Division at the 1987 National ACS Meeting in New Orleans). While I attended this lecture to learn more about this famous early chemist's long-time association with the University of Virginia, I also learned that his Ph.D. dissertation was based upon his work as an "archeological chemist". Mallet (1832-1912), a charter member of the ACS, made many contributions to chemistry including the determination of the atomic weights of Al, Li, and Au. However, I will ignore many of the other fascinating aspects of Mallet's research and focus on his early studies of gold artifacts.

During the summers of 1851 and 1852, young John Mallet traveled from his home in Dublin, Ireland (where he had already begun his study of chemistry at Trinity College) to Göttingen, Germany. He worked in the laboratory of the famous chemist Frederick Wöhler (1800-1882) who was himself a pupil of Berzelius. He brought with him a wide variety of Celtic antiquities from the Museum of the Royal Irish Acad-