The Chemical Revolution:

The new chemistry of airs and rules of chemical combination

Waseda University, SILS,
History of Modern Physical Sciences

The *Phlogiston* Theory, I

Phlogiston was a theoretical substance that was used to explain certain processes of physical change such as *combustion*, *respiration*, *rusting*, and so on.

The theory proposed a *light* substance – a subtile, or imponderable fluid – that is released during chemical processes involving heat (burning, respiration, calcination, and so on).

- Here, *light* means the property of having levity: the opposite of heavy, not less heavy; that is *zero weight* or *negative weight*.

Phlogiston had no color, odor, taste nor any positive weight.

- How could it be detected?

The *Phlogiston* Theory, II

Some examples of combustion:

- wood $\rightarrow$ ash + *phlogiston* (to the air)
- charcoal $\rightarrow$ *phlogiston* (to the air) + impurities

The theory was developed by Becher and Stahl, but its most well-remembered proponent was Joseph Priestley.

We are now confident that there is no such thing as phlogiston. That is, it was a *theoretical substance* whose properties were increasingly seen as strange, and the assumption of which became unnecessary in later theories.

Nevertheless, we can think of the phlogiston theory as a sort of scientific paradigm.

Joseph Black (1728–1799)

- Born in Bordeaux to a entrepreneurial Scottish family. Studied medicine at Glasgow, were he was an assistant in a chemistry laboratory.
- Professor at Glasgow and then Edinburgh, in anatomy, chemistry and medicine. Practiced medicine.
- He was a bachelor, something of a ladies man, and friends with many of the most important Scottish intellectuals of the time – such as A. Smith, D. Hume, and J. Hutton.
- Worked on the chemistry of airs and the physics of heat.

Black's Chemical Experiments

He warmed *magnesia alba* (mostly magnesium carbonate, $MgCO_3$)[1] in a closed chamber and noticed that it gave off a gas.

He collected this gas, by passing it through a liquid filter. He called it fixed air, because it had been *fixed* in the white magnesium. (He did not invent this terminology.)

He studied the chemical characteristics of fixed air and he weighed it – by weighing the magnesia alba before and after warming it and drawing off the fixed air.

- *Experiments upon Magnesia Alba, Quicklime, and Some Other Alkaline Substances*, 1756.

[1] The modern name is theoretically loaded, and is added only for our convenience. Moreover, there were no chemical formulas of the modern sort at this time.

Black's *Fixed Air*

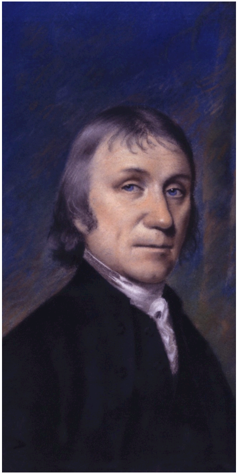
Fixed air (carbon dioxide, CO_2) would support neither combustion nor respiration.

It had a characteristic weight per volume.

Once these properties were identified, Black could show that *the same kind of air* could be derived from other chemical processes – for example, mixing limestone and mineral acids, warming chalk in liquid solution, and so on.

He showed that the process could also be reversed. He separated chalk into quicklime and fixed air. He, then, mixed water with the quicklime and showed that it combined with fixed air to form chalk.

Joseph Priestley (1733–1804)



Born in to a middle class, *dissenting* (non-Anglican) family. Studied languages – Greek, Latin, Hebrew, French, Italian, German, Cuneiform (Akkadian, Sumerian), Syriac and Arabic – and theology at dissenting academies.

Librarian to the Earl of Shelburne. Had his own laboratory; carried out important studies on airs. Toured with the Earl. Met Lavoisier.

Moved to Birmingham. Joined the Lunar Society – E. Darwin, J. Watt, B. Franklin.

Bastille Day Dinner. Priestley did not attend, but his house was sacked and burned anyway. Forced to resign from the Royal Society. Moved to Pennsylvania, USA. Founded the Unitarian Church.

Sheridan. Priestley. Sir Cecil Wray. Fox. Horne Tooke. Dr. Lindsey.

"A BIRMINGHAM TOAST, JULY 14, 1791."

Cartoon depicting a dinner which provoked the "Priestley Riots" in Birmingham, England. (Priestley was not actually there.)

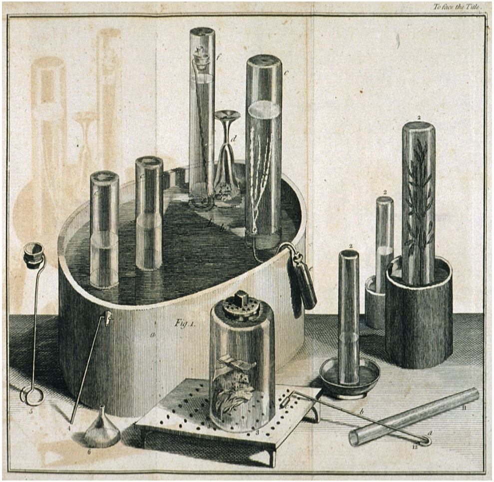
Priestley's house was destroyed in the riots, 14th July, 1791.

Priestley's Pneumatic Trough

Priestley discovered a number of new kinds of air. By isolating these in a *pneumatic trough* he was able to study their properties.

He was especially interested in the relationship between these airs and phlogiston.

His chemical work was written up in *Experiments and Observations on Different Kinds of Air*, 1775.



The Pneumatic Trough

Priestley and *Fixed Air*

He carried out a number of experiments on Black's *fixed air*, and showed that it was also produced in the brewing process.

He showed that air in which combustion had taken place also becomes fixed air.

He showed that this air could not support combustion or respiration – for example, flames would extinguish and animals would asphyxiate when placed in a chamber containing fixed air.

It could, however, support plant growth. In fact, this process would make the air "healthful" again. Plants and animals produced a mutually sustaining balance.

Priestley and Other Airs

By various chemical processes, he discovered a number of new airs. He also studied airs first isolated by Cavendish and others, such as Nitrous Air (NO), Acid Air (HCl), Phlogisticated Air (CO_2, N_2), Inflammable Air (methane CH_4, H_2), and so on.

He explored and tested their properties against various assumptions of the phlogiston theory.

Nitrous air produced red fumes in common air, and if mixed over water the total amount of air *decreased in volume*.

This became a way to test the "goodness" of air without suffocating animals.

Priestley's *Dephlogisticated Air*, I

The discovery of Dephlogisticated Air was regarded by Priestley as his most important.

He heated calx of mercury (mercury oxide, MgO) in a closed chamber and discovered that an air was released. He captured and studied it.

It supported combustion and respiration much better than common air.

- Candles flared.
- Charcoal glowed brighter.
- Recently asphyxiated mice sprang back to life.
- Mice remained conscious longer in it than in common air…

He realized that plants were producing this air, and that it was a factor in common air.

Priestley's *Dephlogisticated Air*, II

He called this gas *dephlogisticated air* (oxygen, O_2), because it seemed to allow more phlogiston to be given off than common air.

It was a sort of modification of common air.

Priestley described these experiments to Lavoisier.

Priestley, Letter to Lavoisier

"There is no history of experiments more truly ingenious than mine … especially on the discovery of dephlogisticated air."

Modification of Common Air

For Priestley, the different kinds of air were modifications of a single substance. They were not different in *kind*, or *nature*, they were different in *degree*.

Priestley, *Experiments and Observations*, 1776

"There are … few maxims in philosophy that have laid firmer hold upon the mind, than that air, meaning atmospherical air … is a simple elementary substance, indestructible, and unalterable, at least as much so as water is supposed to be. In the course of my inquiries, I was, however, soon satisfied that atmospherical air is not an unalterable thing; for that the phlogiston with which it becomes loaded from bodies burning in it, and animals breathing it, and various other chemical processes, so far alters and depraves it, as to render it altogether unfit for inflammation, respiration, and other purposes…"

Priestley's Phlogiston Theory

For Priestley, phlogiston was a substance with *no* weight – in some places he seemed to argue that it must have *negative weight*, but in other places he denied this. (Guyton de Morveau claimed that phlogiston had negative weight.)

It was given off by combustive processes – such as burning, calcination, respiration – and consumed by plants in their growth.

It was contained in all chemicals and airs in different amounts.

Priestley defended the phlogiston theory to his death, long after most other chemists had abandoned it.

Henry Cavendish (1731–1810)

Born in Nice, first son of the House of Devonshire. Educated at Cambridge. Like most nobility, he did not bother to graduate.

He spent his life alone, secluded on his estate, which had a well-equipped laboratory. He devoted his life to experimenting with little inclination toward theorizing.

At the age of 40 he inherited a great fortune. He did not care about his health or his appearance, hated company and communicated with his female servants only through letters.

Cavendish's Work

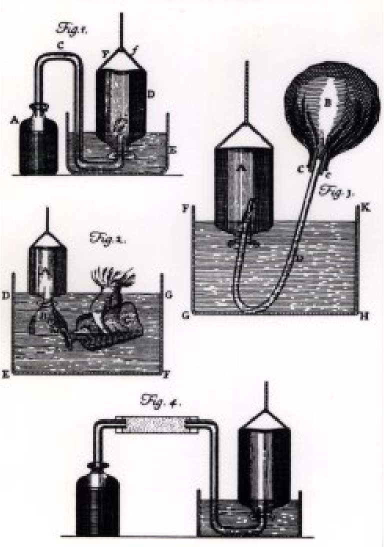
He was an incredibly fastidious experimenter. Although his equipment was crude, he produced results that could not be reproduced for over a century. He published very little and most of his work was discussed only in his extensive laboratory notes.

He worked on the chemistry of airs, electricity, the gravitational constant, and so on.

- *On Fractious Airs*, 1766; *Experiments on Air*, 1784.

His scientific notes were published by James Clerk Maxwell in 1879, around 70 years after his death.

Cavendish's Experiments on Airs



He found a new gas by dropping iron and zinc into various acids.

He found that this air burned explosively, and he thought he may have isolated *phlogiston itself*.

He weighed the gas, however, and it had a definite weight.

He called it phlogiston or *inflammable air* (H_2).

The Composition of Water

Later Cavendish heard that others – such as Priestley – had noticed a dew when plogiston inflammable air was exploded with common air.

He worked for almost ten years, exploding inflammable air – which he then called phlogiston – and dephlogisticated air, using a static electrical spark.

In 1784, he announced to the Royal Society that "water consists of dephlogisticated air united with phlogiston," in parts of one to two – we would say $O_2 + 2\,H_2 = 2\,H_2O$.

He spent many years proving his case by studying the result of burning inflammable air with common air, leaving *foul air* (N_2).

The Successes of Phlogiston Theory

In our view, the phlogiston theory was misguided.

Phlogiston theorists, however, were not cranks. They were careful experimenters, committed to the process of *rational, theoretical explanation*.

The theory could *explain* a large number of chemical processes.

- mercury + dephlogisticated air ↔ calx of mercury
- wood + common air → ash + phlogisticated air
- ore (calx) + charcoal → metal + fixed air
- metal (pure base + phlogiston) + water ↔ calx + inflammable air (phlogiston)
- water ↔ inflammable air + dephlogisticated air

Phlogiston Theory

The theory has all of the characteristics of a Kuhnian paradigm. (Or rather, this is one of the historical episodes that Kuhn used to develop his concept of paradigm.)

It assumed, or posited, a theoretical substance that is without color, odor, taste or mass (weight).

It proposed an encompassing account of the natural processes of combustion, respiration, rusting, plant photosynthesis, and so on.

The paradigm set out a number of interesting research programs.

The fact that phlogiston sometimes appears to have zero or negative weight was treated as an *anomaly*.

Under the influence of this paradigm, 18th-century chemists were able to discover a number of novel facts about the world.

Antoine-Laurent Lavoisier (1743–1794)

- He was a capable chemist but had few profound discoveries. Nevertheless, he is thought to have founded the modern field of chemistry. He also worked on respiration, and with Laplace, on the theory of heat (*caloric*).
- Worked with his wife, Marie-Anne Paulze Lavoisier (1758–1836).
- He was a liberal reformer, and developed progressive economic policy during the early years of the revolution. But, during the Terror, he was guillotined.
- *Traité élémentaire de chimie*, 1789.

On the basis of a number of bold *hypotheses*, Lavoisier was able to reorganize chemical knowledge with little or no new "discoveries." He quite explicitly conceived of himself as a *chemical revolutionary*.

Wurtz, a French Chemistry textbook, 1868

"Chemistry is a French science. It was constituted by Lavoisier of immortal memory."

He introduced a new conception of *chemical processes*, which lead to a new research program.

He cemented the importance of quantitative analysis.

Fundamental Ideas

- The different kinds of air found by Black, Priestley and Cavendish are, in fact, fundamentally different chemical *substances*. Common air is a *mixture* not a *compound*.

Mixtures

Mixtures are simply different substances jumbled together.

Compounds

Compounds are new substances composed of more fundamental substances, which have properties that are different from their components. They are characterized by constant composition (ratios), by weight, of the fundamental substances.

- Fundamental substances are found by chemical analysis. These were also called *simple substances* – related to, but conceptually different from, our elements.

Fundamental Hypotheses

The *measure of matter* is its weight.

Conservation of mass

In every chemical reaction, no matter is created or destroyed.

Chemical equation

So, in every reaction, the weight of all reactants before and after will always be equal. In this way, every chemical reaction is like an equation involving matter and the balance establishes its validity.

Nomenclature

Substances should be named for their constituent parts.

New Language

Lavoisier instituted a new *nomenclature* in which chemical names indicate (1) the substances involved in their compositions and (2) the ratios in which they occur.

He was influenced by Carl Linnaeus' binomial classification of plants and animals and Étienne Bonnot de Condillac's theory of a universal algebra.

Condillac

"We think only with words – languages are the true analytical methods – algebra, the means of expression which is the simplest, most exact and best adapted to its object, is both a language and an analytical method. In short, the art of reasoning can be reduced to a well constructed language."

The results of Lavoisier's work were codified in a report to the Académie, which he wrote with some colleagues, and in his *Elements of Chemistry* (1798).

Because his theory of chemical processes was built into the new naming system, the nomenclature served to reinforce the theory. Thus, oxygen was given that name because it was conceived as the *root of all acids*.

- What does Hydrogen mean?

Examples of the new nomenclature are calcium nitrite ($Ca(NO_2)_2$) and calcium nitrate ($Ca(NO_3)_2$), nitric oxide (NO) and nitrous oxide (N_2O), carbon monoxide (CO) and carbon dioxide (CO_2), iron oxide, magnesium carbonate (magnesia alba), and so on.

Lavoisier's Simple Substances

This theory puts great weight on the building blocks, the simple substances, what we call the *elements* – a word that Lavoisier did not like to use in the modern sense.

Lavoisier stated that the simple substances are identified by *analysis*, laboratory experience. They were not *theoretical entities*.

They might be further broken down at a later point – for example, he considered our chlorine (Cl) to be an oxide.

Lavoisier, *Elements of Chemistry*, 1789

"Chemistry advances toward perfection by dividing and subdividing... these things we at present suppose simple may soon be found quite otherwise. All that we dare venture to affirm of any substance is that it must be considered simple in the *present state of our knowledge*, and so far as chemical analysis has hitherto been able to show."

Lavoisier on Elements

Lavoisier regarded a discussion of what we call *elements* to be outside the scope of true chemistry. Instead, he preferred a practical conceptualization of *simple substances*.

Lavoisier, *Elements of Chemistry*, 1789

"It will be a matter of surprise, that in a treatise upon the elements of chemistry, there should be no chapter on the constituent and elementary parts of matter; but I shall take occasion, in this place, to remark that the fondness for reducing all the bodies in nature to three or four elements, proceeds from a prejudice which has descended to us from the Greek philosophers. The notion of four elements … is a mere hypothesis, assumed long before the first principles of experimental philosophy or of chemistry had any existence.

Lavoisier on Elements (con't)

Lavoisier, *Elements of Chemistry*, 1789

"All that can be said upon the number and nature of elements is, in my opinion, confined to discussions entirely of a metaphysical nature… I shall, therefore, only add upon this subject, that if, by the term elements, we mean to express those simple and indivisible atoms of which matter is composed, it is extremely probable we know nothing at all about them; but if we apply the term elements, or principles of bodies, to express our idea of the last point to which analysis is capable of reaching, we must admit, as elements, all the substances into which we are capable, by any means, to reduce bodies by decomposition."

TABLE OF SIMPLE SUBSTANCES

New Names	Old Names
Light	Light
Caloric	Heat. Principle or element of heat.
Oxygen	Dephlogisticated air. Vital air.
Azote [Nitrogen]	Phlogisticated air or gas. Mephitis.
Hydrogen	Inflammable air or gas.
…	…

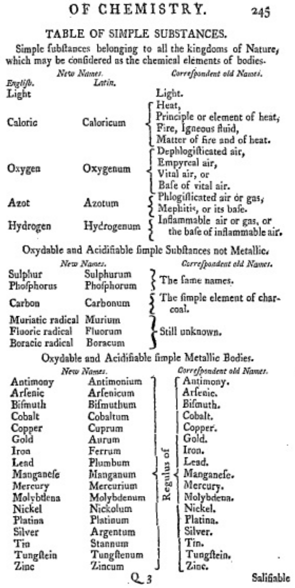


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TABLE OF SIMPLE SUBSTANCES.

Simple fubftances belonging to all the kingdoms of Nature, which may be confidered as the chemical elements of bodies.

New Names. English.	New Names. Latin.	Correfpondent old Names.
Light		Light.
Caloric	Caloricum	Heat, Principle or element of heat, Fire, Igneous fluid, Matter of fire and of heat.
Oxygen	Oxygenum	Dephlogifticated air, Empyreal air, Vital air, or Bafe of vital air.
Azot	Azotum	Phlogifticated air or gas, Mephitis, or its bafe.
Hydrogen	Hydrogenum	Inflammable air or gas, or the bafe of inflammable air.

Oxydable and Acidifiable fimple Subftances not Metallic.

New Names.		Correfpondent old Names.
Sulphur	Sulphurum	The fame names.
Phofphorus	Phofphorum	The fame names.
Carbon	Carbonum	The fimple element of charcoal.
Muriatic radical	Murium	Still unknown.
Fluoric radical	Fluorum	Still unknown.
Boracic radical	Boracum	Still unknown.

Oxydable and Acidifiable fimple Metallic Bodies.

New Names.			Correfpondent old Names.
Antimony	Antimonium	Regulus of	Antimony.
Arfenic	Arfenicum	Regulus of	Arfenic.
Bifmuth	Bifmuthum	Regulus of	Bifmuth.
Cobalt	Cobaltum	Regulus of	Cobalt.
Copper	Cuprum	Regulus of	Copper.
Gold	Aurum	Regulus of	Gold.
Iron	Ferrum	Regulus of	Iron.
Lead	Plumbum	Regulus of	Lead.
Manganefe	Manganum	Regulus of	Manganefe.
Mercury	Mercurium	Regulus of	Mercury.
Molybdena	Molybdenum	Regulus of	Molybdena.
Nickel	Nickolum	Regulus of	Nickel.
Platina	Platinum	Regulus of	Platina.
Silver	Argentum	Regulus of	Silver.
Tin	Stannum	Regulus of	Tin.
Tungftein	Tungftenum	Regulus of	Tungftein.
Zinc	Zincum	Regulus of	Zinc.

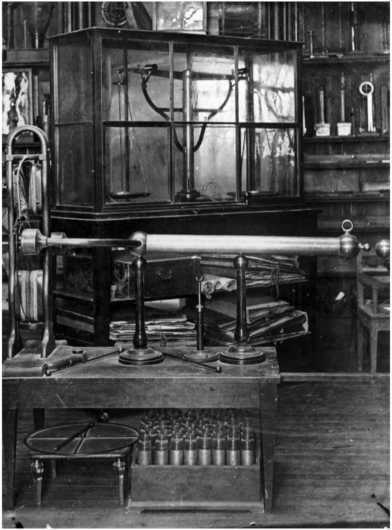
Q 3 Salifiable

Lavoisier's Laboratory, reconstructed

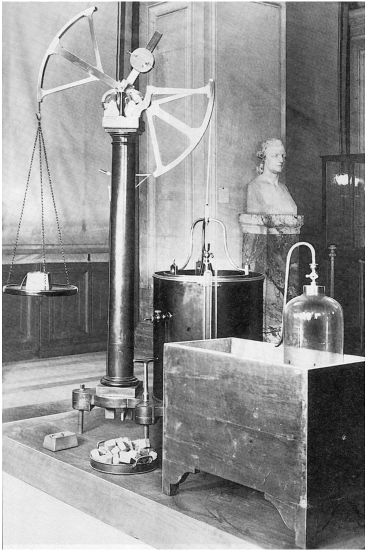
Lavoisier’s balance – in the glass case – was very expensive and very precise, by the standards of that time.

It was made for him by the best instrument makers in Paris.

In the foreground, we see a machine for generating and storing static electricity, with a box full of Leyden jars below it – a so-called “battery” of Leyden jars.

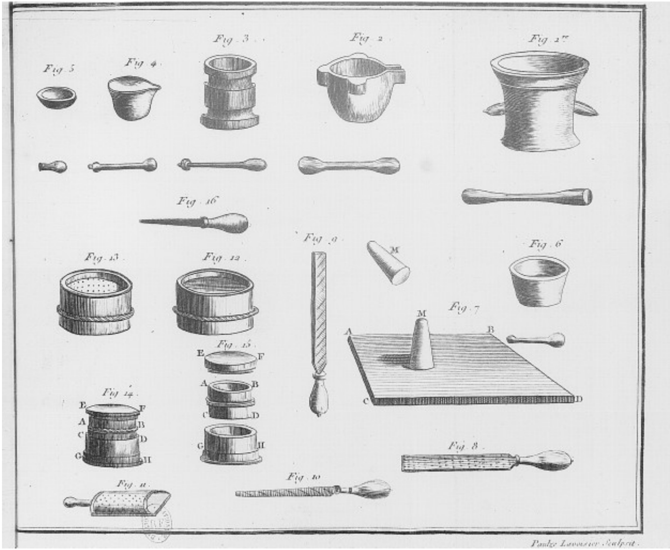


Lavoisier's Gasometer

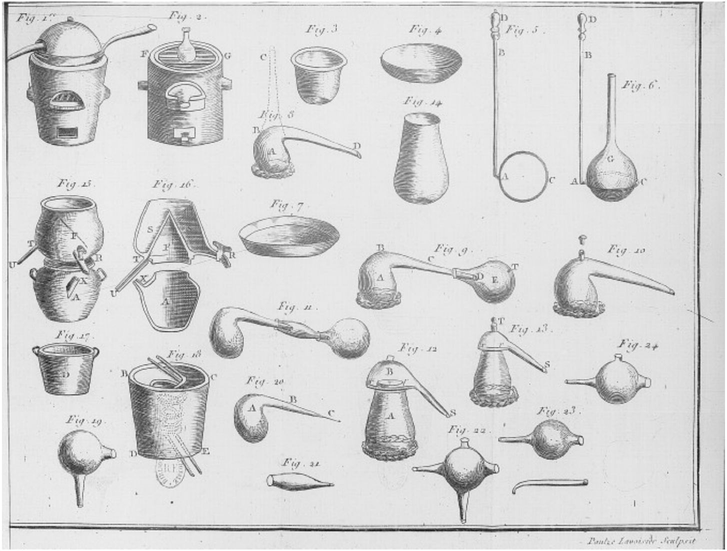


Lavoisier's gasometer allowed him to measure the volume and the weight of gases with high precision.

It was much better than any other equipment at that time, which allowed him to carry out experiments that others could not verify.



A plate of chemical apparatus from *Traité élémentaire de chimie*
(All plates illustrated by M.-A. Paulze Lavoisier)



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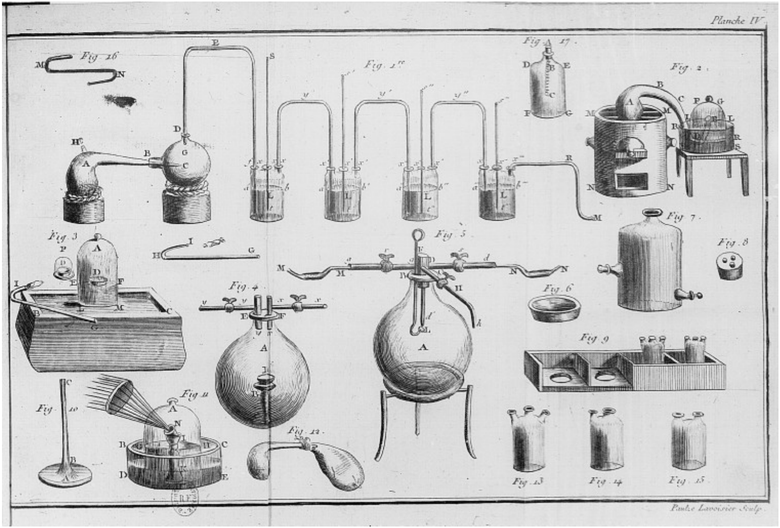
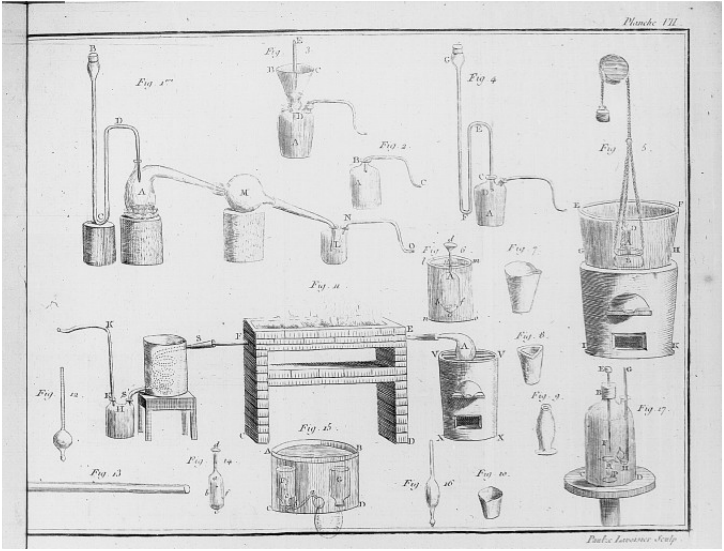
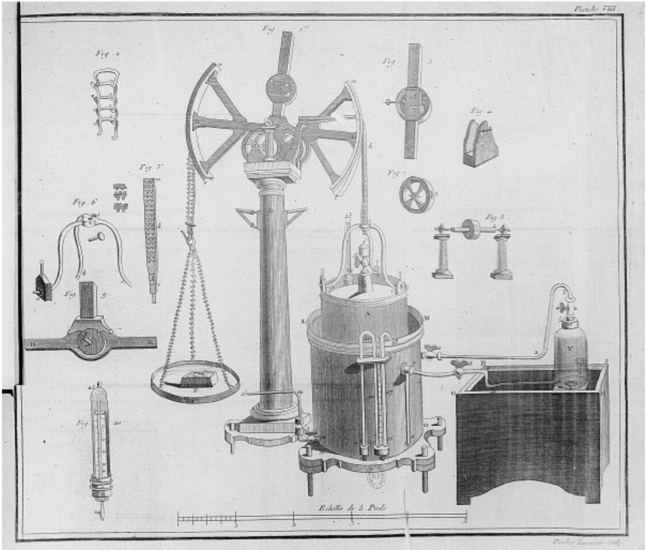


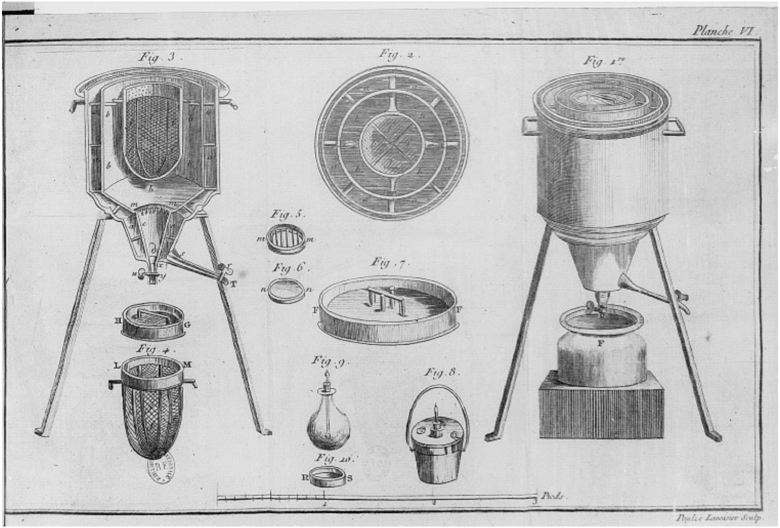
A plate of apparatus for studying airs from *Traité élémentaire de chimie*



A plate of distillation apparatus from *Traité élémentaire de chimie*



A plate of the gasometer from *Traité élémentaire de chimie*



A plate of the calorimeter from *Traité élémentaire de chimie*

Lavoisier's Theory of Combustion

In "Memoir On Combustion," 1777, he argued that the phenomena of combustion always

1 involves fire or light (*caloric*);

2a takes place in the presence of what he then called *pure air* (O_2),

2b such that, pure air is decomposed and the weight of the burning body increases in the amount of the pure air taken in;

2c and, the burning body becomes an acid by the addition of pure air – for example, sulfur → vitriolic acid, or carbon based substance → fixed air (CO_2), carbonic acid.

He argued that all these phenomena can be explained without using phlogiston. *There is no need for phlogiston*.

He proposed that the key lay in the role of pure air, or oxygen (O_2).

Theory of Combustion

Lavoisier, “Memoir On Combustion,” 1777

“I venture to propose to the Academy today a new theory of combustion. Materials may not burn except in a very few kinds of air, or rather, combustion may take place in only a single variety of air: that which Mr. Priestley has named dephlogisticated air and which I name here *pure air*. In all combustion, pure air in which the combustion takes place is destroyed or decomposed and the burning body increases in weight exactly in proportion to the quantity of air destroyed or decomposed… and we see that there is no longer need, in explaining the phenomena of combustion, of supposing that there exists an immense quantity of fixed fire [that is phlogiston] in all bodies which we call combustible; and that on the contrary it is very probable that little of this fire exists in metals, sulfur, and phosphorus and in the majority of very solid, heavy, and compact bodies…”

Theory of Combustion (con't)

He argued that all of these phenomena could be explained without using phlogiston.

- mercury + oxygen $\leftrightarrow$ mercuric oxide
- wood + common air $\rightarrow$ ash + carbon dioxide
- ore (metallic oxide) + charcoal $\rightarrow$ metal + carbon dioxide
- metal (pure base) + water $\leftrightarrow$ metallic oxide + hydrogen
- water $\leftrightarrow$ hydrogen + oxygen

In arguing against the phlogiston theory he said,

> "My object is not to substitute a rigorously demonstrated theory but solely a hypothesis which appears to me more probable, more conformable to the laws of nature, and which appears to me to contain fewer forced explanations and fewer contradictions."

Priestley's Reaction

Priestley, *The Doctrine of Phlogiston*, 1796

"There have been few, if any, revolutions in science so great, so sudden, and so general, as the prevalence of what is now usually termed the new system of chemistry, or that of the Antiphlogistians, over the doctrine of Stahl, which was at one time thought to have been the greatest discovery that had ever been made in the science."

Priestley, however, never accepted the new chemistry.

- He claimed that the new theory gave no better account of rusting than the old.
- He thought there were no grounds for believing that water is composed of hydrogen and oxygen.
- He asserted that the new theory added as many complications as it resolved – such as the relation between hydrogen and water, and the substance of carbon.

Priestly on Hydrogen, Carbon

Priestley, *The Doctrine of Phlogiston*, 1796

"If inflammable air, or hydrogen, be nothing more than a component part of water, it could never be produced but in circumstances in which either water itself, or something into which water is known to enter, is present. But in my experiments on heating finery cinder [our magnetite] together with charcoal, inflammable air is produced, though, according to the new theory, no water is concerned. …

Though the new theory discards phlogiston, and in this respect is more simple than the old, it admits another new principle, to which its advocates give the name of carbon, which they define to be the same thing with charcoal, free from earth, salts, and all other extraneous substances; and whereas we say that fixed air consists of inflammable air and dephlogisticated air or oxygen, they say that it consists of this carbon dissolved in dephlogisticated air."

The Chemical Revolution

- Made phlogiston, as a theoretical substance, unnecessary; but introduced a new theoretical substance of *caloric*.
- Produced a new nomenclature based on a theory of simple substances.
- Provided a definition of elements based on laboratory practice – namely, as simple substances.
- Cemented the methodology of *analysis by weight*.
- Elucidated the role of oxygen in combustion and respiration.
- Developed a new theory of acids, bases and salts.
- Established the importance of quantitative precision.

Overview

The "chemical revolution" shows that some scientific revolutions are small scale, discipline specific revolutions.

- Both the phlogiston theory, and Lavoisier's theory take place within the overall context of the so-called Newtonian worldview.

The issue of oxygen raises the question of what constitutes a scientific discovery? Who discovered oxygen?

When people argue about which paradigm is better, they ague at cross-purposes, or past one another.