

Chemical Revolution

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The chemical revolution

- Narrowly understood, the **chemical revolution** refers to a period from 1775 to 1789 during which phlogiston theory was replaced by oxygen theory.
- However, the broader changes from the chemistry (and alchemy) rooted in the Renaissance period to the **experimental, quantitative, atomistic modern chemistry of elements** occurs over a much longer period, roughly from around 1750 into the 19th century, mostly in Britain, France, and the German countries.

Pre-revolutionary 18th century chemistry

Reminder

- ancient theory of **four elements** by Empedocles (and four qualities)
- Paracelsus and his **principle-based** approach to chemistry
- Pre-revolutionary 18th century chemistry owes much to Paracelsian chemistry of the late Renaissance and the tradition of alchemy evolved since then.
- It is conducted in terms of basic entities: a form of elements captured by “principles”
- These elements resemble substances rather than atoms (which were only identified by Dalton).
- Chemistry does not deal with fundamental constituents, but is sort of a **mid-level theorizing**.

Imponderables and forces

- history of at least 200 years: reign of theorising in terms of imponderables
- Chemical theories deal with 'imponderables' (literally: incapable of being weighed or evaluated with exactness), which are special fluids which pass through 'ponderables' such as ordinary matter
- Examples of imponderables: phlogiston, caloric, electricity, light, magneticism, material aethers
- imponderables have properties and confer properties, and so do explanatory work
- Imponderables are **weightless** and **ineffable**:
 - weightlessness: they don't show up on balance
 - ineffability: that which is not open to common construal, that which is so rarefied that it can pass through ponderables
- interaction often explained in terms of **forces** ('elective affinities'): attraction, repulsion

Principles in chemistry

Characterisation (Principle (in Paracelsus's sense))

A 'principle' (*arché*) is that which begins the beginning, in three ways:

- (a) *ontic: substantial presence, agency*
- (b) *epistemic: brings under classification*
- (c) *methodological*

Remark: Priestley and Lavoisier use 'principles' in sense (a)

Phlogiston theory in a nutshell

Question:

What is phlogiston?

- Phlogiston: a theoretical principle (Priestley: 'alkaline principle') postulated to explain combustion and the chemical transformation of ores into metals
- Combustible substance \rightarrow ash + phlogiston
- Ore + phlogiston \rightarrow metal
- In other words: an imponderable substance emitted during combustion and the calcination of metals: the 'food of fire' or 'inflammable principle'.
- Ahistorically, we could say that where the post-revolutionary chemist sees a gain or loss of oxygen, a phlogiston theorist sees an inverse loss or gain of phlogiston.

Johann Joachim Becher (1635-1682)



- German physician, alchemist
- 1667 *Physica subterranea*
- eliminated fire and air from elements, replacing them with three forms of earth:
 - terra lapidea
 - terra fluida
 - terra pinguis: oily, sulphurous, or combustible properties
- central idea: combustible substances contain ignitable matter, 'terra pinguis'

Georg Ernst Stahl (1659-1734)



- professor of medicine and chemistry in Halle
- 1697 *Zymotechnia fundamentalis*, 1723 *Fundamenta chymiae*
- renamed terra pinguis to **phlogiston** (from Greek: 'burning up', 'inflamm')
- metals \rightarrow compounds of phlogiston + metallic oxides (= 'calces')
- when metal ignited: phlogiston is freed, leaving behind oxide
- when oxide is heated with substance rich in phlogiston (e.g. charcoal), calx takes up phlogiston and regenerates the metal
- **phlogiston is a substance**
- wood \rightarrow ash + phlogiston
- calx + phlogiston \rightarrow metal
- problem known at time: tin and lead increase in weight on combustion

Johann Heinrich Pott (1692-1777), Prussian physician and chemist

- phlogiston: is not a particle, but an essence that permeates substances

Principle (Basic principles of theory of phlogiston according to Pott)

- 1 *The form of phlogiston consists of a circular movement around its axis.*
- 2 *When homogeneous it cannot be consumed or dissipated in a fire.*
- 3 *The reason it causes expansion in most bodies is unknown, but not accidental. It is proportional to the compactness of the texture of the bodies or to the intimacy of their constitution.*
- 4 *The increase of weight during calcination is evident only after a long time, and is due either to the fact that the particles of the body become more compact, decrease the volume and hence increase the density as in the case of lead, or those little heavy particles of air become lodged in the substance as in the case of powdered zinc oxide.*
- 5 *Air attracts the phlogiston of bodies.*
- 6 *When set in motion, phlogiston is the chief active principle in nature of all inanimate bodies.*
- 7 *It is the basis of colours.*
- 8 *It is the principal agent in fermentation.*

In a nutshell

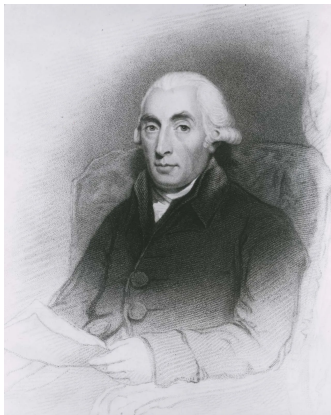


James Bryant Conant, ed. *The Overthrow of Phlogiston Theory: The Chemical Revolution of 1775–1789*.
Cambridge: Harvard University Press (1950)

Conant (1950, 14)

In general, substances that burned in the air were said to be rich in phlogiston; the fact that combustion soon ceased in an enclosed space was taken as clear-cut evidence that air had the capacity to absorb only a finite amount of phlogiston. When the air had become completely phlogisticated it would no longer serve to support the combustion of any material, nor would a metal heated in it yield a calx; nor could phlogisticated air support life. Breathing was thought to take phlogiston out of the body.

Joseph Black (1728-1799)



- Scottish enlightenment figure, professor of medicine and chemistry at the University of Edinburgh
- discoveries of magnesium, latent heat, specific heat, and carbon dioxide
- skilled experimentalist, interest in gases and their chemical properties
- theorises in terms of chemical principles; there are five principles of matter: Water, Salt, Earth, Fire and Metal
- when his experiments showed presence of carbon dioxide (which he called “fixed air”), he added principle of Air
- concept of ‘affinity’: force that holds chemical combinations together

Black's discoveries

- developed '**analytical balance**', balance with high accuracy, permitted to see how gains and losses balanced up (replaced tort)
 - '**latent heat**' (1761): application of heat to ice at its melting point does not cause rise in temperature of ice/water mixture, but increase in water in the mixture; thus, when a body changes (e.g. from solid to liquid), it absorbs/releases heat without changing temperature
 - '**specific heat**'/heat capacity: amount of heat required to raise temperature by 1 degree, different for different substances
- ⇒ both these developments mark **beginning of thermodynamics**
- found that limestone (calcium carbonate) could be heated or treated with acids to yield a gas he called "**fixed air**" (carbon dioxide), denser than air, did not support flame or animal life
 - showed that carbon dioxide is produced by animal respiration and microbial fermentation
 - His student Daniel Rutherford discovered **nitrogen** in 1772: residue of air left after burning ("phlogisticated air", for us a mixture of nitrogen and carbon dioxide), having taken up all of the phlogiston. (cf. Priestley's discovery of oxygen—"dephlogisticated air")

Joseph Priestley (1733-1804)



- English chemist, natural philosopher, separatist theologian, liberal political theorist
- educated at Davetry Academy, dissenting from Church of England
- in British empiricist tradition, experimental approach, Baconian ideology, dissenting Academics have important role
- heartland of Priestley's chemistry: pneumatics, i.e., chemistry of air/atmosphere
- goal: to isolate "fixed air" (oxygen is type of fixed air)
- What fixes air? Plants, alkaline earth,...

Priestley's discoveries

- “nitrous air” (nitrous oxide, N_2O , Davy: “laughing gas”)
- volume relationship important to Priestley
- 1772 discovery of artificially carbonated water led to widespread recognition
- developed many ways of analyzing newly isolated gases, emphasis on physical and mechanical parameters, rather than chemical (flame size and colour of flammable gases)
- 1774 discovery of oxygen (“dephlogisticated air”); Priestley believed it to be capable of combining with more phlogiston
- met with Lavoisier in Paris in 1774, where he demonstrated release of oxygen from mercuric oxide and debated the nature of the gas
- They also debated the interpretation of result by Cavendish as well as Watt's demonstration of the compound nature of water.
- Both these last two points central for the chemical revolution, and both these results formed basis of Lavoisier's new oxidation chemistry.

Antoine-Laurent Lavoisier (1743-1794)



- high-born French aristocrat, darling of French Academy
- 1789 *Traité élémentaire de chimie*, (tr into English by Kerr in 1790 as *Elements of Chemistry*)
- ruthless, systematic, quantitative approach to chemistry; theorising is important
- also in empiricist tradition, great experimentalist, makes measurements of unprecedented accuracy
- emphasis on nomenclature, classification, linguistic precision (catalysed through Condillac)
- invents terms 'oxygen', 'oxidation', 'hydrogen'

Oxygen, begetter of acid

- Lavoisier does not break with chemistry of principles, so we find generating agents in both Priestley and Lavoisier
- ⇒ continuation of Paracelsian principle ontology
- 1770s: Lavoisier studies acids; by 1774, he concluded that phosphoric acid was in part made up of air and this was later shown in experiments on phosphorous and sulfur
- ⇒ “eminently respirable air” is a constituent of all acids and thus contains the principle of acidity
- Lavoisier’s ‘oxygenic principle’: principle of respirable air, begetter of acids
- ⇒ theory of acidity, rather than of oxygen
- By 1778, Lavoisier announces the role of oxygen in combustion and weight gain and its role in acids.

Priestley’s discovery of oxygen and Lavoisier’s understanding of its role in central chemical reactions delivers the first piece of the chemical revolution.

Hydrogen, begetter of water

- Despite the theory of oxygen available, phlogiston still enjoyed a decisive advantage: it explains why metal and acid produced 'flammable air' (i.e., hydrogen), by release of phlogiston by the metal (which is the calx of the metal and phlogiston).

Thus, the second piece of the chemical revolution is to acquire an understanding of flammable air (and to characterize water).

- In 1783, word reached the French Academy of Sciences from Henry Cavendish's assistant, Charles Blagden, that Cavendish had synthesized distilled water by exploding flammable and dephlogisticated air.
- Lavoisier was able to repeat the experiments, and hypothesized that the amount of reactant equaled the amount of product (although he could not be absolutely sure).
- Later in 1783, he announced that water was not an element, but a compound of the oxygenic principle and the 'aqueous inflammable principle' (or, as he called it, 'hydrogen' or the begetter of water).

The pieces come together

- The demonstration of the compound nature of water gave Lavoisier confidence in his attack against phlogiston theory with his alternate theory of combustion (in which oxygen held a central place).
- ⇒ He could now explain the production of flammable air (hydrogen) when acid and metal was combined, for he argued that hydrogen came not from the metal, but from water.
- In 1785, he launched his decisive attack against phlogiston, arguing that **since you could explain chemical phenomena without it, it was rendered extraneous** (and thus, probably did not exist).
- Furthermore, he noted that it was a vague principle, sometimes with 'weight' (mass), sometimes not, sometimes a combination of fire and earth, sometimes free of fire.

Caloric theory

Characterisation (Caloric theory)

Heat consists of an imponderable, self-repellent, weightless fluid or gas ('caloric')—a substance—that flows from hotter to colder bodies. Caloric could exit or enter a solid or liquid through pores.

- In his 'Réflexions sur le phlogistique' (1783), Lavoisier argues that experimental results (e.g. finding a fixed melting point for ice) were inconsistent with phlogiston theory. In its place, he introduced 'caloric' as the substance of heat.
- uses a **calorimeter** to measure heat released in chemical reactions
- **Conservation of heat**: caloric is a material substance that can neither be created nor destroyed—its quantity is constant
- The flow of heat from hotter to colder bodies is explained by the self-repellent nature of caloric.
- Further success: explanation of thermic expansion of substances and of radiation of heat, deduction of many gas laws, Carnot (1824) develops principle of Carnot cycle based on caloric

Challenging the caloric theory

Count Rumford's experiment

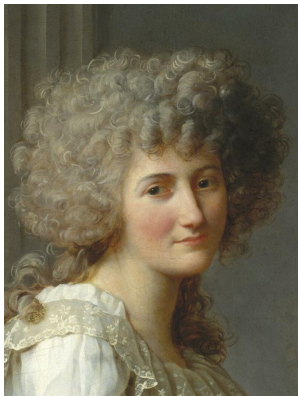


- Sir Benjamin Thompson (1753-1814), Count Rumford, was a British physicist
- experiment in 1798: friction from boring out a cannon heats the metal, but there is no source from which caloric is transferred...
- Also, boring the cannon does not lead to loss of its ability to produce heat.
- However, experiment is too imprecise to be decisive.
- After Lavoisier was executed, Rumford married Mme Lavoisier:

I think I shall live to drive caloric off the stage as the late Lavoisier drove away [phlogiston]. What a singular destiny for the wife of two Philosophers!

But caloric survived Rumford (and Mme Lavoisier divorced him).

Marie-Anne Paulze Lavoisier (1758-1838)



- French aristocrat and chemist, later Countess of Rumford
- married Lavoisier when she was 13 (!)
- developed interest in his work, started to actively participate in work in his lab
- received formal training in chemistry
- almost all lab work was joint work by the Lavoisiers
- With her excellence in French, English, Latin, and her artistic training, she wrote much of Lavoisiers papers, illustrated them, and translated his and other work to and from French (Kirwin, Priestley, Cavendish).
- secured her husband's legacy after his execution
- She did not receive any recognition for her seminal contributions in her lifetime, even though they were so central in enabling Lavoisier's own work.

The new classification and nomenclature

- Antoine Lavoisier, Louis-Bernard Guyton de Morveau, Claude-Louis Berthollet, and Antoine François de Fourcroy: *Méthode de nomenclature chimique*, submitted to the Academy in 1787.
- ⇒ new system of **nomenclature, based on Lavoisier's new oxygen theory** (Black complained that to accept the new nomenclature was to accept the "French theories")
- The ancient elements of earth, water, air, and fire were replaced by **55 new elements which were presumably not further decomposable**:
 - light, caloric,
 - principles of oxygen, hydrogen, and azote (nitrogen), carbon, sulfur, phosphorus,
 - yet unknown 'radicals' of muriatic acid (hydrochloric acid), boric acid, and 'fluoric' acid,
 - 17 metals,
 - 5 'earths' (mostly oxides of yet unknown metals such as magnesia, baria, strontia),
 - 3 alkalies (potash, soda, and ammonia),
 - the 'radicals' of 19 organic acids.

Brock's six necessary and sufficient conditions



William H Brock (1993). *The Norton History of Chemistry*.

Brock lists the following six **necessary and sufficient conditions** for the **chemical revolution**:

- 1 Realization that air did not participate in chemical reactions.
- 2 Abandonment of elementary nature of air.
- 3 Lavoisier's concept of gas as expanded solid or liquid.
- 4 Guyton's discovery that metal increased in weight when 'calcined' in air.
- 5 The ideas of acidity (prioritized by Brock over the debate over combustion).
- 6 Definition of the constituents of acids and bases as elements, operationally defined as that which could not be further analyzed.

Humphry Davy (1778-1829)



- British chemist, professor at the Royal Institution
- used electricity to isolate potassium, sodium, calcium, strontium, barium, magnesium, and boron for the first time
- discovered the elemental nature of chlorine and iodine
- experimented with nitrous oxide (which he named "laughing gas"), discovered its anaesthetic properties
- **destroys Lavoisier's chemistry:**
 - 1 shows that there is no oxygen in 'oxymuriatic acid', overturning the 'acidifying principle' according to which all acids are compounds of oxygen (and so oxidation is not about acids)
 - 2 halogens such as fluorine, chlorine support combustion
 - 3 suggested that acids were substances that contained hydrogen ions, and reacted with metals to form salts and hydrogen gas
- buried in the **Cimetière des Rois**

John Dalton (1766-1844)



- English chemist, physicist and meteorologist
- *New System of Chemistry* (1808)
- Dalton's approach was less that of a chemist than that of a mathematically inclined meteorologist (analysis of atmosphere: different strata of elements fixed by proportions)
- move away from chemistry of principles, elective affinities, quantifiable forces
- instead: consideration of proportions, ratios
- visualisable chemistry, based on ratio combinations, combining of relative weights

Dalton's chemical atomism in brief

- In Dalton's atomistic theory of the chemical elements, there are no chemical reactions, only mechanical combinations of definite proportions, no forces (undercutting Newtonian paradigm of short-range attractive and repulsive forces)
 - rigorously simplified atomistic view: inert, passive elements, understood as the last thing to be experimentally isolatable
 - ab initio creation of heterogeneous atoms, what makes the difference is the way they are combined
- ⇒ static, Democritean atomism
- Dalton shifts debate in chemistry away from Newtonian quantification of forces toward chemical mechanisms, combining elements
 - move away from 'why' (= causes) and 'how', to arithmetic combinations, to 'what' and 'how much'
 - stress on units that combine as fixities
 - strictly realist, empiricist

New System of Chemistry (1808)

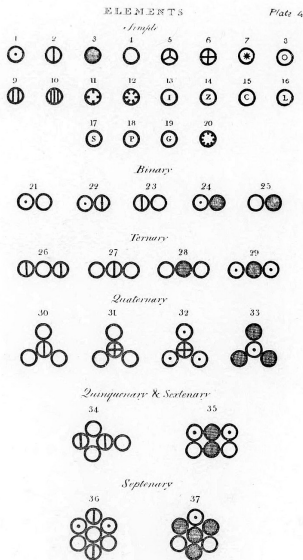
- In the last chapter of Book I, Dalton explains that he wants to show...

'On chemical synthesis'. p. 213; emphases in the original

... the importance and advantage of ascertaining the relative weights of the ultimate particles, both of simple and compound bodies, the number of simple elementary particles which constitute one compound particle, and the number of less compound particles which enter into the formation of one more compound particle.

- two bodies which are disposed to combine can do so in fixed proportions of a whole number of each constituent into a compound
- ⇒ result can be binary combination where both types contribute one atom each, or two different sorts of ternary combinations with one atom of one type and two atoms of the other, or combinations with a higher number
- first rule of combination:

When only one combination of two bodies can be obtained, it must be presumed to a binary one, unless some cause appear to the contrary. (214)



- Dalton assumes uniformity in chemical composition: composition of any chemical substance is constant (today called 'law of constant composition')
- If two elements A and B combine to form more than two compounds, then the various weights of A which combine with a fixed weight of B bear a simple ratio to one another, i.e., a ratio of whole numbers ('law of multiple proportion')
- If two elements A and B combine separately with a third element C , then the weights of A and B which combine with a fixed weight of C bear a simple ratio to each other ('law of reciprocal proportions')

Application to water

- Water is the only known product of hydrogen and oxygen.
- Thus, it must be assumed to be binary: HO
- From the data that the reaction required 87.4 parts oxygen and 12.6 parts hydrogen, Dalton estimated a relative weight of 7 to 1, oxygen to hydrogen, taking hydrogen as the standard weight.

Ultimately, this leads to this:

PERIODIC TABLE OF ELEMENTS

Chemical Group Block

PubChem

1	1	2	Atomic Number										17	35.45	Atomic Mass, u										18
1	H Hydrogen Nonmetal												Cl Chlorine Halogen												He Helium Noble Gas
2	Li Lithium Alkali Earth Me...	Be Beryllium Alkali Earth Me...																							Ne Neon Noble Gas
3	Na Sodium Alkali Metal	Mg Magnesium Alkali Earth Me...																							Ar Argon Noble Gas
4	K Potassium Alkali Metal	Ca Calcium Alkali Earth Me...	Sc Scandium Transition Metal	Ti Titanium Transition Metal	V Vanadium Transition Metal	Cr Chromium Transition Metal	Mn Manganese Transition Metal	Fe Iron Transition Metal	Co Cobalt Transition Metal	Ni Nickel Transition Metal	Cu Copper Transition Metal	Zn Zinc Transition Metal	Ga Gallium Metalloid	Ge Germanium Metalloid	As Arsenic Metalloid	Se Selenium Nonmetal	Br Bromine Halogen	Kr Krypton Noble Gas							
5	Rb Rubidium Alkali Metal	Sr Strontium Alkali Earth Me...	Y Yttrium Transition Metal	Zr Zirconium Transition Metal	Nb Niobium Transition Metal	Mo Molybdenum Transition Metal	Tc Technetium Transition Metal	Ru Ruthenium Transition Metal	Rh Rhodium Transition Metal	Pd Palladium Transition Metal	Ag Silver Transition Metal	Cd Cadmium Transition Metal	In Indium Transition Metal	Sn Tin Transition Metal	Sb Antimony Metalloid	Te Tellurium Metalloid	I Iodine Halogen	Xe Xenon Noble Gas							
6	Cs Cesium Alkali Metal	Ba Barium Alkali Earth Me...		Hf Hafnium Transition Metal	Ta Tantalum Transition Metal	W Tungsten Transition Metal	Re Rhenium Transition Metal	Os Osmium Transition Metal	Ir Iridium Transition Metal	Pt Platinum Transition Metal	Au Gold Transition Metal	Hg Mercury Transition Metal	Tl Thallium Transition Metal	Pb Lead Transition Metal	Bi Bismuth Transition Metal	Po Polonium Metalloid	At Astatine Halogen	Rn Radon Noble Gas							
7	Fr Francium Alkali Metal	Ra Radium Alkali Earth Me...		Rf Rutherfordium Transition Metal	Ds Dubnium Transition Metal	Sg Seaborgium Transition Metal	Bh Bohrium Transition Metal	Hs Hassium Transition Metal	Mt Meitnerium Transition Metal	Ds Darmstadtium Transition Metal	Rg Roentgenium Transition Metal	Cn Copernicium Transition Metal	Nh Nihonium Transition Metal	Fl Flerovium Transition Metal	Mc Moscovium Transition Metal	Lv Livermorium Transition Metal	Ts Tennessine Halogen	Og Oganesson Noble Gas							
			La Lanthanum Lanthanide	Ce Cerium Lanthanide	Pr Praseodymium Lanthanide	Nd Neodymium Lanthanide	Pm Promethium Lanthanide	Sm Samarium Lanthanide	Eu Europium Lanthanide	Gd Gadolinium Lanthanide	Tb Terbium Lanthanide	Dy Dysprosium Lanthanide	Ho Holmium Lanthanide	Er Erbium Lanthanide	Tm Thulium Lanthanide	Yb Ytterbium Lanthanide	Lu Lutetium Lanthanide								
			Ac Actinium Actinide	Th Thorium Actinide	Pa Protactinium Actinide	U Uranium Actinide	Np Neptunium Actinide	Pu Plutonium Actinide	Am Americium Actinide	Cm Curium Actinide	Bk Berkelium Actinide	Cf Californium Actinide	Es Einsteinium Actinide	Fm Fermium Actinide	Md Mendelevium Actinide	No Nobelium Actinide	Lr Lawrencium Actinide								