

PHLOGISTON THEORY AND CHEMICAL REVOLUTIONS

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Introduction

Joseph Priestley was born in 1733 near Birstall, County of Yorkshire, in England. Above the door of his birthplace is the plaque (Fig. 1) that states simply “Joseph Priestley: discoverer of oxygen was born on this site AD 1733.

Priestley is famous among scientists mainly for his discovery of oxygen, but he also achieved many other great “firsts” in science. In this presentation, emphasis will be placed on that aspect of his work for which he became “infamous”. Priestley adopted, developed, and advanced the theory of phlogiston to explain why materials react with oxygen. He continually had to refine the theory, but in the end, he died ignominiously in the eyes of the developing community of chemical scientists. To his dying day, he refused to acknowledge the nonexistence of phlogiston as the driving force for chemical reactions.

The story begins with reference to Batley Grammar School (Fig. 2) where, according to his memoirs, Priestley learned religion, classics, and literacy. He had no formal education in either science or history, as humanities were not taught at the schools in England in the early 18th century.

In the mid 18th century, unlike the present, there was no conflict between science and religion because in those days there was virtually no physical science. One could argue that history is best understood if taught backwards; this is especially true in understanding the history of science. Now, we know essentially everything chemists need to know about atoms and molecules, mass and energetics, to explain the symbolism of chemical equations and the reasons why chemical changes occur. Historians of science tend to start with alchemy and work forward but then stop when science is no longer susceptible to historical reinterpretation. One consequence of this approach to the history of science is that the credit for scientific advance is allocated by contemporaries in an unscientific, often political, manner and is rarely subjected to revision. Priestley, for example, deduced and published the inverse square law of force between electric charges, 20 years before Coulomb, to whom history has credited the discovery. Now it is enshrined in the modern scientific literature, the credit cannot be reallocated.

Coulomb's Law is one of many examples where historians of science have not been kind to Joseph Priestley. This essay is an attempt to re-evaluate Priestley's contributions to physical chemistry 200 years



Figure 1. *Plaque above the front door of 5, Owler Lane, Fieldhead, Birstall, the birthplace of Joseph Priestley.*

ago concerning the first theory of the driving force of chemical reactions: “phlogiston.”

Every chemist knows that Priestley discovered oxygen (1). Some chemists now know that he also discovered and characterized nine other gases, including ammonia. Priestley’s contributions to physical chemistry

been stubborn, but one has to question whether someone who had achieved so much in his life could be so naïve. If, as he surely did, Priestley honestly believed that chemical reactions were driven by phlogiston, particularly since Lavoisier and his antiphlogistonists had “proven” that it cannot exist (7), there must be more substance to the theory.

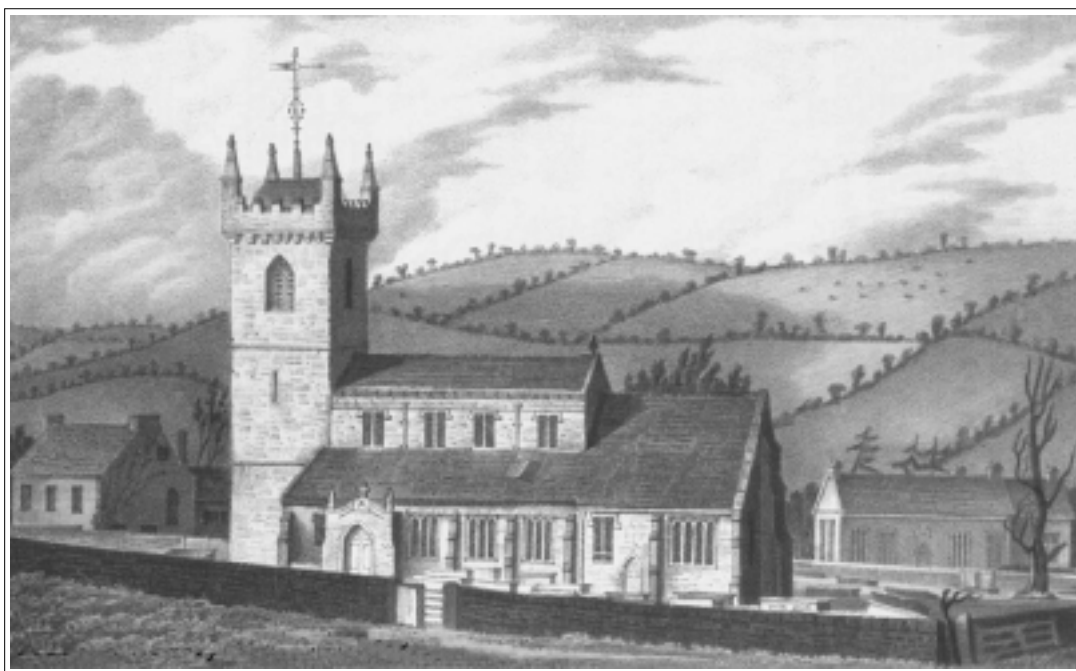


Figure 2. *An old lithograph from 1836 showing the vicarage, the Parish Church, and Batley Grammar School to the right that Priestley attended from 1744-1749.*

or the science of chemical and physical change, however, are largely unknown. Seventy-five years before Faraday, for example, Priestley decomposed the ammonia he had discovered into hydrogen and nitrogen by using electricity. Besides Coulomb’s law 20 years before Coulomb (2) Priestley published many other original firsts. His innovations include a description of atoms 40 years before Dalton (3), hypothesis of division of atoms 150 years before Rutherford (4), forces between atoms 100 years before van der Waals (5), and prediction of black holes 200 years before Stephen Hawking (6). Priestley also first discovered and described the process of photosynthesis and the carbon cycle. He investigated the solubility of carbon dioxide in water and went on to invent the process of carbonation or fizzy drinks industry.

Despite this life of extraordinarily diverse scientific discovery, Priestley died in 1804, “stubborn and stupid,” the last of the phlogistonists. He might have

Here a modern interpretation of phlogiston is presented. It may be argued that phlogiston was the first reasonable scientific theory of chemical change, 100 years before Gibbs got it right. The antiphlogistonists, by contrast, had nothing to contribute to physical chemistry in the form of an answer to the question, “Why do chemical reactions take place?” They were the founding fathers of “inorganic chemistry,” but physical chemistry centers around why and how chemicals react.

By use of Ellingham diagrams, a modern platform for describing the thermodynamic equilibrium of reactions of elements with oxygen, lines of thought of the protagonists of phlogiston theory can be scrutinized. The concept of a state function, for example, which is central to thermodynamics, was first introduced by Black in the caloric theory of heat (8). Both caloric theory and phlogiston theory of combustion, when revisited in the light of modern thermodynamics, can help to explain Priestley’s dogged adherence to the theory until the day he died in 1804.

Every thermodynamic material does indeed have a constitutive state function, (“phlogiston”?), which can be given a definition: “minus the Gibbs chemical potential of oxygen within the material.” It has the dimensions of (free) energy per mole of oxygen, and measures its oxidation propensity. While the antiphlogistonists may have been the first inorganic chemists, Priestley’s conceptual interpretation of phlogiston was the first attempt at the physical chemistry of reactions. If phlogiston is regarded as an alternative description of “Gibbs free energy,” the theory appears to be an intuitively accurate description, as could reasonably be expected at that time, and remains essentially correct today given its precise thermodynamic definition.

Caloric: as a State Function

We now know that the understanding of chemical reactions is inextricably dependent upon an understanding of the concept of “heat.” A big step forward in the 18th century was the introduction of the concept of a state function, “caloric,” by Joseph Black (8). Unfortunately, there was no understanding of the difference between energy the state function and heat, which is energy on the move.

Prior to the advent of thermodynamics, around 1850, all scholars of science believed in the caloric theory: that heat was a conserved fluid with no mass. It was present in various amounts in all materials and flowed from high to low concentrations. The caloric content depended on temperature and physical state; gases had a high caloric content and solids a low caloric content. The basic misconception was that caloric was a conserved substance which was particulate, had a mass, and hence could be “neither created nor destroyed.” We now know that “substance” to be the thermodynamic state function internal energy, or enthalpy. Heat itself is NOT energy, but energy on the move and not a state function.

Of great fundamental relevance, however, and largely overlooked by historians of science, is the fact that Black had for the first time, it appears, introduced the concept of a state function. The properties of a material (in this case the caloric content) depend only upon its equilibrium state and not on its processing history. The total energy of a material is the thermodynamic state function called the “internal energy.” Only differences in energy between two states can be defined and measured. If those two states are at the same pressure, the

energy difference is called the “enthalpy.” This thermodynamic state function can be identified with Black’s “caloric.”

Background to Phlogiston

The concept of phlogiston was introduced around 1700 by the German natural philosopher Georg Ernst Stahl. Until then it was believed by the alchemists that everything was made up of just four elements: earth, water, air, and fire. Observations of combustion by various solid materials, however, showed that the many different kinds of earth required a fifth element that explained why, for example, some materials burn in air much more readily than others. Different kinds of earth, i.e. solids, were deemed to contain variable quantities of “phlogiston” which, from Greek, literally means “fire of the earth.” The precise definition of phlogiston was not clear; some philosophers regarded phlogiston and fire as being synonymous. When a solid burned, it simply transferred its phlogiston to the air. Phlogiston was a concept Joseph Priestley adopted, developed further, and adhered to throughout his life as a natural scientist.

By the mid 1700s natural philosophers such as Priestley were beginning to write down chemical equations. Almost all of the earliest chemical reactions studied by Priestley and his contemporaries involved oxygen.

charcoal (+ Π) + air = fixed air(CO ₂) + phlogisticated air metal (+ Π) + air = calx (pure base) + phlogisticated air charcoal (+ Π) + calx = metal (+ Π) + fixed air metal (+ Π) + water = calx + inflammable air (Π) metal (+ Π) + acid = salt + inflammable air (Π) mercury (+ Π) + dephlogisticated air = calx of mercury inflammable air (+ Π) + dephlogisticated air = water
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Table 1. A list of some early chemical equations; the symbol Π is used to represent phlogiston.

The first attempts at chemical equations, as seen in Table 1, generally involved a material containing its phlogiston reacting with air, so as to give up its phlogiston, which would appear in one of the products. Besides his most famous discovery of all, oxygen, Priestley went on to discover and characterize the reactions involving nine gases. He isolated pure oxygen by heating the oxide of mercury. In keeping with the phlogiston concept, air that was capable of reacting with a solid to accept the transfer of phlogiston was aptly named “dephlogisticated air.”



Figure 3. Antoine Lavoisier (1743-1794) usurped Priestley's discovery and renamed his dephlogisticated air "oxygen."

Soon after the time of his discovery of dephlogisticated air, Priestley met Lavoisier in Paris and told him of his discovery. Lavoisier, however, had invented a balance that could weigh very accurately to 0.0005 g. He was able to confirm that when inflammable air (hydrogen) reacted with dephlogisticated air (oxygen) to give water, there was no mass present except that of the reactants and products of the reaction (7).

Lavoisier had discovered the principle of "conservation of mass" in chemical reactions. He argued that since the mass of the reactants equals the mass of the products, in the reactions he investigated, there was no mass that could account for phlogiston. Phlogiston therefore could not exist. Phlogiston theory effectively died on September 5, 1775, the day Lavoisier presented his paper to the French Academy of Science, and as far as historians of science are concerned, has remained dead and buried. Lavoisier and the antiphlogistonists staged a ceremonial bonfire of all the old chemistry books based on the theory of phlogiston.

The empirical 1st law of thermodynamics, the mechanical equivalent of heat, was discovered in 1850 by Joule. The 2nd law and the concept of entropy were proposed around the same time by Clausius. It was not until Gibbs introduced the concept of chemical potential, however, in the late 1880s that the true driving force for all physical and chemical change was discovered. Gibbs was the first to explain why chemical reactions take place; he introduced the concept of Gibbs free energy and the related concept of chemical potential (9).

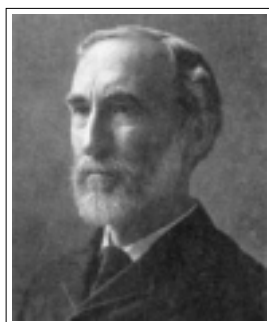


Figure 4. The great American scientist J. W. Gibbs, who discovered the real driving force of chemical reactions.

In 1885 the American mathematician and engineer J. Willard Gibbs finally applied the recently discovered and formulated laws of thermodynamics to explain why one chemical will react with another to form different compounds. Chemical reactions will take place in the direction of equilibrium until the Gibbs free energy of the reactants plus the products is a minimum. Then the reaction ceases.

Ellingham Diagrams

A modern platform for explaining the reactions of various elements with oxygen is the Ellingham diagram (10). These diagrams plot the Gibbs free energy difference between the element plus oxygen, and the metal oxide, and plot it as a function of temperature. The greater the Gibbs free energy difference, the greater the propensity of the element to react with oxygen.

Phlogiston: a Thermodynamic State Function

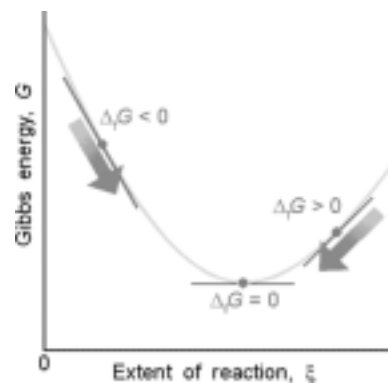


Figure 5. Diagram showing that chemicals react until the Gibbs free energy reaches its minimum: at this point the Gibbs chemical potential of all the species within reactants and products is uniform, the total Gibbs free energy is at a minimum with respect to further change, and the reaction stops. Thus, not all the difference in "caloric content" between reactants and products is available as heat.

In order to see the connection between caloric, phlogiston, and energy, we must now explain in further detail the concept of a state function. Energy in the form of heat (denoted by q) is not a property of a material, i.e. state function; it is energy on the move through or between materials. The total energy content of a chemical is a state function, because it depends only upon its equilibrium state of temperature and pressure. An alter-

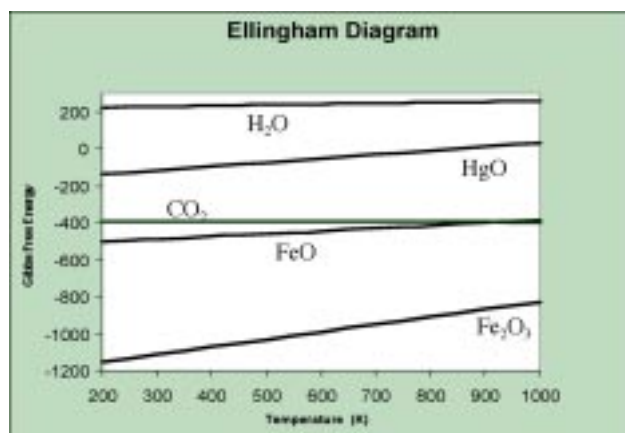


Figure 6. Ellingham diagram for the chemical reaction of the elements hydrogen, mercury, carbon and iron, with oxygen. The Gibbs free energy change, in units of kilojoules per mole of oxygen, is plotted against reaction temperature in degrees Kelvin.

native simple way of stating the 1st and 2nd laws of thermodynamics is to define the status of the energy as being a quantifiable function of state, being available or unavailable, in a material that changes when its state is changed. This change could be in a chemical reaction.

1st law $\Delta H = q$: enthalpy (“heat” content) [a state function]

2nd law $T/\Delta S = q$: entropy (unavailable “heat content”) [a state function]

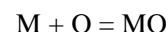
Some of the energy content of a chemical may be unavailable as heat when it burns, the amount of unavailable energy depending on the absolute temperature (T) at which it exists. A combination of the 1st and 2nd laws defines the Gibbs state function, which predicts the position of equilibrium of all chemical reactions (i.e., when $\Delta G = 0$):

$$1^{\text{st}} + 2^{\text{nd}} \text{ Law } \Delta G = \Delta H - T \Delta S$$

Without changing the formal thermodynamic description of chemical reactions, we can readily redefine the Gibbs state function and give it and its two components names consistent with the caloric theory of “heat” and phlogiston theory of reactions of the 18th century. The change in Gibbs free energy for an oxidation is referred to as the chemical potential of oxygen within the material relative to its oxide.

We will simply alter the names and symbols of the energies and revert to specific rather than molar quantities (since phlogiston preceded the mole balance dis-

covered in 1805 by Dalton) for reactions of an element with oxygen:



There will be changes in the state functions for which we introduce the names “entropic energy,” “caloric,” and “phlogiston.” The signs are conventional and can be reversed so that the phlogiston content is a positive concept.

entropic energy: $\Gamma = +T \Delta S / \text{mol wt. of } M$

caloric: $C = \Delta H / \text{mol wt. of } M$

phlogiston: $\Pi = -(C - \Gamma)$

Then, in the spirit of the Priestley equations in Table 1, we can write a simple chemical equation with a driving force on the left and heat given off on the right.



Phlogiston is seen to be equivalent to minus the Gibbs free energy of the oxygen per unit mass of reactant. It is an extensive property of the material, depending upon its state (temperature and pressure). Phlogiston, in this definition, has dimensions of chemical potential, i.e. energy/mass (per mole equivalent of O_2).

We can now proceed to compute the phlogiston content of any element or compound or mixed material with respect to any of its oxidized states. Having done so, we can then plot the phlogiston content as a function of temperature for all elements in the spirit of Ellingham.

The interesting values of the phlogiston content in Fig. 7 reveal that the general theory of phlogiston was in many ways a reasonable description of the driving force of reactions with oxygen before the advent of chemical thermodynamics and Gibbs’ chemical potential nomenclature.

The first observation that we make is that pure oxygen has no propensity to react with itself and its phlogiston content is zero at all temperatures. It is “dephlogisticated air!”

Secondly we note that the phlogiston content of the element hydrogen is so great (above 200) that it is off the diagram. Some of the 18th-century phlogistonists actually believed that pure hydrogen was phlogiston. Such misconceptions are now quite understandable.

We also note that the phlogiston content of mercury is very close to zero; in fact it is positive up to 900 degrees and then it crosses zero and goes negative. It is this simple fact that enabled Joseph Priestley to discover pure oxygen in 1774 by heating the oxide of mercury

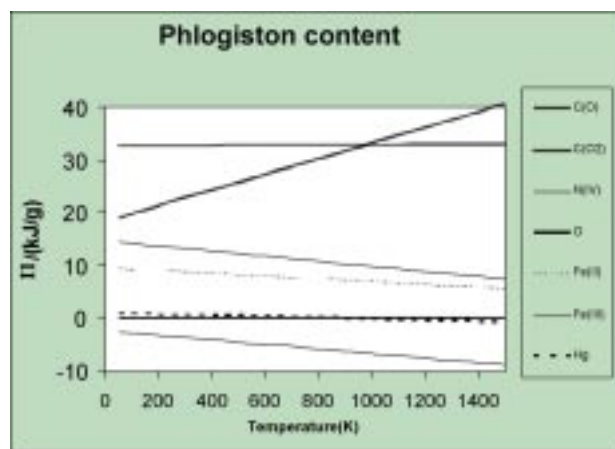


Figure 7. Phlogiston content of carbon, nitrogen, oxygen, iron, and mercury calculated from thermodynamic tables as a function of temperature for a range of elements investigated by Priestley and his contemporaries. The line for hydrogen is too high for this scale (around 250 in the above units of kilojoule per mole of oxygen) compared to all other elements. Notice that the phlogiston content may be both positive or negative. It is negative in the case of nitrogen gas, hence the stability of the earth's atmosphere.

above 900 degrees. He could restore the phlogiston content of mercury and produce "dephlogisticated air."

Revolutions in Chemistry

The discovery of conserved quantities of mass and molecule equivalents in chemical reaction has been identified with the 1st and 2nd chemical "revolutions," respectively. But the real revolution, it seems, was yet to come. The conservation of mass discovered by Lavoisier (7), according to historians of chemistry, gave rise to the first chemical revolution. One could argue that it was the birth of chemistry. The atomic theory of Dalton and the concept of a molecular chemical equation, in the form of Dalton's law of constant proportions, then gave rise to the "2nd chemical revolution;" perhaps the beginning of the degeneration of chemistry, inorganic and organic chemistry, but the real revolution, and the subject of physical chemistry, was yet to come.

	Year AD	discoverer	balance
1 st	1775	Lavoisier	mass
2 nd	1804	Dalton	mole
3 rd	1850	Hess	enthalpy or "caloric"
4 th	1885	Gibbs	free energy or "phlogiston"

Table 2. Chronology of "chemical revolutions" arising from the discoveries of mass and energy balances in chemical reactions.

The protagonists of the first revolution in chemistry were the antiphlogistonists, but they failed to address the fundamental question, "Why do two chemicals react if there is no phlogiston?" The atomic theory of Dalton explains the mole balance in chemical equations, but, again, Dalton's atomic theory neglected to address the question of the driving force for chemical change.

Thermodynamics began with the conservation of energy, in the form of the 1st law of thermodynamics; the appropriate balance law for chemical reactions is Hess' law of constant heat summations. This is merely an alternative statement to "caloric is a state function." Science had to wait another 30 years after the advent of thermodynamics before Gibbs, proposed that the ultimate driving force for chemical equilibrium is the equality of chemical potential of any species on either side of the reaction. Alternatively, we can state that the reactants have zero phlogiston. This surely marks the 4th revolution in chemistry but the first real revolution in physical chemistry, and hence also in chemical engineering

Conclusions

In a Priestley publication of 1796, which he pointedly addressed to the list of French antiphlogistonists, Priestley wrote as follows in his conclusion (11):

The phlogiston theory is not without its difficulties. The chief of them is that we are not able to ascertain the weight of phlogiston, or indeed that of the oxygenous principle. But neither do any of us pretend to have weighed light, or the element of heat, though we do not doubt but that they are properly substances, capable by their addition, or abstraction, of making great changes in the properties of bodies, and of being transmitted from one substance to another.

It can be concluded here that, although the antiphlogistonists might have rightful claim to be the founding fathers of *inorganic chemistry*, they did not

address the question of why chemical reactions take place. They ridiculed the phlogiston theory but had no replacement. We can now see why Priestley adhered stubbornly to the theory until his dying day. It was because he instinctively knew there had to be something to account for the propensity of elements to react with oxygen and for the variations in that propensity from one element to another. Priestley, it might be argued, was not the last phlogistonist, but the first physical chemist. One could speculate that if J. W. Gibbs had been a chemist rather than a mathematician and engineer, he might have given some credit to the phlogiston theory.

Gibbs theory, as it was originally published, was not easy for the uninitiated to understand. It took ten years before his great work was recognized as such by the scientific community (13). This could be yet another reason why historians of science have not been so kind to Priestley and his phlogiston; they themselves may not have fully understood the concepts of Gibbsian thermodynamics, or why chemicals react!

REFERENCES AND NOTES

1. J. Priestley, *Experiments and Observations on Different Kinds of Air*, J. Johnson, London, 1774.
2. J. Priestley, *History of the Present State of Electricity with Original Experiments*, J. Johnson, London, 1772.
3. J. Priestley, "On the Nature and Essential Properties of Matter," in *Disquisitions Relating to Matter and Spirit*, J. Johnson, London, 1777, Section II, p 5.
4. Ref. 3, p 6.
5. Ref. 3, p 7.
6. J. Priestley, "Observations Concerning the Velocity of Light," in *History and Present State of Discoveries Relating to Vision Light and Colours*, J. Johnson, London, 1772, Section III.
7. A. Lavoisier "Memoir on Combustion in General," *French Philos. Soc. J.*, **1775**.
8. J. Robinson, Ed., *Lectures on the Elements of Chemistry*, by Joseph Black, University of Edinburgh, 1809.
9. J.W. Gibbs, *The Collected Scientific Papers, Thermodynamics*, Longmans Green, London and New York, 1906, Vol. I.
10. H. J. T. Ellingham, *J. Soc. Chem. Ind.*, May, 1944. 125-133.
11. J. Priestley, "Considerations on the Doctrine of Phlogiston and the Decomposition of Water," Thomas Dobson, Philadelphia, PA, 1796.
12. T. L. Davis, "Priestley's Last Defense of Phlogiston," *J. Chem. Educ.*, **1927**, 4, 176.
13. C. E. Moore, A. Smolinski, and B. Jaselskis, *Bull. Hist. Chem.* **2002**, 27, 114-127.

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