#### History of Science

# Controversy in Chemistry: How Do You Prove a Negative?—The Cases of Phlogiston and Cold Fusion\*\*

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n our first essay in this series, the two cases of controversy in stereochemistry we examined were temporally widely separated—one from the very beginnings of the field and one quite recent and also quite different in terms of overall scope and impact, not to mention the disparity in experimental methodology and conceptual framework available to the participants. Nonetheless, as we tried to show, they are actually closely related with respect to a most fundamental issue in the historical development of a discipline—namely, how the community comes to agree upon what counts as evidence in resolving disputes.

For our second study we have again chosen two stories that appear to be about as disparate as one could possibly arrange. One, the overthrow of the theory of phlogiston, dates from the origins of modern chemistry, and is now universally considered a central development therein. The other, the cold fusion episode, is only 15 years old, and is now generally (though by no means universally) considered as just a stumble in the long historical march of chemistry. Why have we paired them? Because we feel that, as with the previous study, closer examination reveals certain con-

nections that are instructive for a general understanding of how controversies play out and, in doing so, serve as a powerful engine for the advancement of science. The question of what counts as evidence is important here as well, but we will focus in particular on the persistence of belief, associated with the difficulty of demonstrating the *non-existence* of a theoretical or hypothetical entity.

#### Case 1: The Eventual Death of Phlogiston—What are the Lessons?

Phlogiston has long served as a hobby horse that various commentators have ridden for their own purposes, particularly textbook authors, who often use historical incidents as vehicles for their personal philosophies. This situation is hardly a new phenomenon. For example, Roscoe and Schorlemmer, like many 19th century chemists, were concerned with the status of chemistry. In their Treatise on Chemistry of 1881 they asserted that "It is only after Stahl's labours [on phlogiston] that a scientific chemistry becomes possible".[1] Closer to our own time, Linus Pauling also emphasized the strengths of Stahl's conception in providing a coherent theoretical framework for chemistry:

"The phlogiston theory thus provided a general explanation of the chemical processes of oxidation and reduction ... It is interesting to consider the other ways in which chemical phenomena were accounted for by the phlogiston theory. The success of the theory in providing these explanations explains the fact that it had many strong adherents". [2]

These appreciative comments are not, however, representative of the general opinion among textbook authors. The history of phlogiston is usually presented as a cautionary tale: "The phlogiston theory ... long outlived its usefulness, and the tenacity with which it maintained itself is an instructive illustration of the difficulty which most men have of freeing their minds from the authority of a long held theory", a theory that "delayed the development of chemistry as an exact science for three-quarters of a century". [3]

In addition to what the phlogiston episode supposedly tells us about the frailties of the human mind, it has the additional merit (according to some authors) of highlighting the virtues of science:

"Although the phlogiston theory is of no importance today, the way in which it was discarded is a good illustration of the manner in which the scientific method operates ... It remained for Lavoisier, who had developed good equipment and a facility for accurate experimentation, to deliver the crushing blow to the theory". [4]

Since the phlogiston theory is generally believed to have expired by 1800, it would seem to have little relevance today. Yet the lessons encapsulated in its history apparently have not been appreciated sufficiently by all scientists. Thus, in 1991 the journal *Chemtech* thought it necessary to recount the story yet again under the headline, "A timely analysis of the persistence of lousy ideas". [5] In this part of our article we will address two questions: Was the phlogiston theory indeed a lousy idea, and why did it persist for a century or more?

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We can begin answering the first question by noting how misleading the Chemtech headline is—a situation not at all uncommon in the treatment of this subject. The article itself is an adaptation of a chapter by James Bryant Conant, one of the major historians of phlogiston. [6] Nowhere in Conant's work does the phrase "lousy idea" appear, and he neither sneers at the theory nor derides its advocates. Rather, he notes that the concept "provided a pattern into which a mass of otherwise unrelated phenomena could be fitted".[7] As we shall see, Conant's respectful treatment of phlogiston and the phlogistonists was entirely appropriate.[8]

Although the conceptual structure of the phlogiston hypothesis was laid down by Johann Joachim Becher in the mid-17th century, phlogiston only became a centerpiece of chemical thinking through the efforts of his student Georg Ernst Stahl, later Professor of Medicine at the University of Halle (1694–1715), who coined the term phlogiston. [9] The concept was founded upon a common contemporary belief, namely, that the properties of substances were a consequence of their containing carriers of those properties, which were called principles. For example, substances that were metallic, saline, or acidic had those characteristics because they contained the principles for metallicity, salinity, and acidity, respectively. A single principle could be the carrier of more than one property, and the diversity of substances was accounted for by the differing proportions of the principles that were present in each substance.[10]

The exact nature of these principles was a matter of dispute. Some authors categorized them as purely hypothetical, some as real but imponderable (most assigned phlogiston to this category), and some as real and ponderable (late on, phlogiston was in this category as well). The general view was that principles could not be isolated in an uncombined state, but instead were passed from one substance to another during chemical reactions.

The doctrine of principles was in fact able to make sense of a wide range of well-established phenomena, many of them connected with practical arts such as mining and metallurgy. For example, it was common knowledge that flammable substances such as charcoal and sulfur would convert earthy, metallic ores (called calces) into shiny, ductile metals. Stahl and his followers attributed this conversion to the transfer of phlogiston (the principle of flammability and metallicity) from the charcoal or sulfur to the ore. Note that according to this theory, metals (which consisted of a calx and phlogiston) were more complex than their calces (oxides). The oxygen theory maintained just the opposite that metals were less complex than their calces. This difference was to be a major point of disagreement between the phlogistonists and antiphlogistonists.

Describing the reduction of metal ores by charcoal in terms of phlogiston transfer was more than mere word play. It was supported empirically by the observation of reversible chemical transformations, such as the combustion of sulfur to sulfuric acid and its eventual recovery from the derived potassium sulfate by reaction of the salt with charcoal. The phlogistonists asserted that since the combustion of sulfur involved the loss of phlogiston, the sulfur could be regained by combining the product with a phlogiston-rich material such as charcoal—which is exactly what was observed [Eq. (1)].<sup>[11]</sup>

$$\begin{split} \mathbf{S} & \xrightarrow{\text{gair, water, heat}} & \mathbf{H}_2 \mathbf{SO}_4 \xrightarrow{\mathbf{K}_2 \mathbf{CO}_3} & \mathbf{K}_2 \mathbf{SO}_4 \\ & \xrightarrow{\text{charcoal, heat}} & \mathbf{K}_2 \mathbf{CO}_3 + \mathbf{KS}_n \xrightarrow{\text{vinegar}} & \mathbf{S} \end{split} \tag{1}$$

The phlogiston theory also enabled Stahl to realize that the reverse of ore reduction (the calcination of metals) was a form of combustion that differed from the burning of charcoal only in its rate. Even Stahl's most determined opponents conceded that this was a discovery of prime importance. Furthermore, Stahl included respiration under the rubric of phlogiston transfer, thus making a conceptual bridge between the animate and inanimate realms. He further believed that phlogiston was conserved, so that when charcoal or sulfur was burned in air (then thought to be a single substance) the emitted phlogiston was absorbed by the air. For the air itself to remain respirable, the phlogiston was in turn absorbed by living organisms, thus establishing a complete phlogiston cycle in nature.[12] Finally, it is noteworthy that the phlogiston theory was the first truly chemical theory of chemical phenomena, deliberately set in opposition to the prevailing mechanical theory, which could not convincingly explain the qualitative changes so characteristic of chemical processes. Thus, in 1770, at about the time that Lavoisier began to interest himself in the problem of combustion, the phlogiston theory "was not a decaying relic tradition ... but a work that symbolized for most chemists the achievement of autonomy for chemistry". [13]

Phlogiston's most passionate advocate was Joseph Priestley, who continued to believe in it up to the time of his death in 1804.<sup>[14]</sup> Phlogiston's most effective and implacable opponent was Antoine-Laurent Lavoisier, who in 1772 began a series of experiments that would eventually convince him, and subsequently the chemical community, that the phlogiston concept was completely superfluous.<sup>[15]</sup> Yet Priestley and Lavoisier relied on the same set of experiments to buttress their contradictory conclusions

Many of these experiments involved the production and differentiation of a variety of new gases ("airs", as they were then known). One of the most important, which led to the discovery of a new "air", was the thermal decomposition of HgO to give "an eminently respirable air" that supported combustion and living organisms far better than ordinary air. To Priestley the gas was "dephlogisticated air"—ordinary air deprived of phlogiston. To Lavoisier it was "oxygen", a "simple substance" that combined with materials undergoing combustion or calcination. Deciding between these alternatives involved observing and interpreting the behavior of various airs under different chemical and biological conditions.

In the standard version of phlogiston's fall from credibility Lavoisier is supposed to have discovered unexpectedly that substances gain weight when they burn, even though they are allegedly losing phlogiston. This discovery then forced the adherents of phlogiston to embrace an absurdity—that phlogiston had negative weight—which then convinced all but a few diehards of the superiority of the oxygen theory of combustion.

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As is often the case, the actual history is not nearly so tidy. It had been established already in 1630 by Jean Rey that metallic calces weighed more than the metals from which they were derived, and 18th-century investigators further confirmed this observation. [16] Phlogistonists did not view this result as fatal for their theory, but rather as an observation that could be explained within the theory's framework.

There were in fact several competing explanations that all relied on the plausible assumption that phlogiston was lighter than air. For example, one explanation held that, as a metal was calcined, air replaced phlogiston in its internal spaces, thus leading to the weight increase. The fact that weight increases were not invariably observed in calcination—temperatures were sometimes high enough to vaporize portions of the product leading to a weight decrease—further blunted the impact of this line of attack.

Other experimental results were also thought to have invalidated the phlogiston hypothesis. As noted above, one particularly important set of data concerned the thermal decomposition of the calx of mercury (HgO).[17] In this experiment, a gas is released and metallic mercury is left as a residue. To Lavoisier the results furnished decisive support for the oxygen theory, since mercury regained its metallic state without any external source of phlogiston such as charcoal. However, the phlogistonists had an alternative explanation at hand. By the 1780s most of them accepted the proposition that during calcination air replaced phlogiston within the pores of the metal. This so-called "fixed air" (about whose composition there was much disagreement) was presumed to be rich in phlogiston. Upon heating the sample, the phlogiston was supposed to be transferred to the mercury calx, thus restoring it to the metallic state. The dephlogisticated air that remained was expelled, as observed.

The picture that emerges from even this abbreviated history is that of two competing theories, one of which eventually prevailed by a steady accretion of new experimental results linked to a more coherent explanatory framework. [18] Lavoisier's balance sheet method, which accounted for the weights of

all reactants and products and showed that nothing ponderable was created or destroyed, was very effective in converting other chemists to his system. Yet the rigorous application of this method required Lavoisier to adopt some premises of the scheme he had set out to overthrow. For example, to account for the three states of matter and for the heat released in oxidation reactions, Lavoisier posited that all substances contain varying amounts of caloric, the material basis of heat. Since he obtained nearly perfect agreement between the weights of reactants and products—to the extent that some of his opponents had understandable doubts about his claim<sup>[19]</sup>—Lavoisier found it necessary to assume that caloric, although real, was an imponderable fluid. Shades of phlogiston!

In fact, it was precisely with respect to the imponderable aspects of chemical phenomena, such as heat, light, and electricity, that the oxygen theory was found wanting. Thus, a small band of natural philosophers was able to welcome oxygen as being "among the greatest discoveries in physics" (in the words of the eminent geologist James Hutton) while still embracing phlogiston. The reality of phlogiston, Hutton claimed, would always be hidden from "those philosophers, who, with the balance in their hands refuse to admit into the rank of chymical elements substances which do not ponderate...". [20] Until the elaboration of the energy concept in the mid-19th century, Hutton's critique could not be totally dismissed.

In addition, phlogiston's fortunes were temporarily boosted by the unraveling of parts of Lavoisier's system. For example, caloric was rendered superfluous by the kinetic theory of heat.<sup>[21]</sup> An even harsher blow resulted from the discovery that oxygen was not an essential component of acids. It is often forgotten that Lavoisier's theory was as much about acidity as it was about combustion.[22] (The word "oxygen" was derived from the Greek words for "acid former".) Lavoisier described oxygen as the principle of acidity, which uncomfortably echoes Stahl's description of phlogiston as the principle of flammability. When Humphrey Davy showed in 1810 that muriatic acid (HCl) contained no oxygen and that so-called "oxygenated muriatic acid" was in fact elemental chlorine, doubts arose in some quarters about the viability of the oxygen theory. Davy himself entertained a sympathetic attitude toward phlogiston in the first decade of the 19th century, and his results with HCl and Cl<sub>2</sub> provoked concerns that "future discoveries shall ... utterly destroy the merits of the later improvements in pneumatic chemistry and bring us back to the doctrine of phlogiston ..." [24]

Yet the oxygen theory of combustion, the nomenclatural reform, and other pillars of the Chemical Revolution remained unshaken. As we noted in an earlier report, it usually takes more than just experimental disconfirmations to destroy a theory that has had predictive success with respect to crucial issues.[25] So, at the end of the day, how can we explain the contrasting fates of the oxygen and phlogiston theories? By the last two decades of the 18th century, phlogistonists could do no more than provide explanations of known results, while Lavoisier and his adherents were able to predict as yet unknown phenomena. To even account for those experimental data that played so conclusive a role in the struggle between the two theories, phlogistonists had constant recourse to ad hoc hypotheses. Ultimately, Lavoisier was fully justified in characterizing phlogiston as "a veritable Proteus that changes its form every instant!"[26] Yet the longevity of this protean concept was derived in large part from the great difficulty involved in proving its nonexistence.[27]

# Case 2: The Short Life (but Longer Afterlife) of Cold Fusion

Our previous essay dealt with a recent controversy, that of bond–stretch isomerism, which was relatively unfamiliar even to the majority of practicing chemists, and completely unknown outside their ranks. The roughly contemporaneous case of cold fusion was entirely the opposite. For several months in 1989 it was one of the hottest topics around—not just in scientific journals, but also in newspapers, popular magazines, TV shows, etc. We can think of no chemistry story that has attained comparable vis-

ibility. Indeed, how it played out in the public eye would merit a fascinating and valuable examination in its own right, but one that would far exceed the scope of this Essay. Nor do we have space to consider the claims and counterclaims in any detail; in any case, most readers are probably fairly familiar with at least the basic outline. We present below a very brief summary. For those who want to know more, several full-length book accounts, written from a variety of perspectives (including scientist-nonbeliever, [28] scientist–agnostic/skeptic, [29] scientist/science writer-nonbeliever,[30] scientist/science writer-believer,[31] and science writer-nonbeliever<sup>[32]</sup>) were published within the first few years. There are also a number of internetbased bibliographies which can easily be located on-line.

The controversy opened in March 1989, when University of Utah electrochemists Stanley Pons and Martin Fleischmann held a press conference to announce that electrolysis of D<sub>2</sub>O at a palladium electrode produced anomalous effects, including liberation of energy in excess of the input—in one case to such an extreme extent as to melt the Pd cathode and destroy the apparatus. A publication appearing shortly afterwards (but submitted prior to the press conference) provided some details and also reported neutron fluxes, γ-rays at the right energy to indicate protonneutron reactions, and accumulation of tritium in the electrolyte.<sup>[33]</sup> Related, but much less dramatic, findings (many fewer neutrons, no excess heat) were published around the same time by Steve Jones, a physicist at Brigham Young University.[34] (The two research groups were aware of each other's work; concerns over priority issues—patent rights in particular-no doubt prompted the unorthodox publication-by-press-conference and substantially set the tone for ensuing developments.) The authors concluded that nuclear fusion, which had been somehow catalyzed within the Pd lattice, was the only possible explanation for these observations.

The clear potential importance of such a discovery, coupled with the apparent experimental simplicity, inspired many to attempt replication. Within a matter of weeks a number of positive findings were announced (mostly by press release, like the original), including excess heat (Texas A&M, Stanford), neutrons (Georgia Tech), and tritium (Washington, a different group at Texas A&M). A special session on cold fusion at the April 1989 ACS national meeting attracted an audience of around 7000 (mostly) enthusiastic chemists. Almost immediately, though, strong skepticism set in, as several of the highly publicized "confirmations" were retracted, with explanations of the experimental problems responsible. A special session at the American Physical Society meeting at the beginning of May featured a number of negative presentations; one in particular (by Nate Lewis, subsequently published<sup>[35]</sup>) reported his research group's inability to detect any excess heat, possible experimental reasons why one might (erroneously) detect excess heat, and a deconstruction of the assumptions used by Pons and Fleischmann that, he argued, led to deducing excess heat evolved from unconvincing data. Later in May, a publication appeared demonstrating that the claimed y-ray signature was artifactual.[36]

Over the next year or so the controversy continued, as further positive as well as negative results appeared regularly. A Department of Energy (DOE) panel investigated the topic during the summer, and issued its report—strongly negative—in October. In August 1989 the National Cold Fusion Institute (NCFI) was inaugurated in Salt Lake City, funded by the state of Utah (after federal support was refused). The First Annual Conference on Cold Fusion was held there in March 1990; the participants were primarily (by design) those with positive findings to report. In any case the majority of critics had concluded there was little left that needed to be criticized, and ceased paying much attention. By late 1990 both Pons and Fleischmann had left Utah, and the NCFI closed the following June. The cold fusion controversy was effectively over.

But *not* cold fusion. Research has continued at a moderate level of activity right up to the present day. A good deal of the work has been published in non-mainstream journals (some created for the purpose) or electronically; but occasionally papers have appeared in presti-

gious locations, such as the 1993 paper by Pons and Fleischmanns on calorimetry, which was accepted by Physics Letters A. [37] This publication merits notice on further grounds: it reports what appears to be the last joint experimental work by Fleischmann and Pons on cold fusion. Perhaps more importantly, it is one of the last reports to be formally challenged on technical grounds by a cold fusion skeptic.[38] Subsequent claims have been almost completely ignored by the scientific mainstream, and the popular media has generally followed suit, with a few exceptions. Compilations of this work may be found on a number of websites, notably the LENR-CANR (low energy nuclear reactions/chemically assisted nuclear reactions) site,[39] which features bibliographic material and summaries, written from the strong proponents' point of view. A quite different (and intriguing) perspective may be found in a recent book by the sociologist of science Bart Simon, who proposes a new model for understanding how and why research persists beyond the point where the vast majority of the community considers the field finished: he calls it "Undead Science".[40]

Two somewhat less fanciful, but rather contradictory, conceptual models have been offered for the consideration of scientific controversies: one from an internal point of view and one more external. In fact they *both* seem to fit the cold fusion saga pretty well. The first is that of "pathological science", first described by Irving Langmuir in a 1953 lecture (a transcription was republished in *Physics Today* in 1989<sup>[41]</sup>) and subsequently reprised and updated by Denis Rousseau. [42] According to Rousseau, pathological science has three fundamental characteristics:

- Observed effects are near the limits of detectability and/or statistically marginally significant; their magnitudes cannot be controlled in any systematic way by varying experimental parameters.
- Incompatibility with accepted theories or principles is readily ignored.
- Investigators avoid carrying out critical, potentially disconfirming experiments, and refuse to accept any such experiments carried out by others as conclusive.

Rousseau argued that all three applied to Pons and Fleischmann (the other two cases he examined were "polywater" and Benveniste's "infinite dilution"), in which he called particular attention to the complete lack of correspondence between the excess heat claimed and the levels of nuclear byproducts detected (point 2), and the failure to perform any control experiments with ordinary water (point 3). The first point applies to the question of excess heat itself (although Rousseau does not specifically comment on that): even in the original paper<sup>[33]</sup> some of the data (Table 2) appear to show effects varying inversely with input, and subsequent analysis established that many of the most striking claims were actually tiny numbers inflated by dubious assumptions.[35]

A quite different perspective has been proposed by the sociologist of science Harry Collins. The "Experimenter's Regress", which was introduced in a discussion of the search for gravity waves, argues that it is impossible to separate questions about the existence or non-existence of a novel phenomenon from questions about the validity of the experiments designed to detect it:

"When the normal criterion—successful outcome—is not available, scientists disagree about which experiments are competently

Where there is disagreement about what counts as a competently performed experiment, the ensuing debate is coextensive with the debate about the proper outcome of the experiment". [43]

Clearly this may be applied to cold fusion (as Collins and a colleague did<sup>[44]</sup>): any negative finding can always be (and has been) challenged as incorrectly performed, such as claims that the wrong kind of electrode was used, etc.

The fact that these dueling descriptors are both operative has much to do with the continued survival of cold fusion research—if only as a ghostly entity, as Simon would have it. How should we view the more recent findings in light of the earlier, substantially discredited work? Pons and Fleisch-

mann, and others, made some rather major errors that led to reports of large effects—excess heat exceeding 1000%, high levels of neutrons or tritium-so a skeptic comfortably concludes that the generally much smaller effects now claimed are the result of more subtle errors. Conversely, proponents can reasonably argue that their later experimental designs do take previous criticisms into account, and should not be automatically assumed to be tainted by the same old mistakes; but they never get the opportunity to defend themselves, since nobody even bothers to criticize them. A (rather plaintive) letter to this effect, published in Chemical & Engineering News in 2003, [45] elicited no response at all. As Simon comments:

"No matter what kinds of new experiments and data CF researchers present, their critics (if even listening) always drag them back to debates from 1989. There seems to be no escape ... Their collective identity as a group as well as their scientific practice is organized to a large degree around reclaiming scientific legitimacy by constantly revisiting the criticisms of 1989–1990. In part they have no choice, since there are few extant criticisms of work after 1990 that they can address". [46]

Another factor in the post-mortem survival of cold fusion has been its decidedly chimerical nature. Which of the various phenomena that have been reported in the context of cold fusion excess heat, neutrons, tritium, X-rays, yrays, helium, even transmutation[47]\_\_\_ are fundamental to whatever (if anything) is going on? At least some of these reports are indisputably erroneous, but what does that imply about others? For example, the philosopher of science William McKinney, in arguing that one can escape from the "Experimenter's Regress" on the basis of objective analysis of experiments, suggested that the unequivocal demonstration of the artifactual γ-ray signature (thus undermining the claim for neutrons) was the real "knockout blow" for cold fusion. [48] However, cold fusion researchers are committed to no theory, so (on their account) excess heat need not be tied to neutrons. Since nobody has seriously claimed to understand the phenomena on the basis of any unifying theory, there need not be any real links between the various types of phenomena studied. From a strictly logical point of view, every individual experiment would need to be evaluated on its own merits: if one set of claims is debunked to everyone's satisfaction, that does not necessarily disprove another.

Indeed, one of the more recent studies (by the above-cited letter-writer Melvin Miles) reports detecting <sup>4</sup>He along with excess heat in more or less commensurate amounts, if it is assumed that the heat is produced by fusion of two deuterons to produce 4He and energy [Eq. (2)]. Furthermore, he claims that although the generation of excess heat is not always reproducible, the two phenomena correlate well, and the long-demanded control experiment was performed: light-water experiments exhibit neither excess heat nor 4He.[49] Of course, in "standard" D+D fusion, Equation (2) represents a very lowprobability pathway compared to reactions that generate neutrons and tritium,[50] and one would also need to explain why the energy liberated shows up entirely as heat rather than radiation (and many more things besides). But if one is willing to accept the possibility of some kind of nonstandard nuclear process going on within the Pd lattice (a big if for many, but one that does not seem to have much troubled cold fusion researchers), there are no apparent a priori grounds for dismissing these and other findings. They might well be subject to criticism on a variety of experimental grounds; but as noted above, work from the last ten years or more has received little, if any, scrutiny at all.

$$D + D \rightarrow {}^{4}He + \gamma (23.77 \,MeV) \tag{2}$$

So there matters stand: no cold fusion researcher has been able to dispel the stigma of "pathological science" by rigorously and reproducibly demonstrating effects sufficiently large to exclude the possibility of error (for example, by constructing a working power generator), nor does it seem possible to conclude unequivocally that *all* the apparently anomalous behavior can be attributed to error. Under these circum-

stances, the DOE has decided to carry out another review, which is underway at the time of writing (summer 2004). From the range of comments made in response to that announcement, [51] though, it seems most unlikely that their report will settle matters:

"There are quite a few people who are putting their time into this. They are working under conditions that are bad for their careers. They think they are doing something that may result in some important new finding. I think scientists should be open minded. Historically, many things get overturned with time."

"The critical question is, How good and different are [the cold fusion researchers'] new results? If they are saying, 'We are now able to reproduce our results', that's not good enough. But if they are saying, 'We are getting 10 times as much heat out now, and we understand things', that would be interesting. I don't see anything wrong with giving these people a new hearing."

"I think a review is a waste of time. But if you put together a credible committee, you can try to put the issue to bed for some time. It will come back. The believers never stop believing."

There are clear differences between our two cases: whereas the phlogiston controversy involved choosing the best theoretical framework to rationalize a set of experimental observations, with cold fusion there are essentially no theoretical frameworks among which to choose. Instead we have a set of observations that cannot be rationalized in terms of existing standard theory, and need to decide whether they (or some fraction thereof) are real anomalies that require new ideas, or mere mistakes. The majority of the scientific community has (explicitly or implicitly) opted for the second interpretation, just as the majority decided against phlogiston at the end of the 18th century. But the minority positions, then and now, were sustained for a considerable period. It is easy, but (as we have tried to show) much too simplistic, to invoke irrationality to explain this persistence of heterodoxy. Instead, these two cases illustrate that, once the human imagination has conceived an idea, it can sometimes be very difficult to prove its non-existence.

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- [4] R. A. Day, Jr., R. C. Johnson, General Chemistry, Prentice-Hall, Englewood Cliffs, 1975, p. 5.
- [5] J. B. Conant, Chemtech 1991, 592-596.
- [6] a) J. B. Conant, Science and Common Sense, Yale University Press, New Haven, 1951; b) Conant's major work on phlogiston is one of his famous case studies: "The Overthrow of the Phlogiston Theory: The Chemical Revolution of 1775–1789": Harvard Case Studies in Experimental Science, Vol. 1 (Eds.: J. B. Conant, L. K. Nash), Harvard University Press, Cambridge, 1966, pp. 65–115.
- [7] Ref. [5], p. 592.
- [8] The phlogiston story has been of great interest to those in science studies as well as to scientists themselves. It has served as a paradigmatic case for one controversial philosophical theory of scientific change: T. S. Kuhn, The Structure of Scientific Revolutions, 2nd ed., enlarged, University of Chicago Press, Chicago, 1970, pp. 52-56, 69-72. An early sociological study is by H.G. McCann, Chemistry Transformed: The Paradigmatic Shift from Phlogiston to Oxygen, Ablex, Norwood, 1978. Two additional books that deal significantly with phlogiston (although it does not appear in their titles) are E. Ströker, Theoriewandel in der Wissenschaftsgeschichte: Chemie im 18. Jahrhundert, Klostermann, Frankfurt am Main, 1982; and K. Hufbauer, The Formation of the German Chemical Community (1720-1795), University of California Press, Berkeley, 1982.
- [9] W. H. Brock, The Norton History of Chemistry, W. W. Norton, New York, 1993, pp. 79–84.
- [10] a) B. Bensaude-Vincent, I. Stengers, A History of Chemistry, Harvard University Press, Cambridge, 1996, pp. 57-63;
  b) for an extensive discussion of principles and their role in chemistry, see M. G. Kim, Affinity, That Elusive

- Dream: A Genealogy of the Chemical Revolution, MIT Press, Cambridge, **2003**, pp. 84–110.
- [11] Ref. [9], p. 82. We thank Professors Lawrence Principe and William Brock for helpful correspondence about this process.
- [12] Ref. [9], p. 83.
- [13] Ref. [10a], p. 58.
- [14] T. L. Davis, J. Chem. Educ. 1927, 4, 176– 183.
- [15] There was of course a third party who played a major role in the discovery of oxygen, the Swedish apothecary Carl Wilhelm Scheele (1742-1786): W. A. Smeaton, Endeavour 1986, 45, 28-30; W. A. Smeaton, Endeavour 1992, 51, 128-131. Although the first to isolate the gas, Scheele worked in relative obscurity and died before both Lavoisier and Priestley, and was thus not a major participant in the phlogiston controversy. The near simultaneous discovery of oxygen by three independent investigators has provided prime material for examinations of the meaning of "discovery": A. Musgrave in Method and Appraisal in the Physical Sciences (Ed.: C. Howson), Cambridge University Press, Cambridge, 1976, pp. 181-209, on pp. 194-195. The three contenders have even been turned into characters in a drama: C. Djerassi, R. Hoffmann, Oxygen, Wiley, New York, 2001.
- [16] Musgrave, Ref. [15], pp. 182-185.
- [17] Ref. [6b], pp. 93-104.
- [18] F. L. Holmes, *Isis* **2000**, *91*, 735–753.
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