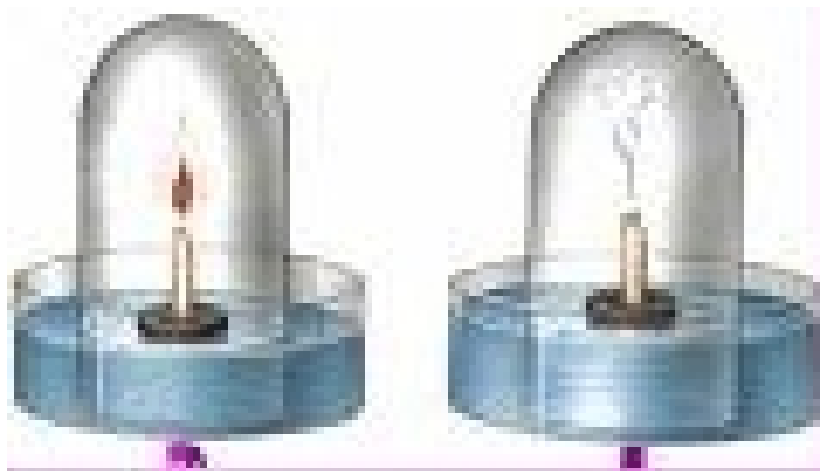


OXIDATION/REDUCTION

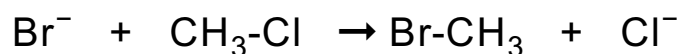


Modern Definitions

- oxidation is:
 - i) the addition of oxygen
 - ii) the removal of hydrogen
 - iii) loss of electrons
- reduction is:
 - i) the loss of oxygen
 - ii) the addition of hydrogen
 - iii) addition of electrons

- modern chem interprets all redox reactions as electron transfer ones, but only ones that result in changes in “oxidation number”, ie, ones that can be interpreted as complete gain or loss of an electron

- simple motion of electrons does not, by itself, result in a redox reaction, ie, consider



is Br oxidized or reduced: Yes___, or No___



is Br oxidized or reduced: Yes___, or No___

- all considerations of redox reactions begin with the most fundamental and spectacular reaction - **fire**

The Phenomenon of Combustion

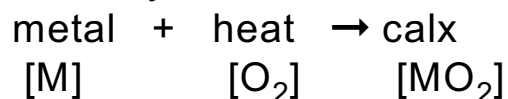
- for early Greek philosophers, combustion was the most dramatic chemical reaction, and “fire” was concluded to be one of the four prime elements, and one that could be perceived as heat and light
 - since combustion of wood, for example, seemed to involve loss of component materials, in the earliest thinking

☆ combustion was interpreted as a decomposition reaction

- in combustion elemental fire was lost from a substance leaving behind incombustible earths, and the product ash weighed less than the starting materials, ie,



- Egyptian metallurgists were aware that the base metals, such as lead or tin, could be converted into heavier calxes by heating in air, a process they called **calcination**, ie,



- ancient metallurgists believed calcination and combustion were quite different processes

- in general, those doing early chemistry, such as the alchemists, saw no need to follow weight changes of combustion processes because one of the products, fire, had no absolute weight; thus,

use of a balance in any reaction that involved fire was a useless activity

- an early attempt to explain the weight gain in metal calcination came from the French physician Jean Rey in 1630
- Rey proposed that on heating, air became separated into lighter (less dense) and heavier (more dense) components and the heavier components adhered to the metal making it heavier after calcination, just as wet sand weighs more than dry sand
- Rey believed his theoretical explanation was far superior to any explanation that was based on mere experiment, and was proud of the “brilliance” of his own thinking (see p.03)

The Role of Air

- in 1664, the inventive Robert Hooke (a paid assistant of the wealthy Robert Boyle), proposed a revised theory of combustion based on his many experiments. He discovered

i) glowing charcoal was extinguished when covered by a glass vessel, and

ii) sulfur heated in an evacuated glass vessel (prepared with the newly invented air pump) could be made to burn if saltpetre [KNO_3] were dropped on it

- Hooke concluded that combustion was:

i) the loss of a volatile, sulfurous component from a combustible substance, and

☆ ii) air, or saltpetre, was required as a solvent for the released substance

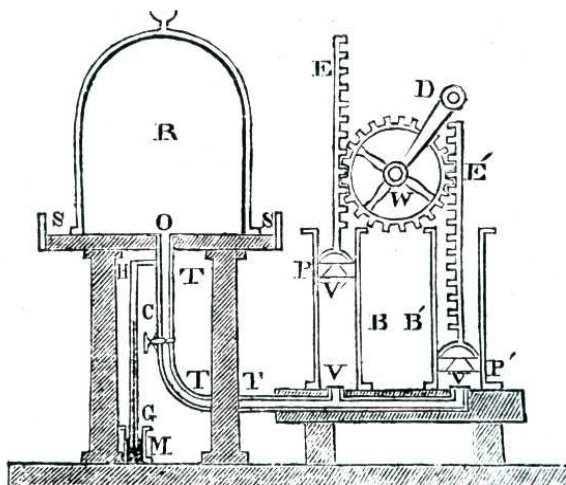


Robert Hooke
(1635-1703)

- Hooke's employer, Robert Boyle, in 1670 also used the air pump

to discover that combustion ceased in an evacuated glass vessel, and small animals died in an airless vessel. Boyle concluded that

☆ biological respiration was a process very similar to chemical combustion



Boyle's air pump, schematic

The Phlogiston Theory

- in 1669, the German alchemist/metallurgist Johann Becher suggested that the principle of combustibility was a combustible earth which conferred flammability, colour, odour and taste to materials in which it was present (see inside cover of text for Becher quote on the "joy" of chemistry)

- a German physician **Georg Stahl** (1660-1734) gave the name **phlogiston** (Gr = inflammable) to Becher's combustible earth
- Stahl proposed a comprehensive interpretation of combustion that was based on the release of phlogiston [ϕ], ie,

wood \rightleftharpoons ashes + flame

and, metal \rightleftharpoons calx



Johann Becher (1635-1682)

- air was required for both processes to dissolve and carry off the released ϕ
- Stahl's ideas included that of a reversible reaction; any substance rich in ϕ could (in theory) reverse combustion and calcination reactions
- Stahl also proposed that the ϕ released by combustion and respiration was removed from atmospheric air by plants, since plants when dried were rich in ϕ (ie, they burned very well)
- respiration was a slow biological combustion of food, generating body heat and requiring air
- an excellent, almost pure, source of ϕ was charcoal, which therefore could reconvert a calx to its metal, ie

$$\text{calx} + \text{charcoal} \rightarrow \text{metal}$$



- ☆☆☆ Stahl's phlogiston theory became chemistry's first great unifying theory, explaining the fundamental requirements of combustion, calcination and respiration, their need for air to proceed, and the crucial role of plants in the purification of the air and nutritive basis of life
- the theory had an enormous impact on chemistry and medicine in the 18th century (for example, windows were opened in sick rooms and plants were introduced to speed recovery; sanatoriums began letting their patients 'take the air' instead of shutting them up in isolated rooms)
- Stahl believed ϕ was
 - i) a weightless principle, imperceptible to the senses (in its purest form) and not confinable in vessels
 - ii) the source of a substance's colour
 - iii) the medium through which fire particles could move

- the phlogiston theory was almost universally accepted by 1750

Pneumatic Chemistry

- pneumatic chemistry is a term used to describe the processes used to discover and characterise new gases discovered after 1750

- as we saw in **Composition**, Black discovered the first new, chemically distinct air, “fixed air” in 1755 by heating and decomposing magnesia [MgCO_3]

- fixed air was very different from common air. It

i) would not support combustion

ii) was denser than common air

iii) was a product of burning charcoal, respiration and fermentation

- Black did not involve phlogiston in his discussion of fixed air, but his work started the era of pneumatic chemistry and an expansion of phlogiston theory

- **Henry Cavendish** (1731-1810) was a very wealthy, intelligent and eccentric natural philosopher who began to study “factitious airs” - any airs contained in solid substances that could be released by chemical reactions; he published his first discoveries in 1766

- he collected the air released by the solution of metals in marine [HCl] and vitriolic [H_2SO_4] acids, ie,

metal + acid \rightarrow salt + new air



- Cavendish obtained the same quantity of the new air from a fixed weight of tin or lead on solution in either marine or vitriolic acid

- therefore concluded the new air was released from the metal (not the acid)

- the properties of his new air were remarkable. It

i) exploded when tested with a glowing splint

ii) was 11x lighter than common air

- Cavendish called the new air **inflammable air**, and suggested it was nearly pure phlogiston

☆ inflammable air = ϕ = $[H_2]$

- Cavendish explained salt formation as the following reaction



- in Cavendish's view, ϕ became a material substance, with weight and physical properties, in accord with Newton's mass/weight laws; this interpretation became very popular, especially in England and Scotland

- **Carl Scheele** (1742-1786) , was a Swede who had no formal education before apprenticing as an apothecary at age 14; he began to carry out chemical experiments in his teens and had a photographic memory - he could remember everything in a book after a single reading

- in 1770 he heated saltpetre (nitre) and collected the released gas, ie,



- Scheele found the new air to be tasteless, colourless, odourless but an excellent supporter of combustion; glowing splints burst into brilliant flame when exposed to it

- he named the new air **fire air**, and later also isolated it from 'red precipitate' [mercuric oxide]

- he collected his experiments on this novel fire air, and other first-time chemical experiments, in a book entitled Chemical Treatise on Air and Fire, and asked the leading Swedish chemist of the time, Torbern Bergman, to write an introduction, which he finally did several years later. The book was published in 1777, by which time the new gas had been discovered and reported by Priestley



Carl Scheele (1742-1786)

- Scheele measured the decrease in volume when combustion occurred in a closed vessel over water, ie,

- since he could see no visible combustion products

Scheele considered two possible explanations for the observed volume decrease:

i) the combustible material in the candle combined with a portion of common air to form a non-gaseous product; this was

considered unlikely because he could find no combustion products in the reaction vessel after combustion

ii) the ϕ released by the candle reduced the interparticle repulsions in the vitiated air [our nitrogen], thus causing a volume reduction; if true Scheele realised the density of the vitiated air should be greater than common air, but he found it to be less dense

- faced with these difficulties of interpretation, Scheele opted for explanation ii), thereby giving a new property to ϕ

- Scheele accepted the common view that combustion ceased when common air became saturated with ϕ

- Scheele observed that a gas identical with common air resulted if 3 parts of vitiated air were combined with 1 part of fire air

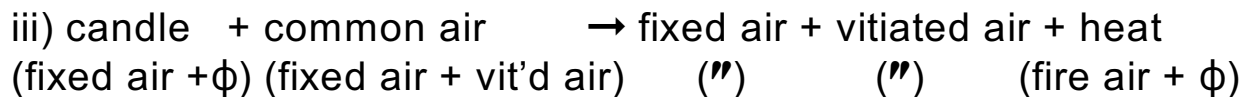
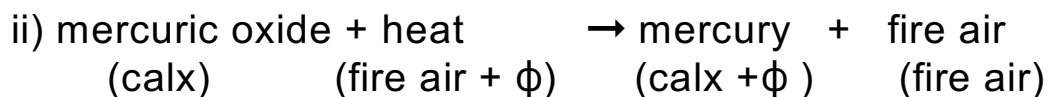
- Scheele also (following Priestley) burned a candle in a closed vessel over mercury and found a volume reduction of only 1/80 and the production of fixed air; he concluded ϕ did not always reduce interparticle repulsions

- also (following Cavendish) he burned inflammable air in common air over water, and could find no combustion products; only heat was produced

- Scheele explained all these observations as follows:

i) inflammable air + common air \rightarrow heat
 (ϕ) (fire air + vit'd air) (ϕ + fire air)+ vitiated air

therefore heat = fire air + ϕ



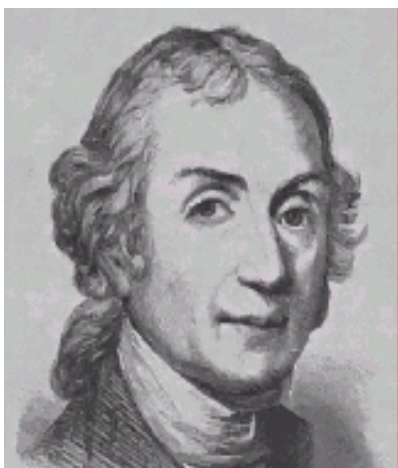
- Scheele's proposal made heat into a material substance, altho the presence in it of ϕ rendered it weightless and able to pass through solid substances

- **Joseph Priestley** (1733-1804) was a non-conformist minister who held radical views in religion, politics and science

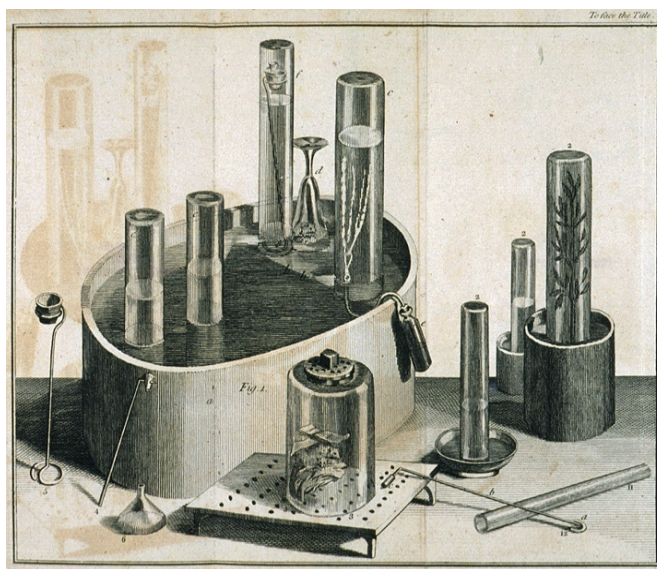
- a radical non-conformist minister who could read 8 languages and equated science with hunting, ie, "*...where a passer-by may sometimes blunder on the quarry while the serious experts weary themselves without starting any game*"

- began his study of chem in 1770 by collecting the fixed air from the brewing of beer at a nearby tavern

- he pioneered the use of mercury as the liquid seal to collect gases that were soluble in water and in a few years isolated and characterised N_2O (laughing gas), NO , NO_2 , HCl , CO , NH_3 , SO_2 and SO_3

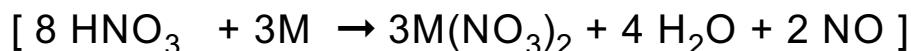


Joseph Priestley, 1733-1804

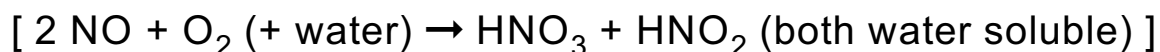


Priestley's water trough

- in 1772, isolated “nitrous air”, [NO] by solution of metals in nitric acid, and collecting the gas over mercury, ie,

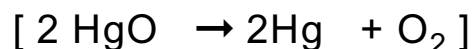


- he discovered that nitrous air reacted rapidly with common air to form a ‘brownish gas’ [NO₂]; this reaction caused a 1/5 volume reduction when carried out over water



- Priestley observed that the remaining air could no longer sustain combustion or respiration, and concluded that nitrous air acted as a direct measure of the “goodness of air”

- in 1774 he heated ‘red precipitate’ [HgO] with a 12 inch burning lens and collected the gas evolved



- he noted the unique properties of the gas:

i) it supported combustion and respiration 5x better than common air, and

ii) it was completely consumed by reaction with nitrous air

- thus Priestley concluded the new air could dissolve ϕ 5x better **than common air, and named it dephlogisticated air**

☆ dephlogisticated air = air - ϕ = [O₂]

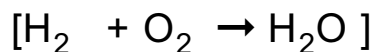
- Priestley published this result in late 1774, two years before Scheele’s report of “fire air”; Priestley believed in hasty publication “*when I made a discovery, I did not wait to perfect it by more elaborate research but at once threw it out to the world, that I might establish my claim before I was anticipated*”

- Priestley named the air that remained in a vessel after **combustion ceased phlogisticated air**

☆ phlogisticated air = air + ϕ = [N₂]

- thus by 1775 the major gases discovered in England, [H₂], [O₂] and [N₂], had all been explained in terms of the ϕ theory

- in 1781, James Watt made a 'spark eudiometer' for Priestley so he could ignite with an electrical spark a mixture of ϕ , inflammable air, with dephlogisticated air in an anhydrous vessel, ie,



- by repeatedly sparking a mixture of the two gases Priestley could see no products of the reaction, except for a few drops of water on the walls of the eudiometer

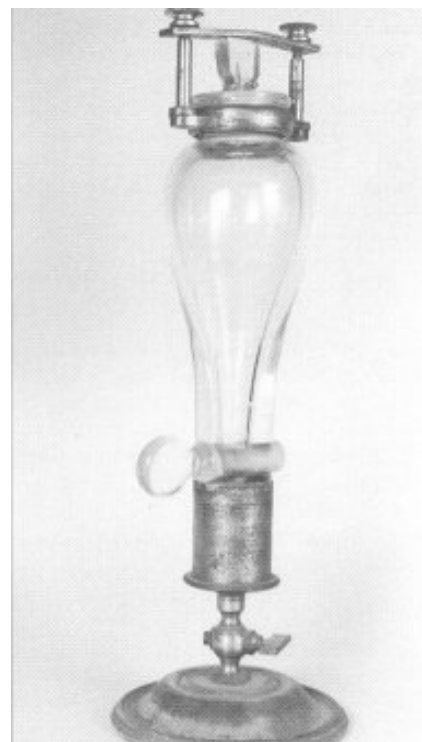
- he concluded the water had ppt'd out from the product air, in which it was less soluble than in inflammable air, ie



- Priestley remained convinced of the validity of phlogiston theory until his death (in Pennsylvania, USA) in 1804

Cavendish (again)

- on learning of Priestley's eudiometer results, Cavendish repeated the [H₂] and [O₂] combination in a eudiometer, but dried



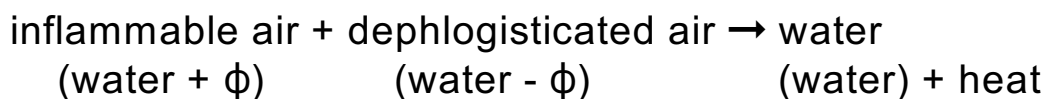
Cavendish's gas eudiometer

the $[H_2]$ before reaction (by repeated passage through anhydrous [calcium chloride]); he found the two gases combined in the ratio

$$[H_2] : [O_2] = 2.02 : 1 \quad \text{a very accurate result}$$

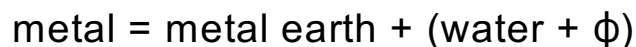
- Cavendish, who was a very careful experimenter, found that no product other than quite pure water appeared in the eudiometer, and the weight loss of the two gases was equal to the weight of water produced

- he rejected the idea that the water had come from 'wet' $[H_2]$, and concluded instead that the 'inflammable air' was = (water + ϕ), and that Priestley's 'dephlogisticated air' was really = (water - ϕ)
- thus

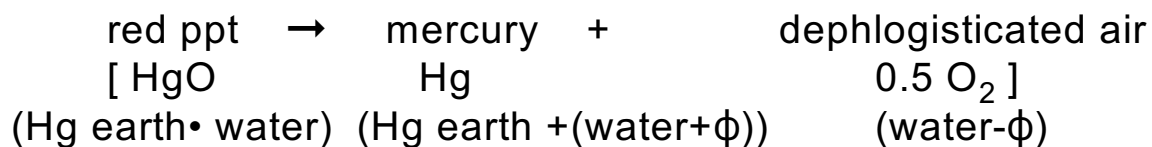


- Cavendish considered the outlandish idea that the fundamental element water might be a compound substance (of inflammable and dephlogisticated airs), but favoured the interpretation above because the two airs did not combine with each other spontaneously unless a spark was applied, which meant that an affinity force (of water for ϕ) had to be overcome before products could form

- he then used his new compositional ideas to reinterpret calcination of metals; instead of metals being composed of metal earth combined with ϕ , ie, metal = metal earth + ϕ , they were composed of a metal earth + inflammable air, ie,



- and to explain Priestley's production of $[O_2]$ by heating red ppt of mercury, Cavendish proposed that all calxes contained hydrated water, and thus



- see that Cavendish's explanation fits the experimental observations, but the presumed composition of metals and their calxes has changed, but water is maintained as a simple substance
- there was soon to be a 'revolution' in the interpretation of chemical combination, pneumatic chemistry, fire and the nature of water

Antoine Lavoisier (1743-1794); the founder of modern chemistry

- Lavoisier was born in Paris into a wealthy family and trained as a lawyer; in 1768 he augmented his personal income by purchasing shares in a tax collection venture know as the Fermé Générale
- in 1771 he married 14-yr old Marie-Anne Paulze, daughter of a business colleague who became his english translator, secretary, laboratory assistant and wife (see text cover); they had no children

- Lavoisier was very ambitious and an extremely hard worker, doing most of his chemical researches when his business tasks were done

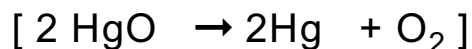
- in 1772 he studied the combustion of diamond on heating in air

[$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$]

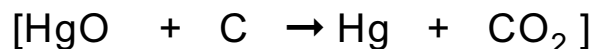
and observed that fixed air was produced as the weight of diamond and volume of air both decreased



- even at the beginning of his chemical investigations, Lavoisier used balances (many specially made for him and accurate to a fraction of a milligram) to follow weight changes in reactions and, although taught the phlogiston theory in chemistry lectures, he began to suspect that weight relationships were key to understanding the conversion of starting materials into products
- also in 1772 he studied the combustion of sulfur and phosphorus in a water-sealed combustion vessel and found that combustion was accompanied by a decrease in weight of S and P, a decrease in volume of common air, and the production of aqueous acids (sulfuric and phosphoric)
- in a notebook entry for early 1773, Lavoisier proposed to carry out an exhaustive investigation of pneumatic chemistry with the intent of bringing about “a revolution in physics and chemistry”
- after restudying Black’s work on magnesia, Lavoisier began to suspect that during combustion the burning material combined with a portion of common air to give combustion products whose weight would be equal to the loss in weight of reactants
- in Oct, 1774, Priestley visited Paris, dined with the Lavoisiers and told them of his recent discovery of ‘dephlogisticated air”; in Nov, 1774 Lavoisier repeated the experiment and collected the new air [O₂], ie,

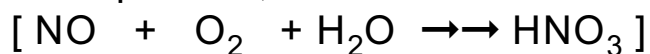


- in early 1775, Lavoisier had verified that the new air had the unique properties attributed to it by Priestley, and that the weight of Hg and the new air equalled the weight of HgO decomposed
- also, heating the ‘red ppt of mercury’ with charcoal generated fixed air, ie



- on publication in 1778 (of work done in 1775), Lavoisier concluded that metals (such as Hg) on heating in air combined with a portion of atmospheric air (the new air, O_2) and that calxes (such as HgO) were compounds of metals and the new air, without mention of Priestley!

- in 1776, Lavoisier combined 'nitrous air' [NO] with the new air (as Priestley had done previously) and observed that nitric acid formed as product, ie



- he concluded that the new air imparted acidity to compounds and gave it the new name **oxygen** (Gr = acid former)

- in 1777, Lavoisier repeated the key expt in phlogiston theory, the burning of a candle; he found that when a candle was burned in oxygen,

- i) all the oxygen was consumed
- ii) fixed air was formed and found as carbonic acid in the water, and
- iii) the results could be explained without involving ϕ

- he then publically rejected the phlogiston theory, saying combustion could be explained without it

- in 1783, Lavoisier learned of Cavendish's expts on the burning of [H_2] with the appearance of water; he repeated the expt and determined that the wt of water produced equalled the weights of oxygen and [H_2] consumed and then concluded, without mentioning the contributions of Cavendish:

- i) the reaction of [H_2] with oxygen was a combustion process, and
- ☆ii) that water was a compound substance made up of oxygen and [H_2]

- he then renamed [H₂] as **hydrogen** (Gr = water former)

- in his revolutionary Traité Elementaire de Chimie of 1789, Lavoisier concluded that all combustion reactions were reactions in which substances combined with oxygen, ie,

combustion = oxidation

- to explain the heat and light evolved during combustion, Lavoisier proposed that elemental oxygen was surrounded by a sphere of “**caloric**”, and the release of caloric gave rise to the heat and light of flame, ie,

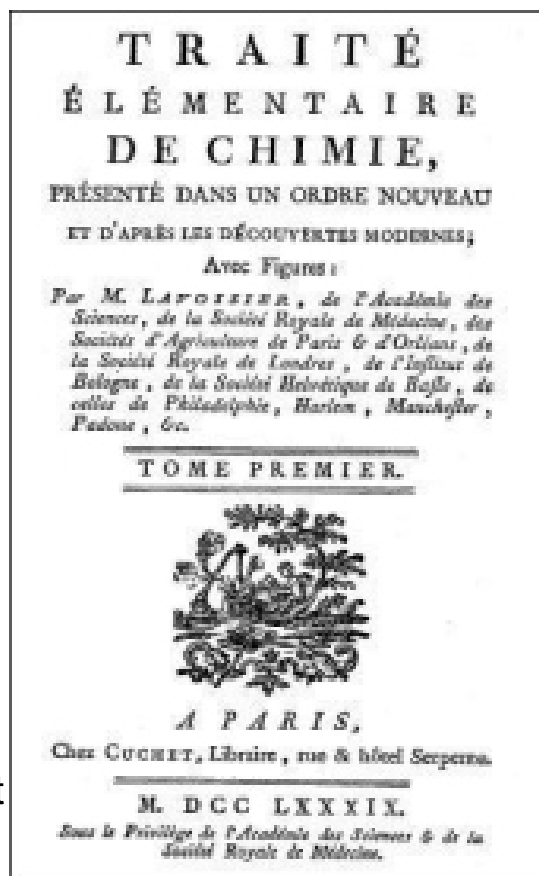
carbon + oxygen → fixed air + heat/light
(carbon) (O₂ + caloric) (CO₂) (caloric)

- supporters of φ theory (like Priestley) claimed that Lavoisier’s theory did little more than change the name of phlogiston to caloric, and move its location from the combustible to oxygen

- nonetheless Lavoisier’s theory of combustion became generally accepted within a few years of the publication of the Traité, and the balance became the most important instrument in chemistry

Further Developments

-thus by 1800



combustion = oxidation = addition of oxygen
 reduction = deoxidation = removal of oxygen

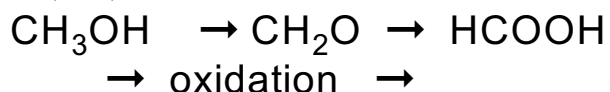
- in 1809 Humphry Davy discovered that the newly isolated phosphorus reacted violently with chlorine in a manner similar to combustion, and within a few years sulfur, bromine and iodine were added to the list of elements that could react other materials with flame-like appearances, but the explanation of “fire” remained elusive

- in 1870 Salet defined combustion as any chemical process energetic enough to emit heat and light

- as early as the 18th century compounds became known that existed in different levels of combination with oxygen, eg
 CO and CO₂, N₂O, NO and NO₂

and the 19th century added
 H₂O and H₂O₂, and CH₃OH, CH₂O and HCOOH

- these examples demonstrated that oxidation could result from removal of hydrogen as well as addition of oxygen, ie,



- in the early 20th century, the great physical chemist Ostwald recognized that electrolysis could change an element from one oxidation level to another, ie,

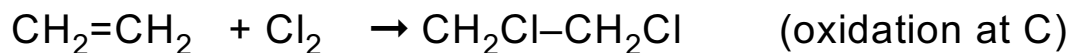
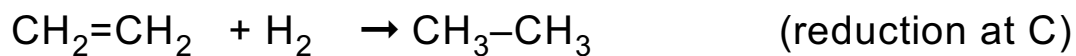


Wilhelm Ostwald
 1853-1932

- by 1913, oxidation had become reinterpreted as a loss of electrons, and reduction as a gain of electrons

- in modern chemistry, oxidation or reduction is defined as such when one or more electrons is actually transferred to or from an atom or when such transfer is assumed to have occurred during a change in oxidation number

-compare



even though the differences in electron positions are similar in both reactions