Rekindling Phlogiston

Douglas Allchin

For 18th-century chemists, phlogiston (proounced FLOW-**JIST**-ON) was the material stuff of fire. It's what allowed things to burn. It produced heat and light. It was also the substance in charcoal that was transferred to ores, transforming them to their metals (reduction), and that was released again when the metals were roasted (calcination). It's also what made metals metal: shiny, malleable, and conductive. Phlogiston was a powerful concept for unifying combustion, reduction, calcination, and, later, the chemical composition of fuel in sunlit plants.

Today, phlogiston has a mixed reputation. For many, perhaps most, phlogiston does not exist. It was an imaginary entity, like the Philosopher's Stone of the alchemists or cold fusion in the 20th century. We explain combustion by oxygen, not phlogiston. Heat is movement, not a material substance. Phlogiston is thus appropriately relegated to the scrap heap of misleading, erroneous — and even embarassing — ideas in the history of science (Conant 1958; Musgrave 1976; McCann 1978; Cohen 1985; Melhado 1989; Thagard 1990, pp. 184, 201). Sir John Herschel epitomized this view in his virulent 1830 criticism:

> The phlogistic doctrine impeded the progress of science, as far as science of experiment can be impeded by a false theory, by perplexing its cultivators with the appearance of contradictions, . . . and by involving the subject in a mist of visionary and hypothetical causes in place of true and acting principles. (pp. 300-301)

Others, however, have seen the concept as more fruitful, even in a modern perspective. For them, phlogiston reflects, even if crudely, reducing potential, or perhaps available electrons (Odling 1871a, 1871b; Scott 1958; Allchin 1992; Kim 2008; Chang 2009; Boanza & Gal 2011). While we now have a more sophisticated view of combustion, especially of the role of gases, phlogiston still functions well as a unifying concept, as it once did. The noted chemist Alexander Crum Brown nicely expressed the more accommodating view in 1864:

> There can be no doubt that this [potential energy] is what the chemists of the seventeenth century meant when they spoke of phlogiston.
>
> We have only to regret that the valuable truth embodied in it [the phlogistic theory] should have been lost sight of; that the antiphlogistonistic chemists, like other reformers, destroyed so much of what was good in the old system.

Accordingly, several science educators have suggested that there is a place for phlogiston as a simple concept or model in the modern classroom (Scott 1958; Allchin 1996; Guinta 2001; Mamlok-Naaman, Ben-Zvi, Hofstein, Menis & Erduran 2005).

Here I profile how the historical concept of phlogiston was used to organize a series of lessons in a high school classroom on the nature of metals, their formation and oxidation, and on oxidation-reduction reactions on a macroscopic scale (Allchin 1996). Phlogiston also served as an occasion to discuss models and realism in science, the possible tension between simple and complex models or theories, and conceptual change.

While the lessons were inspired and guided by history — and included periodic historical commentary — the students were not explicitly engaged in the historical context. That is, this was not a historical case study, with a guiding historical narrative, following (say) the work of a famous scientist from the past (Chapter 10). Rather, the scope of the historical concept

circumscribed a bounded "investigative space" for inquiry learning. Four classes were free to explore this space based on their own questions. While each ultimately explored all the relevant topics, they followed different trajectories, encountering a set of core activities in their own order (discussed further below). The nature of science reflections occurred mostly at the end of the unit, with the introduction of additional historical information and discussion. The whole unit spanned 7-8 class days.

A Primer on Phlogiston

A fully developed notion of oxidation and reduction reactions as we now conceive them did not emerge until after an atomic model provided a framework for characterizing the reactions in terms of electron transfer. But knowledge of reduction has ancient roots. The reactions were known to the first miners and metallurgists who reduced ores to their corresponding metals. Originally, they sometimes attributed the metallic property to a substance from the fire — a conclusion emerging no doubt from the resemblance of the reflective metal surface to the light of the fire. Oxidation reactions were familiar too, of course, to anyone who built a fire. By the early 18th century, these phenomena had become linked by the notion of a material principle of fire or inflammability: phlogiston. Using the concept of phlogiston, chemists could explain why things burned and why they emit heat and light when they did. Wood, oils, alcohol, charcoal, metals, sulfur and phosphorus were rich in phlogiston. Metals also contained phlogiston, which was released when they were "burned," or calcined. Combustion (of organic material) and calcination (of metals) — both oxidations in today's terms — each involved the release of phlogiston. Phlogiston thus powerfully unified the mineral kingdom with the plant and animal kingdoms, earlier considered wholly distinct, by using a shared chemical principle. Chemists also related reduction to its reverse reaction, calcination. Metals lost phlogiston in becoming an earthy material, the metal's calx; while ores or calxes gained phlogiston to yield metals. The basic notion of phlogiston may be summarized in the more familiar form of modern chemical equations:

combustion:

charcoal (rich in phlogiston)	--->	earthy residue	+	light, heat

calcination:

metal (compounded of calx + phlogiston)	--->	calx <for us, the metal oxide>	+	light, heat (released phlogiston)

reduction:

calx (or ore)	+	phlogiston (from charcoal)	--->	metal

In today's terms, phlogistonists had identified something akin to chemical energy or reducing potential (Brown 1864; Odling 1871; Scottt 1958; Kim 2008; Chang 2009). That is, phlogistonists had identified the importance of energy relations in these reactions and then reified them as the gain or loss of a material substance (Partington & McKie 1937-1939; Brock 1992).

Phlogiston also intersected with interpretations of acidity. For example, sulfur was considered a compound of acid and phlogiston. So, when an acid reacted with a metal, phlogistion from the metal was transferred to the acid, yielding the metal's corresponding calx and (in this case) sulfur. In addition, phlogiston was considered to contribute to the unique properties of metals: their luster, malleability and ductility. Late in the 1700s, chemists saw an analogy between fire and electric spraks and explored the relationship between phlogiston and electricity — even being led to use electricity to reduce calxes to their metals (Sudduth 1978;

Allchin 1992). These detailed (and, to modern perspectives, sometimes more convoluted) conceptions became peripheral in our relatively simple classroom project.

As the 18th century progressed, chemists began to collect gases, or various "airs." They realized that they could be involved in chemical reactions — as products or reactants. Pneumatic chemistry flourished. Without knowing fully about oxygen, for example, they realized that combustion in a closed vessel was limited by the amount of air. In addition, burning "fouled" the air for further burning. For breathing, too. A burning candle reduced the time a mouse could live when placed in the same vessel. Drawing on the image of smoke leaving a burning substance, some chemists extended the notion of phlogiston. During combustion, air would become "phlogisticated." When the air became saturated with phlogiston, it failed to support further burning. Likewise, "dephlogisticated air" — oxygen, in today's terms — could support extended combustion.

Another "air" was produced by the reaction of acids with metals. The new "air" (hydrogen, in today's terminology) burned remarkably well and earned the name "inflammable air." Since metals lost their metallic properties, the gas surely contained the lost phlogiston. For some, it *was* phlogiston, perhaps! One of the most productive pneumatic chemists, Joseph Priestley, envisioned the reverse reaction: shouldn't this new "air" be able to reduce calxes back to their metals? And this he subsequently demonstrated (Carrier 1991, pp.29-30; Partington 1962, v. III, pp. 268-270).

In the late 1700s, Antoine Lavoisier identified oxygen as a distinct elemental gas, able to combine with other elements in solid compounds. For Lavoisier, explanations using oxygen made the role of phlogiston unnecessary. Metals were simple substances, not compounds with phlogiston. Calxes were compounds with oxygen, not simple substances. Lavoisier began crafting what he called a "revolution" in chemistry. He developed a new nomenclature for the elements, which now included the gases hydrogen, nitrogen and oxygen, while eliminating water and air. That system helped fruitfully reorganize thinking. Lavoisier's view of combustion (and of heat and light, which were also now chemical elements, as well!) were inscribed in the new terminology and was widely adopted with it. In the following decades, the concept of phlogiston waned. Since then, phlogiston has become notorious as a substance that never was (as exemplified in Herschel's assessment above). Today, many histories (shaped by Lavoisier's perspective) portray phlogistic theory as "overthrown" or "supplanted" by the oxygen theory of combustion (Conant 1957; Musgrave 1976; McCann 1978; Thagard 1990). Yet, by today's reckoning, Lavoisier failed to adequately explain aspects of heat, light and why things can burn at all (Chang 2009). Even our simplest notions of fire include a role for both oxygen and fuel. Late phlogistonists criticized these very deficits in Lavoisier's scheme. They underscored the original strengths in the concept of phlogiston (as above, not related to "airs"). Thus, many accepted the discovery of oxygen, while still maintaining the original role for phlogiston — say, in explaining the heat and light of burning (Allchin 1992; 1994). Understanding this overlap allows one to approach phlogiston and its role in metals without addressing its separate, and less secure, role in pneumatic chemistry. Indeed, because phlogiston helped guide early understanding of combustion and related phenomena, apart from any concerns about gases, it seems ideally suited — despite its maligned reputation among some — for conceptualizing oxidation and reduction at an introductory, macroscopic level.

Orientation and Classroom Strategy

We "rekindled" phlogiston for teaching chemistry in a modern classroom. The original motivation was to teach about metals and to lay the foundation for oxidation-reduction reactions. The teacher in this project, while experienced, had found teaching these topics (especially motivating students) particularly challenging. Our approach to the material was structured by the organization in Figure 1.

METALS	**calcination** (and corrosion, rusting and tarnishing)	**reduction** ("reverse calcination")
ORGANICS (Carbon/Wood)	**combustion**	

Figure 1. Relationship of reduction, calcination, combustion. The Metals/Organics categories follow a more familiar distinction between mineral and animal-vegetable. Phlogiston is lost in the processes on the left (oxidations), gained in processes on the right (reductions).

That is, we wanted the students to address and find relationships among the following:

1. reduction of "ores" (metal oxides, chlorides, etc.) to metals
2. oxidation of metals (calcination)
3. calcination and reduction coupled together
4. combustion.

This provided a fairly well bounded "problem-space" that each class could explore in a context of inquiry. Students would easily be able to generate and draw on a set of observations largely available in the early and mid-18th century, when the concept of phlogiston flourished.

Pedagogically, then, our strategy was to situate the students as a group of investigators in a historically informed scenario, while not making the history explicit or dominant (Johnson and Stewart 1991). We guided four classes in finding their own way through the problems and their solutions, occasionally asking simple questions to help them see adjacent areas of the problem-space. The students conducted simple experiments and demonstrations, punctuated by sometimes quite extended discussions in which they collaborated to interpret their results and to map out successive phases of their inquiry. Each class was free to pursue its own path, and each eventually tackled the material in a different sequence.

An inquiry curriculum is by its very nature unscripted. Applications are highly contextual and contingent on local features, such as teacher strengths, student abilities and class profiles, curricular setting, institutional resources, time, etc. Our context was a 10th-grade chemistry class in a relatively affluent college-prep school. Interest in chemistry itself was relatively low, but the teacher enjoyed a good rappore with the students. The following account may thus be viewed as just one instance of the activity. I try to profile local factors that shaped its development and implementation. Other teachers thus may thus find here a scaffold or flexible model only, to be adapted to their own local circumstances.

Introduction for Students

We wanted to motivate students at the outset to reflect on the relevance of metals — their cultural role and historical emergence. That would ideally lead to questions about industrial processes and, of course, metals as substances subject to chemical reactions. We used a video ("The Age of Metals: Can it Last?" from the public television series *Out of the Fiery Furnace*). We might equally have discussed the local mining industry (here, taconite, a form of iron ore — but metal ores of some sort are mined nearly everywhere). Or one might compile a list of all the metal objects found just in the classroom and note their importance, perhaps typically taken for granted. Or one might profile the historical impact of metals. For example, in a dramatic battle

at Cajamarca, Spanish conquistador Francisco Pizarro and 168 soldiers were able to subdue over 80,000 Incass in one afternnon in part because of their steel swords, armor and guns (Diamond 1997, pp. 67-81). In our classes, we also noted the centuries-old problem arising from the economic value of metals: how does one transform an ore into its corresponding metal?

We then allowed students to observe and record in lab the differences between metals and their "ores" (or their oxides — their "calxes" in 18th-century terminology). (We refrained from providing any chemical formulae, however.) We primed the problem further by showing how a metal can apparently "burn," producing once again its chalky calx (our surrogate ore). First, we burned steel wool. That raised a few eyebrows. Then, for sheer spectacle, we burned magnesium ribbon. The desired effect was achieved. These observations served to guide subsequent work, organized around the questions: what is the nature of the difference between a metal and its "ore," and how does one interpret the transformation from one to the other? (And where did all that light from burning the magnesium come from?!)

Inquiry into Reduction

One class was particularly intrigued by the smelting process. They started off by researching this for homework. Fortunately for them, we could direct them to a convenient chapter section in their text. One could well have used this opportunity, though we did not, to delve deeper into the history of metal technology — elaborating on discoveries in the Iron and Bronze Ages, their implications for civilization, etc.

Once students had acquainted themselves with the critical role of "coke" or charcoal, they were ready to reduce their own "ores." They used partially covered crucibles as mini-furnaces. Different groups used $CuCl_2$ (as tolbachite or eriochalcite) and CuO (cuprite) to provide some variation in trials — and to establish the benefit of sharing results. Using their makeshift smelting apparatus, students successfully produced small granules of metal. In some cases they found a thin but unmistakably-colored lamina of copper on the outside of their crucible (from vapors which had rolled over the crucible lip and condensed, we concluded). They confirmed the presence of their products through observable traits and tests for conductivity which they had learned on the first day of the unit. The charcoal had been able to confer some metallic properties to the ores. In this laboratory exercise, then, they had established one piece of the overall picture, summmarized in their reaction equation:

calx / "ore" + carbon ---> metal (1)

The remaining question was, of course: what is carbon's role? They would need to pursue other inquiries, especially about the burning of coal, before being able to answer this directly. In subsequent investigation, in fact, this class would also learn that they had inadvertently omitted a key product from their equation: where had the carbon gone, or was it part of the metal?

Inquiry into Calcination and Combustion

The initial demonstration of "burning" metals prompted other classes to focus first on the role of the heat of the fire. We provided samples of metal powder for them to roast, or "calcine," in simple crucible set-ups. Again, they noted the recognizable feautres of the metal-calx change. In group discussion, we posed the question whether there was a basis for comparison: did the transformation between metals and their ore-like versions occur elsewhere? Their observations of different samples now provided clues and some cases were forthcoming; others we teased out by suggestion:

tarnishing — of brass candlesticks or doorknobs; of silver jewelry or cups, silverware or other cutlery
corrosion — of bronze statues or copper roofs and pipes, each signaled by distinctive color changes
rusting — or iron nails or fenceposts, cast-iron frying pans, etc., also marked by

color change.

Our intent, clearly, was to link the science with more familiar phenomena and to use that familiarity as a channel for introducing their emerging theory into a vernacular perspective. By comparing these cases with their own, students were able to notice that heat was not exclusively responsible, though it did seem to hasten the process. Most students seemed satisfied by this conclusion and we passed over the opportunity to construct a more carefully controlled experiment. In all cases, however, the metals were exposed to the air or rain or water.

When students reconsidered calcination as burning, they were able to draw on their prior knowledge about the combustion of wood or coal as possibly applicable to "metal-burning." They speculated about the role of oxygen as a reactive agent or catalyst. (Addressing such common prior knowledge was one reason we had not endeavored to follow a strict historical scenario.) Students were able collectively to design experiments to test their hypothesis: compare metals in pure oxygen test chambers with those in oxygen-deprived atmospheres. We recalled that during the early 18th century chemists had discovered different "airs" and devised the equipment to collect and manipulate them. So we challenged our modern students to create on their own any special lab materials: how did one obtain this sample of pure oxygen, for example? (How might a modern chemical supplier get it?) The students were forthcoming in suggesting that burning a candle in a closed system would create the requisite oxygen-free atmosphere. They were a bit more baffled about the oxygen. But some remembered a reaction they had done with red mercury powder in chemistry class some time earlier. Others suggested gathering the "air" from plants or seaweed. Again, we had the opportunity to pursue a tangent — here, into pneumatic chemistry — but we opted for a narrower focus, acknowledged the fruitfulness of their experimental design, and assured them that their tests would confirm their expectations. Another piece was thus added to the puzzle, summarized again in their equation:

metal + oxygen [+?] ---> calx/"ore" [= an oxide?] (2)

This still left open the questions of the light, so dramatically exhibited by the magnesium fire, and of the heat known to accompany burning. Many were ready to speculate that something — akin to smoke, perhaps — was given off during the burning process. (Here, they re-expressed the naive chemical views documented in many cognitive studies and we did nothing immediately to suppress the misconception. We trusted their own investigations and discussions as a route to a proper conception.) One may note, here, that a role for phlogiston was being established, even as they spoke about oxygen.

Inquiry into Coupled Calcination and Reduction

Given these preliminaries (and in one case, even prior to completing them), we were ready to introduce formally the notion of phlogiston. We asked rhetorically whether it might not be possible to transfer the metallic qualities from one metal to another, producing a new metal from its ore without charcoal. We then proceeded with what was perhaps the theatrical highlight of the unit, a demonstration of the thermite reaction (American Chemical Society 1999). In this reaction aluminum reduces iron ore to iron, while it is oxidized to aluminum oxide. The reaction produces spectacular fireworks and enough heat to melt the iron product. In our demonstration, performed on the school's baseball infield, the molten iron exhibted an impressive orange glow as it dripped nicely out of our flower-pot reaction vessel.) The pyrotechnics were calculated to have an effect — and the students did not disappoint us, even given our deliberately hyperbolic promises.

Students confirmed the cooled iron product as metal by measuring conductivity (resistance). We then returned to the blackboard to summarize the reaction:

aluminum + iron "ore" ---> iron + aluminum "ore" + LIGHT, HEAT! (3)

Although the thermite reaction was not discovered until 1893 (hence unknown to the 18th-

century phlogistonists), we confidently interpreted the results in terms of phlogiston. We announced to the students that they had witnessed the transfer of an inflammable (and metal-conferring) substance from the aluminum to the iron ore, while some was lost, accounting for the light and heat. We called the subtance *phlogiston*. This, clearly, was what had allowed carbon to reduce their metal "ores" earlier: carbon was a rich source of phlogiston (witness, for example, the combustibility of coal). While many students remained suspicious, the demonstration allowed them to recognize and address the strong link between calcination (here, of the aluminum) and reduction (of the iron calx). A transfer of properties of some kind had occurred (and we referred back to some of their speculations about things emitted during burning). We sent them home with an excerpt from the 1771 *Encyclopedia Britannica:* "Of the PHLOGISTON" (see chapter appendix). The results of all the investigations were ready to be integrated.

Combustion Revisited and Student Synthesis

Through several days of following leads, students had accumulated a wealth of disparate information: about the roles of oxygen in calcination and of carbon in reduction (though this was cast in doubt by the thermite reaction), and about the release of heat and light. To facilitate the synthesis of information from the different contexts, we constructed the table in Figure 1. Once the elements of the table had been explored separately, the organization suggested some broader comparisons and posed several questions. Some of the details of this discussion are included here to illustrate the multiple possibilities and to alert the teacher to prepare properly. It may also help to show a modern chemist how to think like a phlogistic chemist.

(a) How did the thermite reaction involving aluminum metal (eq. 3) relate to the reduction exercise involving organic carbon (eq. 1)? (How did top and bottom rows relate?) Can charcoal reduce ore precisely because it can combust — the phlogistic explanation? Does charcoal "burn" at the same time it reduces metal ores?

(b) Metals become calxes (top row), but what does wood or coal become when it burns (bottom row)? As one student expressed it — catching us off-guard, but delighting us nonetheless: what is the "calx of carbon"? Alternatively, substituting coal for aluminum in the thermite reaction (eq. 3): what is "coal ore" as a product?

(c) If oxygen is acquired during combustion and calcination (left column), is oxygen lost during reduction, as the reverse process (right column)?

(d) If light and/or heat are released in combustion/calcination, is heat or light therefore required for reduction (in addition to whatever carbon does)?

(e) If reduction and calcination are complementary processes, is there a process complemetary to combustion? That is, how would one characterize "*reverse combustion*" — the gaping hole in the chart?

Each comparison provided an entry into bringing information together and for filling in the holes. Students plumbed their own knowledge to realize that coal ore was the more familiar carbon dioxide: a gas, not an earthy material. It must be formed in reducing metals (revealing an additional, missing product in eq. 1). They concluded that calxes must be metal oxides and that reduction must involve the loss of oxygen. Carbon can be a reducing agent partly because it reacts with the oxygen. Oxygen is lost in the processes in the right column, but oxygen is gained in the processes on the left. Hence, we could provide a new label: *oxidation*. The new term expressed the unity between metallic and organic reactions. Similarly, phlogiston — or some equivalent — must be lost on the left, yielding light and heat, and gained (or required) on the right. The reactions also seem to be coupled: every loss entails a gain somewhere else, and vice

versa. But what was reverse combustion? They reconstructed the necessary equation:

$$? + \text{phlogiston (light)} \quad \text{---}> \quad \text{carbon fuel} + O_2 \qquad (4)$$

Again, they did not disappoint us: they identified this as photosynthesis: familiar, but now with a new and deeper meaning in the context of similar reactions with metals.

All the reasoning here was straightforward, but the students needed time to cross the observational ground several times and notice and talk through all the connections. But this itself can be a lesson about how real research in science proceeds: as a balance between blind groping, reasoned guesses about where to go next, and empirical confirmations. We were satisfied that patience on our part was rewarded with the appreciation by students that they had largely reached their conclusions on their own.

Ironically, our students had already learned atomic theory. Thus, they were well prepared to appreciate further lessons about what some perceived as the fuzzy concept of phlogiston. Phlogiston, they could interpret in modern terms, was a form of energy that one might construe crudely as chemical bonds. But they also knew that light, produced by the release of phlogiston under one conceptual system, was to them associated with the release and capture of electrons (associated with spectra lines). They thus re-mapped what they had just learned about phlogiston onto what they already knew about atoms. They could easily reinterpret oxidation (calcination and combustion) and reduction in terms of a more sophisticated or more deeply articulated notion of electron transfer. This reinterpretaion is significant, because it demonstrates that one need not follow a strict historical sequence across the curriculum. Historical episodes can be used intermittently, even perhaps anachronistically, to great effect.

Reflecting on the Nature of Science

The students at this point were well positioned to appreciate the observations of renowned chemist Alexander Crum Brown in 1864:

> There can be no doubt that this [potential energy] is what the chemists of the seventeenth century meant when they spoke of phlogiston.
>
> The truth which [Lavoisier] established, alike with that he subverted, is now recognizable as partial truth only; and the merit of his generalization is now perceived to consist in its addition to — its demerit to consist in its suppression of — the not less grand generalization established by his scarcely remembered predecessors. . . . Accordingly, the phlogistic theory and antiphlogistic theory are in reality complementary and not, as suggested by their names and usually maintained, antagonistic to one another.

The occasion was ripe to pose deeper questions about the nature of scientific theories. Is phlogiston "real"? In particular, is it any more or less real than electrons? For many of our students, phlogiston was not real: it was not in their textbooks — and it did not appear on the periodic table! Once we had re-introduced the more familiar concept of electrons, they quickly abandoned the "old," outmoded concept. As an idea from history, it no longer had currency and could thus be rejected as imaginary, not real. We emphasized the explanatory adequacy of the concept, how it could guide their own interactions with the materials, and asked how else they would judge the concept. Our strategy was to create a discrepant event *about the nature of science*. How would one know or prove what is real or not?

Philosopher of science Ian Hacking (1983) has proposed that our criteria for realism should not be evidence for particular *representations*. Rather, our judgments about what is real and what is not typically rely on our *interventions* in the world. In this case, our students (like their 18th-century counterparts) could intervene by transfering phlogiston from one substance to another. Historical chemists were even able to predict such interventions — reducing metals with inflammable air (hydrogen) and with electric sparks. In such a *functional* framework, phlogiston can indeed be considered real. It has *instrumental* reality (Kim 2008).

We also turned the students' skepticism on its head: how would the students know if electrons (as a preferred explanation) were any more "real" than phlogiston? Did phlogiston, like electrons, not explain things in a definable context? Did phlogiston not help describe and predict the reactions for them now just as effectively as it had for chemists in the 18th-century? Students gradually recognized that phlogiston and electrons were both humanly developed, possibly limited concepts. Still, they were grounded empirically and extraordinarily powerful in interpreting the world around us. Even if a scientific theory is limited, we may still want to construe it realisitically, at least in a particular context. The concept of phlogiston, they admitted, was certainly reliable and warranted within a prescribed domain of application — and had been accepted historically within this domain. It could be "wrong" and "right" at the same time, depending on context. Phlogiston was as real for 18th-century chemists as electrons are for us now. Scientific theories are not universal or absolute. They have contexts and limits. This, we felt, was a profound lesson about the history and nature of science.

Not every student was deeply engaged in this level of thinking. But our success in provoking philosophical reflection may be indicated, perhaps, by the students who stayed after class to argue about whether the phlogiston concept is still relevant — and who also arrived in class the next day brimming with fresh thoughts.

Other Inquiry Opportunities

The encounter with phlogiston opened several tangential excursions we wanted to pursue more fully, but could not due to our particular schedule. Each could extend the phlogiston/ox-redox unit and/or serve to segue to other units of study.

(1) *Sulfuration*. Despite the term oxidation, oxygen is not the only element capable of converting metals into earthy ores. The sulpheration of iron was known early in the 18th century, but did not become a major component in the debates over combustion and phlogiston. Some, however, used the phenomenon to argue that the oxygen theory of combustion was incomplete, and that it could not therfore fully replace the notion of phlogiston in burning, as many at the time contended (Allchin 1994). Some students in one class found that they could get a fine-grained metal to lose its metallic properties by heating it with sulfur powder. With creativity, an instructor might expand to chlorine, or to carbonates, sulfates, nitrates, etc.

(2) *Acid-metal reactions, reduction by hydrogen*. Some students, prompted by the similarity of calcination with corrosion, wondered if acid could calcine (corrode) a metal. By heating zinc with hydrochloric acid under the hood, they demonstrated that indeed they could. Had they been able to isolate the gas released (clearly evidenced by the fizzing bubbles), they might have been surprised that it was highly flammable. In fact, hydrogen had been called "inflammable air" when it was first isolated by phlogiston-minded chemists. It seemed to have taken phlogiston from the metal as it was calcined by the acid. With a bit of guesswork, the students might have predicted that a phlogiston-rich gas such as this could reduce calxes — a speculation that could be confirmed by further testing, as it was historically by Joseph Priestley (see Primer above).

(3) *Electrochemistry*. The thermite reaction offers a suggestive model for the reactions in a galvanic pile. Indeed, Humphrey Davy used a phlogiston-like concept to interpret some of his early work on electrolysis (Siegfried 1964). For others, phlogiston was the "principle of the negative pole of the galvanic apparatus." One can thus pose a challenge to students: given the concept of phlogiston, and the knowledge that some metals seem to be able to release it to others (as in the thermite reaction), can one generate or harness a flow of phlogiston? The reducing potential of different metals (at two poles in a battery) can certainly be interpreted as reflecting characteristic levels or amounts of phlogiston. Here, one would be building on work of many chemists in the 18th century who saw a connection between phlogiston and electricity. The light of electrical sparks, they speculated, was analogous to combustion and indicated the release of

phlogiston. Indeed, some researchers successfully reduced metals with electricity — a prediction students might also make under appropriate circumstances (see Sudduth 1978; Allchin 1992).

(4) *Respiration*. In a classroom prepared to make cross-disciplinary leaps, the discussions of phlogiston, carbon and photosynthesis could lead to a further pursuit of biological oxidations and reductions. Here, the burning of wood would be an explicit analog of the "burning" of plant fuel by an animal.

(5) *Mining and metallurgy*. As noted above, the encounter with metals and ores provides an opportunity to linger on the metal industry and the historical developments of the Bronze Age, Iron Age, etc. For example, how does one determine the purity of a metal extracted from its ore, especially of gold or silver, whose values are closely related to their purity?

Assessment

This project was ripe for several alternative modes of assessment. For example, we asked the students to keep scientific notebooks/journals of their lab results and their thinking along the way. Initially, we planned to have each student summarize his or her observations and interpretations, along with the class's collective reasoning — all in the format of a modest scientific paper, as though they were reporting original research. By the end of this relatively complex project, however, this seemed somewhat daunting. We also passed up the opportunity for peer review — made even more promising by the possible exchange of papers between classes that had reached their own results in slightly different ways. Nor did we ask students to plan a research agenda or experiments that might investigate one of the Opportunities above.

The solution for the teacher, in this case, was to have students write an essay on one of several topics. One option was to write a letter to a phlogistonist and to explain, in terms he could understand, how we now interpret the four processes in Figure 1. A more straightforward version asked about the role of light and heat in the same set of reactions, comparing explanations using phlogiston and electrons. Another, more philosophical topic invited the students to comment on the claim that "phlogiston is just as real as the electron." The most challenging (and least selected) question asked students to consider the results of combining of carbon or silicon with (a) coal, (b) iron ore and (c) an acid. The intention, here, was that they might predict or articulate the properties of a semi-metal.

Commentary

What does one gain from rekindling phlogiston in the chemistry classroom? How might one generalize from this case to others? What lessons from this activity apply to science education more broadly?

In terms of scientific content, we found that by using the concept of phlogiston, students developed a concrete knowledge of oxidation and reduction that does not rely on atomic theory and its sometimes foreign abstractions. We felt confident that they could relate a broad spectrum of phenomena: they were able to view tarnishing or corrosion as analogous to an extremely slow form of burning (both as a loss of phlogiston). They could connect (non-intuitively) photosynthesis and the production of metals from ores (both as a gain of phlogiston), all without having to refer to electrons. By reifying chemical energy or reduction potential as phlogiston, they were prepared to see that oxidation and reduction reactions will always be coupled, where every transfer of phlogiston involves both donor and recipient (and some release of heat and/or light). While one might convey these concepts of oxidations and reductions in more conventional terms, phlogiston seems to provide a comprehensive scheme for organizing the fundamentals before one understands the more detailed mechanism. Perhaps most importantly, on this more basic level, students can participate in framing their own knowledge; one can engage their interest more and give them a greater sense of authority over the concepts.

Nature of Science. Teachers often adopt elementary theories from history — even those we now construe as "wrong" — as simple models. For example, the Bohr model of the atom is a standard part of teaching atomic theory and spectra lines, though by the next week we often celebrate how it was replaced and shown to be "wrong" by quantum theory. Likewise, textbooks frequently draw on the fluid model of electricity to explain current, resistance, capacitance, etc., especially in complex circuits, although scientists abandoned the notion of an electrical fluid in the mid-19th century. Such models are useful because they can help lead students from simple to more complex ideas. We may need to dwell on their simple applications and contrast their adequacy in certain contexts with their inadequacy in others. These models are excellent opportunities for introducing students to the role of models as conceptual maps, and the ways in which any model is selective in what it represents. They can both inform *and* mislead at the same time (Judson 1981, Chap. 5; Turnbull 1993; Wimsatt 2007). We may profitably reflect and comment on the virtues and qualifications of scientific models or theories as we teach them.

As a result of the explicit reflections, we think our students learned something about conceptual change, or the history of ideas in science. Their final letters to the historical phlogistonist, in particular, demonstrated that they could see the same data in two ways. That is, when comparing interpretations using phlogiston and electrons, they were able to appreciate the historical change in concepts, along with the merit and context of the original interpretation. They thus understood that ideas can change: even an entry in an encyclopedia (our excerpt from *Encyclopedia Britannica*) can later be considered "wrong." Finally, they were able to realize that the development of knowledge is not the mere accumulation of facts. Sometimes there are dramatic reconceptualizations, exemplified in the long-term shift from phlogiston to electrons. By having used the concept of phlogiston themselves, however, they were less likely to see current ideas as self-evident, or to regard as ignorant or foolish those scientists of the past who advocated ideas we now regard as mistaken. Some students also clearly appreciated, by analogy, the tentative status of our current knowledge (about electrons, etc.). Working with the historical ideas, rather than merely learning about them through a presentation, may have been critical to appreciating their legitimacy and thus understanding the historical moral.

The Role of History in Science Education. We borrowed the concept of phlogiston from history, but ultimately our project used history creatively rather than adhering to it strictly. First, our students had learned about combustion and the role of oxygen — and even about electrons — well before our unit on metals and phlogiston. This clearly contradicted the actual historical unfolding. In addition, we used the thermite reaction anachronistically and interpreted it as phlogistonists might have decades earlier, before it was actually known. By contrast, we entirely omitted discussions about phlogiston and air, and metals and acids (but see section on "Opportunities"). Our lesson was historically inspired, not a historical simulation. Our aim was not to replicate or recapitulate history. Rather, we used history as a tool (Chapter 2). The history sensitized us to initial and simplified impressions about reduction and oxidation reactions. It also highlighted the relevant observations for developing the concepts fully. Our scenario was not so much historical as historically informed. Still, a teacher that delves into this case will ideally develop some fluency in the historical way of thinking, to help converse with students on the same level.

While we may have taken liberties with historical events, we did not, however, abandon the perhaps more important historical principle: *respecting historical perspective* (Chapter 5). That is, we preserved the context in which talking about phlogiston did — and still does — make sense. Our application of phlogiston to the thermite reaction, anti-historical in one respect, was governed by just this principle. Nor did we corrupt the original phlogiston concept to fit modern ones. Nor did we treat it as a historical precursor to electron theory, or as an elementary or primitive version of potential energy or reduction potential. Thematically, these links exist; historically, they do not. Throughout, we were sensitive to the historical context, its virtues and limitations both.

According to some models, the individual student "recapitulates" history in learning scientific concepts. Some regard history as *the* model for designing appropriate instructional

sequences. While the notion is intuitively appealing, our experience demonstrates that history need not be the exclusive authority in specifying a conceptual sequence. While we taught oxidation-reduction in a historical context, students had already learned certain relevant concepts developed only later in history. We introduced the 18th-century concept of phlogiston *after* the students had learned about oxygen and Lavoisier's system of the elements, *after* they had learned the role of oxygen in combustion, even *after* they had learned about electrons, atomic models and the electron's role in light and spectra lines. We allowed students to construct their notions on concepts that, historically, were not available at the time of their historical counterparts. Our chronological juggling, nonetheless, yielded a penetrating interpretation that reconciled phlogiston and oxygen.

Managing a Classroom in Historical Inquiry Mode. As noted above, we allowed students to make errors early in the unit without correcting their misconceptions: about carbon possibly combining with ores to constitute metals, or about smoke indicating the release of something material from the fire. Withholding comments at such times was difficult, and required a fair amount of confidence that the students' ensuing research would isolate such errors and correct them. By the end of the unit, these tensions had indeed resolved themselves. The danger, of course, was that individuals might not recognize these connections or transformations. In many cases, therefore, we tried to re-introduce the early conceptions into their final discussions, so that they could couple them with their later knowledge and reinterpret them explicitly using their more sophisticated conceptual frameworks. Where possible, we directed questions specifically to the student who originally introduced the simpler notion. Here, we emphasized the revisions and the reasons for shifting explanations. These provided good occasions to acknowledge and celebrate the students' own discoveries and learning.

Experimentally, our lab experience was modest technically, but hopefully rich and challenging cognitively. For example, the question-oriented framework allowed us to ask students to design experiments. Students reasoned both from hypothesis or question to experiment and from experiments to new concepts. Our physical movement back and forth between the discussion area and lab benches, we hope, reinforced their appreciation of the close interactions between theory and observation, and between investigation and interpretation.

Authentic research involves uncertainty. Admittedly, the problem-space we selected was carefully bounded. But it was also shaped by historical awareness. Through historical precedent, we expected students to be able to make discoveries by exploring on their own without getting lost. Still, the students faced (for themselves) genuine unknowns. Sometimes, in fact, we found it necessary to adopt the role of fellow investigators and pose new questions — in context, from the partial knowledge at hand — to guide further research. Each class seemed to present its own limits or thresholds. We recognize this as the challenge in any truly inquiry framework in a targeted domain.

History can be a guide for inquiry. But inquiry must be based on the students' own understanding, not on trying to re-enact history. That is, the cognitive recapitulation model may be taken too strictly. Our four chemistry classes found four different ways through the problem space described above. Each class pursued topics in its own distinctive order, but all eventually passed through every item on our original list of phenomena:

Class A*	4 --> 2 --> 5 --> 3 --> 1
Class B	2 --> 1 --> 3 --> 4
Class C	2 --> 3 --> 4 --> 1
Class D	1 --> 3 --> 2 --> 4

(*One class also considered sulfuration and treatment of metals with acid, labeled #5.)

Each class also raised and addressed its final synthesis questions in a different order. We obviously facilitated the ability of all classes to develop a common set of information by

choosing a problem-space that was well cross-linked and by guiding students along the way. Yet given a rich collection of phenomena, there were many different ways to reason to a conclusion. For this style of project, it may be important to select a field of observations that has multiple ways of reaching the same concept or that overdetermines the conclusions.

Our ideal was student-based inquiry. At the same time, as student autonomy and freedom increased, so too did the teacher's workload. To be able to pursue contingencies as they arise, one must be ready to accommodate them. In principle, this is simple. In the classroom, it is not. In planning the unit, we felt the need (confirmed in retrospect) to scout the territory ourselves and be prepared for the many possibilities. Many prospective experiments were not fruitful.

Planning our phlogiston unit (which covered 7-8 class days) involved six 1-1½-hour sessions. Preparing for contingency, we found, is extraordinarily time-consuming. In addition, the teacher sometimes needed to prep the lab for four different set-ups on the same day. This was challenging. Thus, in subsequent years, the teacher opted to guide all classes more strongly through a common sequence.

We were also concerned that students not only learn the content, but have a rewarding experience in scientific investigation as well. That is, we were sensitive to the *affective* dimension of inquiry and wanted to ensure *closure* and *success* in problem-solving in an educational setting. We thus carefully selected a problem-space that was relatively simple to explore. We are well aware that students can learn from their own errors. At the same time, students can be enormously discouraged by such perceived "failures." We thus invested considerable time in preparing the unit by trying several investigations and materials that the students might likely have selected on their own. For example, we focused on copper compounds after finding that alternatives with magnesium and zinc did not readily yield clear results. We also abandoned intentions to replicate Lavoisier's measuring of the weight in calcining metals after finding how difficult it was experimentally to get a complete reaction. We used that knowledge to shape and limit the students' inquiry. We established boundaries that would allow the students to explore the phenomena successfully without getting lost or bogged down in the complexity of the real world. Again, the effective teaching scenario was, in some ways, student-based in appearance only.

In summary, by rekindling phlogiston, we were able to teach a difficult concept in simple terms while also fostering learning about conceptual change and the nature of scientific models and theories. Because the concepts that we teach in K-12 are typically simplified (Chapters 7, 8), such lessons seem important in conveying the limits of science and how to interpret the reliability of its claims.

References

Allchin, D. 1992. Phlogiston after oxygen. *Ambix* 39, 110-16.
Allchin, D. 1994. James Hutton and phlogiston. *Annals of Science* 51, 615-635.
Allchin, D. 1996. Rekindling phlogiston: from classroom case study to interdisciplinary relationships. *Science & Education* 6:473-509.
American Chemical Society. 1999. Thermite reaction. URL: jchemed.chem.wisc.edu/jcesoft/cca/cca3/main/thermit/page1.htm.
Boanza, V.B. & Gal, O. 2011. The 'absolute existence' of phlogiston: the losing party's point of view. *British Journal for the History of Science* 44, 317-342.
Brock, W.H. 1992. *History of Chemistry*. New York: W.W. Norton.
Brown, A. C. 1866. Note on phlogistic theory. *Proc. Roy. Soc., Edin.*, 5, (V) 328-30.
Chang, H. 2009. We have never been Whiggish (about phlogiston). *Centaurus* 51, 239-264.
Cohen, I. B. 1985. *Revolutions in Science*. Harvard University Press, Cambridge, Mass.
Conant, J. B. 1957. The overthrow of the phlogistic theory. In J. B. Conant & L. K. Nash (eds.), *Case Histories in Experimental Science*, Harvard University Press, Cambridge, Mass., 1,

65-115.
Diamond, J. 1997. *Guns, Germs and Steel*. New York: W.W. Norton.
Encyclopedia Britainnica. 1771. Of the phlogiston. I, 68-69. URL: books.google.com/books?id=xnW408_9_SMC&pg=PA68#v=onepage&q&f=false.
Guinta, C. 2001. Using history to teach scientific method: The role of errors. *Journal of Chemical Education* 78, 623-627.
Hacking, I. 1983. *Representing and Intervening.* Cambridge, UK: Cambridge University Press.
Herschel, J. F. W. 1830. *A Preliminary Discourse on the Study of Natural Philosophy*. Reprinted with a foreword by A. Fine. University of Chicago Press, Chicago (1987), pp. 300-301.
Johnson, S. and Stewart, J. 1991. Using philosophy of science in curriculum development: an example from high school genetics. *International Journal of Science Education* 12, 297-707.
** Johnson, Johnson and Holubec.: 1986,
Judson, H. F. 1981. *The Search for Solutions*. New York, NY: Holt, Rinehart & Winston.
Kim, M.G. 2008. The 'instrumental' reality of phlogiston. *HYLE* 14, 27-51.
Mamlok-Naaman, R. Ben-Zvi, R., Hofstein, A., Menis, J. & Erduran, S. 2005. Learning science through a historical approach: Does it affect the attitudes of non-science-oriented students towards science? *International Journal of Science and Mathematics Education* 3, 485-507.
McCann, H.G. 1978. *Chemistry Transformed.* Norwood, New Jersey.
Melhado, E.M. 1989. Toward an understanding of the Chemical Revolution. *Knowledge in Society* 8, 123-27;
Musgrave, A. 1976. Why did oxygen supplant phlogiston? Research programs in the chemical revolution? In *Method and Appraisal in the Physical Sciences: the Critical Background to Modern Science, 1800-1905*, C Howson, ed., pp. 181-210. Cambridge, UK: Cambridge University Press.
Odling, W. 1871a. On the revived theory of phlogiston. *Proceedings of the Royal Society* 6, 315-25.
Odling, W. 1871b. *Pharmaceutical Journal* (3rd series),1, 977-981.
Partington, .J. R. & McKie, D. 1937-1939. Historical studies on the phlogiston theory, I-IV. *Annals of Science* 2, 361-404; 3, 1-38, 336-371; 4, 113-149.
Scott, J.H. 1958. Qualitative adequacy of phlogiston. *Journal of Chemical Education* 29, 360-363.
Siegfried, R. 1964. The phlogistic connection of Humphrey Davy. *Chymia* 9, 117-24.
Sudduth, W. M. 1978. Eighteenth-century identifications of electricity with phlogiston. *Ambix* 25, 131-47.
Thagard, P. 1990. The conceptual structure of the Chemical Revolution. *Philosophy of Science* 57, 183-209,
Turnbull, D. 1993. *Maps Are Territories: Science Is an Atlas*. Chicago: University of Chicago Press.
Wimsatt, W.C. 2007. *Reengineering Philosophy of Science for Limited Beings*. Cambridge, MA: Harvard University Press.

of fire actually exiſting as a principle in the compoſition of bodies, and thoſe which it exhibits when exiſting ſeparately and in its natural ſtate: nor have proper diſtinct appellations been deſigned to it in thoſe different circumſtances. In the latter ſtate we may properly give it the names of fire, matter of the ſun, of light, and of heat; and may conſider it as a ſubſtance compoſed of infinitely ſmall particles, continually agitated by a moſt rapid motion, and of conſequence eſſentially fluid.

This ſubſtance, of which the ſun may be called the general reſervoir, ſeems to flow inceſſantly from that ſource, diffuſing itſelf over the world, and through all the bodies we know; but not as a principle, or eſſential part of them, ſince they may be deprived thereof, at leaſt in a great meaſure, without ſuffering any decompoſition. The greateſt change produced on them, by its preſence or its abſence, is the rendering them fluid or ſolid: ſo that all other bodies may be deemed naturally ſolid; fire alone eſſentially fluid, and the principle of fluidity in others. This being preſuppoſed, air itſelf might become ſolid, if it could be entirely deprived of the fire it contains; as bodies of moſt difficult fuſion become fluid, when penetrated by a ſufficient quantity of the particles of fire.

One of the chief properties of this pure fire is to penetrate eaſily into all bodies, and to diffuſe itſelf among them with a ſort of uniformity and equality: for if a heated body be contiguous to a cold one, the former communicates to the latter all its exceſs of heat, cooling in exact proportion as the other warms, till both come to have the very ſame degree of heat. Heat, however, is naturally communicable ſooneſt to the upper parts of a body; and conſequently, when a body cools, the under parts become ſooneſt cold. It hath been obſerved, for inſtance, that the lower extremity of a heated body, freely ſuſpended in the air, grows cold ſooner than the upper; and that when a bar of iron is red-hot at one end, and cold at the other, the cold end is much ſooner heated by placing the bar ſo that the hot end may be undermoſt, than when that end is turned uppermoſt. The levity of the matter of fire, and the vicinity of the earth, may poſſibly be the cauſes of this phenomenon.

Another property of fire is to dilate all bodies into which it penetrates. This hath already been ſhewn with regard to air and water; and it produces the ſame effect on earth.

Fire is the moſt powerful agent we can employ to decompoſe bodies; and the greateſt degree of heat producible by man, is that excited by the rays of the ſun collected in the focus of a large burning-glaſs.

Of the PHLOGISTON.

FROM what hath been ſaid concerning the nature of fire, it is evidently impoſſible for us to fix and confine it in any body. Yet the phenomena attending the combuſtion of inflammable bodies ſhew that they really contain the matter of fire as a conſtituent principle. By what mechaniſm then is this fluid, ſo ſubtile, ſo active, ſo difficult to confine, ſo capable of penetrating into every other ſubſtance in nature, ſo fixed as to make a component part of the moſt ſolid bodies? It is no eaſy matter to give a ſatisfactory anſwer to this queſtion. But, without pretending to gueſs the cauſe of the phenomenon, let us reſt contented with the certainty of the fact, the knowledge of which will undoubtedly procure us conſiderable advantages. Let us therefore examine the properties of fire thus fixed and become a principle of bodies. To this ſubſtance, in order to diſtinguiſh it from pure and unfixed fire, the chemiſts have aſſigned the peculiar title of the *Phlogiſton*, which is indeed no other than a Greek word for the inflammable matter; by which latter name, as well as by that of the ſulphureous principle, it is alſo ſometimes called. It differs from elementary fire in the following particulars. 1. When united to a body, it communicates to it neither heat nor light. 2. It produces no change in its ſtate, whether of ſolidity or fluidity; ſo that a ſolid body does not become fluid by the acceſſion of the phlogiſton, and *vice verſa*; the ſolid bodies to which it is joined being only rendered thereby more apt to be fuſed by the force of the culinary fire. 3. We can convey it from the body with which it is joined into another body, ſo that it ſhall enter into the compoſition thereof, and remain fixed in it.

On this occaſion both theſe bodies, that which is deprived of the phlogiſton and that which receives it, undergo very conſiderable alterations; and it is this laſt circumſtance in particular that obliges us to diſtinguiſh the phlogiſton from pure fire, and to conſider it as the element of fire combined with ſome other ſubſtance, which ſerves it as a baſis for conſtituting a kind of ſecondary principle. For if there were no difference between them, we ſhould be able to introduce and fix pure fire itſelf where-ever we can introduce and fix the phlogiſton: yet this is what we can by no means do, as will appear from experiments to be afterwards produced.

Hitherto chemiſts have never been able to obtain the phlogiſton quite pure, and free from every other ſubſtance: for there are but two ways of ſeparating it from a body of which it makes a part; to wit, either by applying ſome other body with which it may unite the moment it quits the former; or elſe by calcining and burning the compound from which you deſire to ſever it. In the former caſe, it is evident that we do not get the phlogiſton by itſelf, becauſe it only paſſes from one combination into another; and in the latter, it is entirely diſſipated in the decompoſition, ſo that no part of it can poſſibly be ſecured.

The inflammability of a body is an infallible ſign that it contains a phlogiſton; but from a body's not being inflammable, it cannot be inferred that it contains none; for experiments have demonſtrated, that certain metals abound with it, which yet are by no means inflammable.

We have now delivered what is moſt neceſſary to be known concerning the principles of bodies in general. They have many other properties beſides thoſe abovementioned; but we cannot properly take notice of them here, becauſe they preſuppoſe an acquaintance with ſome other things relating to bodies, of which we have hitherto ſaid nothing, intending to treat of them in the ſequel as occaſion ſhall offer. We ſhall only obſerve in this place, that

that when animal and vegetable matters are burnt in ſuch a manner as to hinder them from flaming, ſome part of the phlogiſton contained in them unites intimately with their moſt fixed earthy parts, and with them forms a compound that can be conſumed only by making it red-hot in the open air, where it ſparkles and waſtes away, without emitting any flame. This compound is called a *coal*. We ſhall inquire into the properties of this coal under the head of oils: at preſent it ſuffices that we know in general what it is, and that it readily communicates to other bodies the phlogiſton it contains.

A general View of the Affinities or elective Attractions that ſubſiſt between Bodies.

Before we can reduce compound bodies to the firſt principles above pointed out, we obtain, by analyſing them, certain ſubſtances which are indeed more ſimple than the bodies they helped to compoſe, yet are themſelves compoſed of our primary principles. They are therefore at one and the ſame time both principles and compounds; for which reaſon we ſhall call them by the name of ſecondary principles. Saline and oily matters chiefly conſtitute this claſs. But before we enter upon an examination of their properties, it is fit we lay before the reader a general view of what chemiſts underſtand by the relations or affinities of bodies; becauſe it is neceſſary to know theſe, in order to a diſtinct conception of the different combinations we are to treat of.

All the experiments hitherto made concur in proving, that different bodies, whether principles or compounds, have ſuch a mutual conformity, relation, affinity, or attraction, as diſpoſes ſome of them to join and unite together, while they are incapable of contracting any union with others. This effect, whatever be its cauſe, will enable us to account for, and connect together, all the phenomena that chemiſtry produces. The nature of this univerſal affection of matter is laid down in the following propoſitions.

Firſt, If one ſubſtance has any affinity or conformity with another, the two will unite together, and form one compound.

Secondly, All ſimilar ſubſtances have an affinity with each other, and are conſequently diſpoſed to unite; as water with water, earth with earth, *&c.*

Thirdly, Subſtances that unite together loſe ſome of their ſeparate properties; and the compounds reſulting from their union partake of the properties of thoſe ſubſtances which ſerve as their principles.

Fourthly, The ſimpler any ſubſtances are, the more perceptible and conſiderable are their affinities: whence it follows, that the leſs bodies are compounded, the more difficult it is to analyſe them; that is, to ſeparate from each other the principles of which they conſiſt.

Fifthly, If a body conſiſt of two ſubſtances, and to this compound be preſented a third ſubſtance that has no affinity at all with one of the two primary ſubſtances aforeſaid, but has a greater affinity with the other than thoſe two ſubſtances have with each other, there will enſue a decompoſition, and a new union; that is, the third ſubſtance will ſeparate the two compounding ſubſtances from each other, coaleſce with that which has an affinity with it, form therewith a new combination, and diſengage the other, which will then be left at liberty, and ſuch as it was before it had contracted any union.

Sixthly, It happens ſometimes that when a third ſubſtance is preſented to a body conſiſting of two ſubſtances, no decompoſition follows; but the two compounding ſubſtances, without quitting each other, unite with the ſubſtance preſented to them, and form a combination of three principles: and this happens when that third ſubſtance has an equal, or nearly equal, affinity with each of the compounding ſubſtances. The ſame thing may alſo happen even when the third ſubſtance hath no affinity but with one of the compounding ſubſtances only. To produce ſuch an effect, it is ſufficient that one of the two compounding ſubſtances have to the third body a relation equal, or nearly equal, to that which it has to the other compounding ſubſtance with which it is already combined. Hence it follows, that two ſubſtances, which, when apart from all others, are incapable of contracting any union, may be rendered capable of incorporating together in ſome meaſure, and becoming parts of the ſame compound, by combining with a third ſubſtance with which each of them has an equal affinity.

Seventhly, A body, which of itſelf cannot decompoſe a compound conſiſting of two ſubſtances, becauſe they have a greater affinity with each other than it has with either of them, becomes nevertheleſs capable of ſeparating the two by uniting with one of them, when it is itſelf combined with another body having a degree of affinity with that one ſufficient to compenſate its own want thereof. In that caſe there are two affinities, and thence enſues a double decompoſition, and a double combination.

Theſe fundamental truths, from which we ſhall deduce an explanation of all the phenomena in chemiſtry, will be confirmed and illuſtrated by applying them to the ſeveral caſes, of which our deſign in this treatiſe obliges us to give a circumſtantial account.

Of Saline Subſtances in general.

If a particle of water be intimately united with a particle of earth, the reſult will be a new compound, which, according to our third propoſition of affinities, will partake of the properties of earth and of water; and this combination principally forms what is called a *ſaline ſubſtance*. Conſequently every ſaline ſubſtance muſt have an affinity with earth and with water, and be capable of uniting with both or either of them, whether they be ſeparate or mixed together: and accordingly this property characteriſes all ſalts or ſaline ſubſtances in general.

Water being volatile, and earth fixed, ſalts in general are leſs volatile than the former, and leſs fixed than the latter; that is, fire, which cannot volatilize and carry off pure earth, is capable of rarefying and volatilizing a ſaline ſubſtance; but then this requires a greater degree of heat than is neceſſary for producing the ſame effects on pure water.

There are ſeveral ſorts of ſalts, differing from one another in reſpect either of the quantity or the quality of the