18th Century chemistry

From Alchemy to Chemistry

Alchemy…

- **Alchemy**
  (from the Arabic الخيمياء al-khimia) meaning 'the Black Land' is now seen as a possible origin for the word alchemy.
- The Greek word khumos, meaning 'fluid' has also been suggested as an alternate origin for the word alchemy,
- Alchemy is often described as a “philosophical and spiritual art known as the spagyric art from the Greek words meaning to separate and to join together.
- Alchemy combines elements of chemistry, metallurgy, physics, medicine, astrology, semiotics, mysticism, spiritualism and art.

ALCHEMY AND HERBALIST SYMBOLS

WEIGHTS AND MEASURES

- ℳ ℈ one pound
- ℨ ℈ one ounce
- ℨ ℈ one dram
- ℈ one scruple
- ℙ ℈ one pinch
- ℴ ℈ one pint

ANA equal amounts

THE FOUR ELEMENTS

Earth	cold & dry	Melancholy
Water	cold & wet	Phlegmatic
Air	hot & wet	Sanguine
Fire	hot & dry	Choleric

THE THREE PRINCIPLES

- Salt — the contractive force; crystallisation, contraction
- Sulphur — the expansive force; dissolution, evaporation
- Mercury — the integrative force; balancing salt & sulphur

PROCESSES

- calcination
- congestion
- fixation
- solution
- digestion
- precipitation
- sublimation
- separation
- ceration
- fermentation
- multiplication
- caput mortuum

- ☉☾ day
- ☽☾ night
- sugar
- honey
- alcohol
- spirit
- wax
- oil
- essence
- powder
- digest
- still
- distil
- filter
- take
- mix
- boil
- purify
- compose
- retort
- receiver

MINERALS

- Nitre — Saltpeter
- Realgar — Ore of Arsenic
- Quicklime
- Cinnabar — Ore of Mercury
- Salammoniac — Ammonium Chloride
- Tartar
- Litharge — Lead Monoxide
- Marchasite — Iron Pyrites

ACIDS

- Aqua Fortis
- Aqua Regina
- vinegar
- distilled vinegar
- oil of vitriol

PLANETRY METALS

gold	Sun		
silver	Moon	tin	Jupiter
iron	Mars	lead	Saturn
mercury	Mercury	copper	Venus

Alchemy: From the ancient world to the 18th century

Alchemy…

- The vast majority of the ancient Greeks did not believe in the atomic theory of Democritus.
- Rather, they believed in Aristotle's theory of continuous matter in which all matter consisted of four elements, earth, water, air and fire.

- They had a quite different theory of the nature of matter that did not involve the idea atoms at all.
- In this scheme the earth was cold and dry, water was cold and wet, air was hot and wet and fire was hot and dry.
- These elements could be transformed one into another. Water (cold and wet) could easily become air (hot and wet) by being boiled, for example.

Alchemy: Examples …

- Start with a red powder, heat it and watch it miraculously transform into a silver liquid.

  (As we understand it today, cinnabar. or mercuric oxide, was heated to release oxygen leaving behind pure mercury).

- Take a yellow/red metal (copper) heat it together with a yellow powder (sulphur) and the result is a black powder (copper sulphate).

  (In alchemical thought, the means of producing metallic qualities was demonstrated by the first reaction).

- In the second reaction, metallic qualities were removed (along with the yellowness of both copper and sulphur).
- This had to be a transmutation in action!

Alchemy…

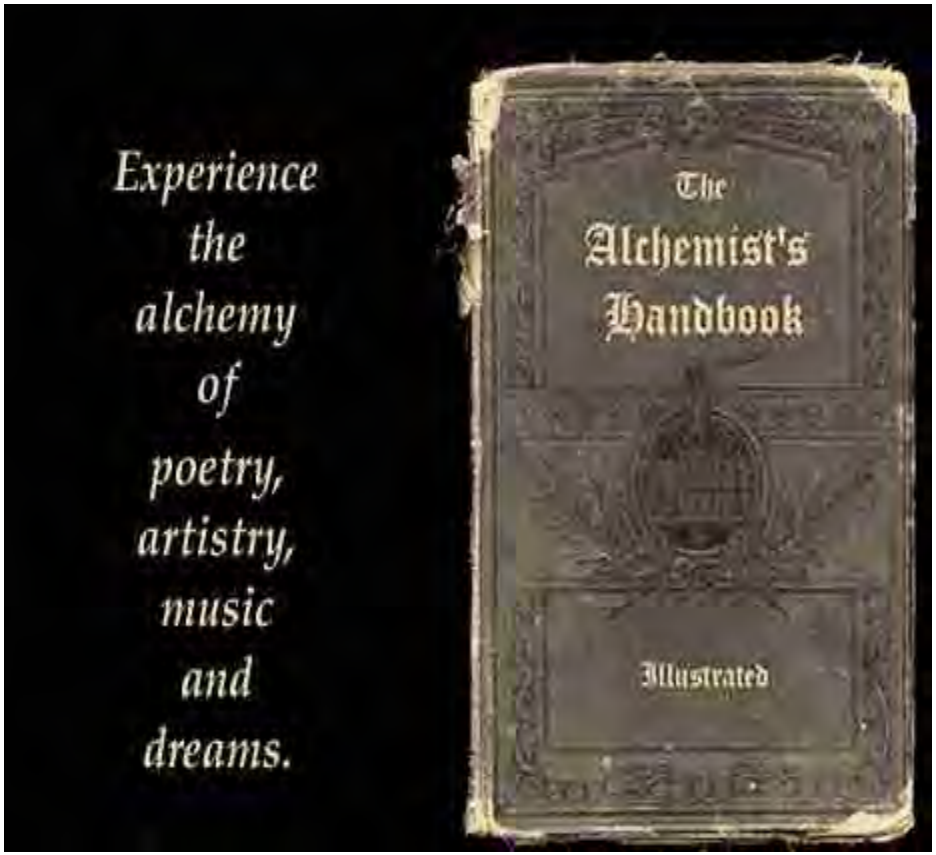
- Such impressive demonstrations of transformation were the routine of alchemy.
- No wonder then that alchemists believed that if they could only find the all-elusive formula, gold was there for the making.
- But, alchemy was conceived more broadly than the hunt for gold.
- Many other useful processes, like the production of metal alloys, perfumes, acids and alcohol, were all seen as progress.

Alchemy…

- Alchemy in Europe, Arabia and China made significant advances and laid the basis from which the science of chemistry developed in the 18th century.
- It produced a good deal of lasting chemical knowledge.
- There was a wide-ranging knowledge of the alloys of precious and other metals.
- The procedure of distillation was invented by alchemists that fascinated them.
- Take a rose, crush up the petals, add alcohol and distil. What you get is concentrated rose oils, of the sort that are used to make perfumes.

- But, alchemists believed this to be a pure and active 'essence of rose' which contained 'all that makes a rose into a rose'.
- Because acids and bases (alkalis) had interesting reactions with metals, the alchemists developed stronger and stronger ones.
- Particularly aqua fortis (concentrated nitric acid) and aqua regis (a mix of concentrated nitric and hydrochloric acids) which could dissolve gold.

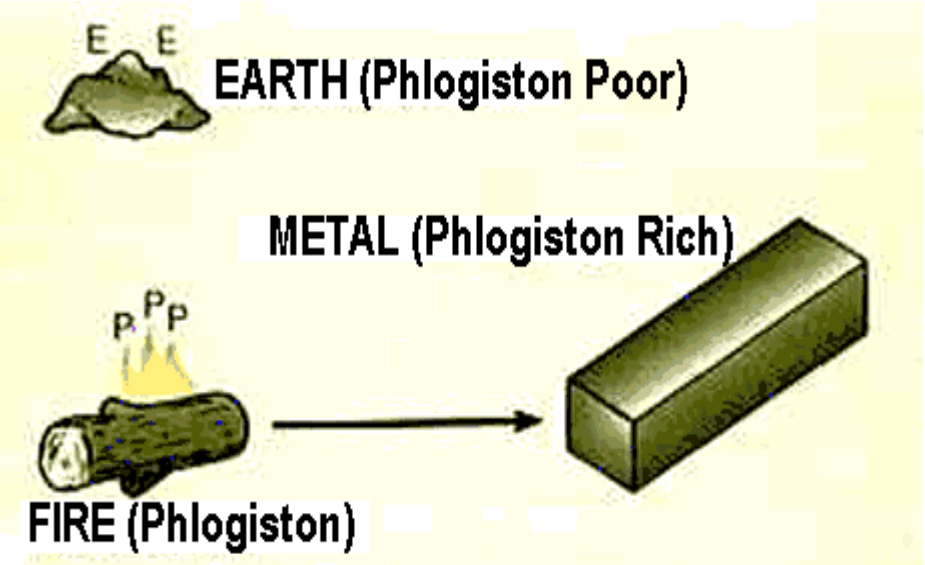
Alchemy…


Experience
the
alchemy
of
poetry,
artistry,
music
and
dreams.
The
Alchemist's
Handbook
Illustrated

The Phlogiston Theory

- Joachim Becher (1635-82):

  He believed substances to be composed of three “earths”, the vitrifiable, the mercurial, and the combustible. He supposed that when a substance burned, a combustible earth was liberated.



- Georg Stahl (1660-1734):

  Used the ideas of Becher and developed the Theory of phlogiston in 1703, which was the main theory for chemists for almost 100 years!

Notes on The Phlogiston Theory

From Stephen Mason:] Joachim Becher (1635-82): Theory of 1669

- Chemical Substances contain three essences or principles:
- *Sulphur* (princ. of *inflammability*)
- *Mercury* (princ. of *fluidity and volatility)*
- *Salt* (princ. of *fixity and inertness*)
- Solid Earthy Substances contain 3 constituents:
- *terra lapida* (fixed earth = Salt Principle)
- *terra pinguis* (oily or fatty earth present in all combustible material = Sulphur = Principle of Inflammability)
- *terra mercurialis* (fluid earth = Mercury)

- **Process of Burning and Calcination:**
- *Calcination* is the process of converting Limestone (or marble or chalk), to Lime.
- (In modern terms, $CaCO_3$ to CaO by means of heat. In fact, CO_2 is driven off in the process.
- involves *decomposition* of compound body into constituent parts; viz., sulphureous terra pinguis and fixed terra lapida in simplest cases.
- simple bodies cannot undergo combustion; only those with terra pinguis and another earth.

Georg Ernst Stahl (1660-1734): Theory of 1703

- Stahl renames 'terra pinguis' or the Principle of Inflammability '**Phlogiston**' (from Greek 'to set on fire') which is 'the motion of fire', 'the motion of heat', 'the sulphurous principle', 'the oily principle'.
- Metal = compound of Calx and Phlogiston
- Heat liberates Phlogiston and leaves the Calx.
- Phlogiston is the essential element of all combustible material

. Phlogiston escapes with burning of combustibles and enters atmosphere or joins with substances like calx to form metal.

- Combustible objects are rich in Phlogiston.
- The process of burning involves loss of Phlogiston to the air.
- What is left over after combustion is without Phlogiston and so cannot burn.
- Wood has Phlogiston but not ash.
- Rusting of metals is analogous to the burning of wood; so metals possess Phlogiston while their rust (or 'calx') does not.
- (The difference in the presence and absence of fire in combustion is explained by speed at which Phlogiston leaves the combustible.)

Phlogiston theory

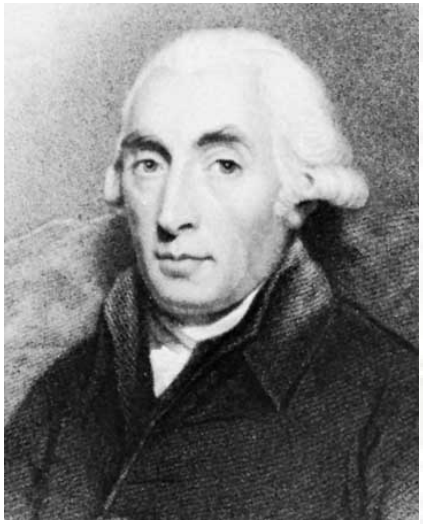
- Phlogiston theory had great explanatory power and guided alchemical research.
- Problem: Why is it that certain substances when heated become *lighter* than they were before combustion (wood to ash) while others become *heavier* than they were before (metal to calx) if combustion involves a *loss* of Phlogiston?
- Answer: Phlogiston is the spiritous aerial part of matter so that it has *negative weight* or *positive lightness* and so its loss increases the weight of the remaining calx.
- Gabriel Venel (1723-75): Positive Lightness Theory.
- "Phlogiston is not attracted towards the centre of the earth but tends to rise; thence comes the increase in weight in the formation of metallic calxes and the diminution of weight in their reduction."
- Phlogiston is an anti-gravity material.

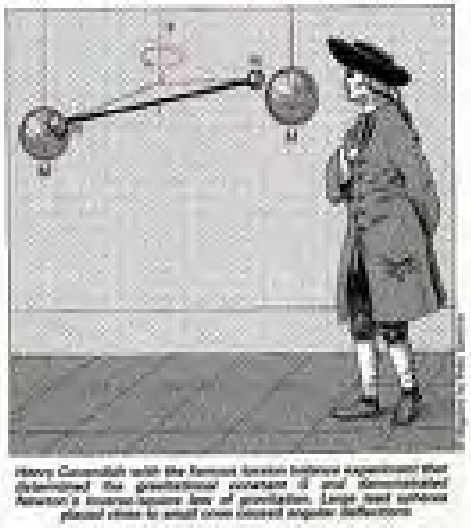
Chemistry of the 18th century

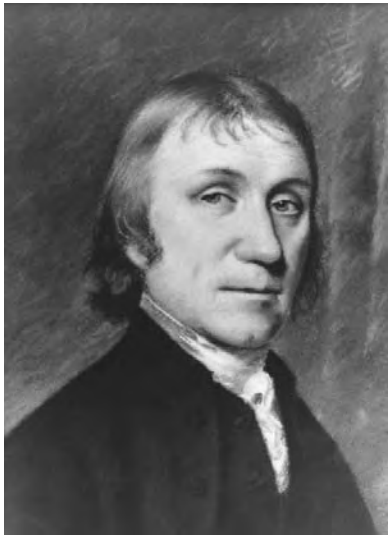
- The Phlogiston theory was accepted by the greatest chemists of the middle and late 18th century: Joseph Black (1728-99), Henry Cavendish (1731-1810), and Joseph Priestley (1733-1804), and even by Lavoisier (until about 1780).

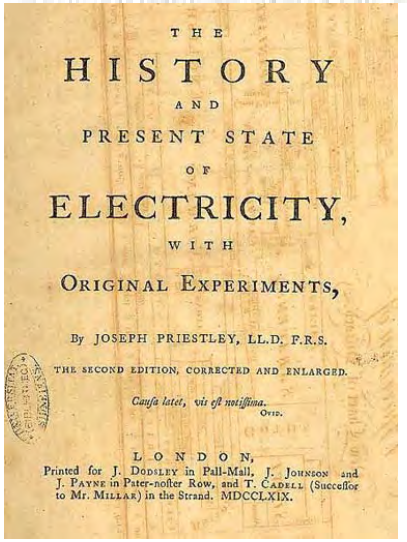
- However, they did overthrow the Greek doctrine of 4 elements, Earth, Air, Fire, Water with recognition of many kinds of 'earths' (elementary substances) but insisted on the retention of air, fire, water as elements.

- Phlogiston = Element of Fire or Agent Activating Fire.









Chemistry of the 18th century

- Joseph Black (1728-1799) isolates 'fixed air' or Carbon Dioxide (1754).
- Henry Cavendish discusses preparation 'inflammable air' (Hydrogen) in 1766, as well as the production of 'sulphurous vapours' and nitreous vapours' using sulphuric and nitric acids on metals.
- Priestley, in the 1770s, discovers what we now call ammonia, hydochloric acid gas, nitrous oxide, nitric oxide, oxygen, nitrogen, carbon monoxide, sulphur dioxide.

- Carl Scheele (1742 - 86):
- "Atmospheric Air" is not an elementary substance but a mixture composed of 2 gases: 'fire air' (Oxygen) and 'foul air" (Nitrogen) in a 1 to 3 ratio by volume.
- The function of "fire air" is to take up the Phlogiston given out by burning substances. The amount that could be absorbed was limited so that when air in a confined space was saturated with Phlogiston it could no longer support combustion

(Explanation as to why a fire will go out in a confined space).

Alchemical chart (1682)

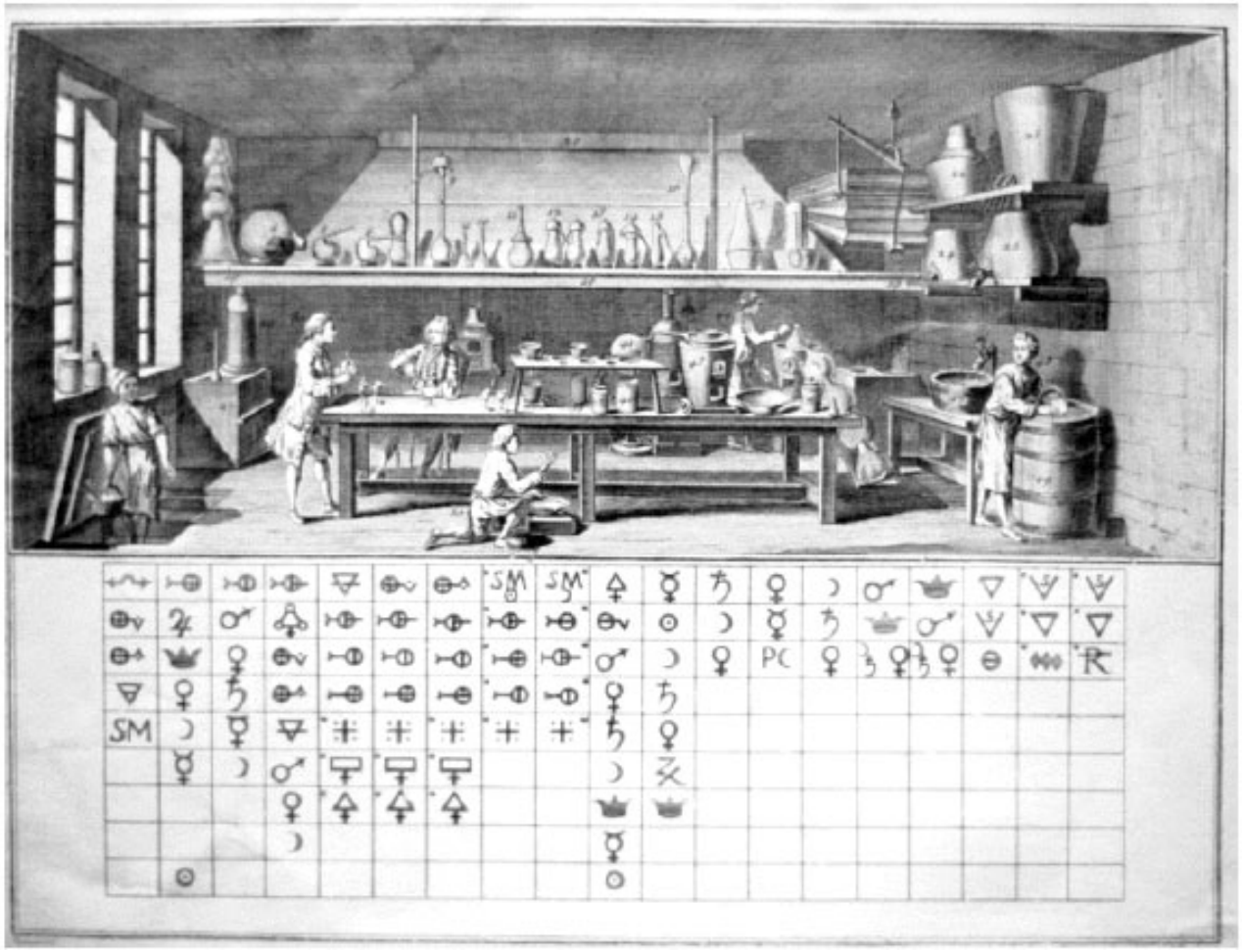
TAke reddish rich Virgin Earth in ♈, impregnate it with ☉, ☽, serene and dew, till the end of *May:* Then imbibe sprinklingly with dew gathered in *May*, and dry in ☉, expose all Night to the ☽ and Air, securing it from Rain. Still when it is dry, imbibe and turn the Earth often. Continue this till ♎mation. The hot ☉ (especially in the Dog-days) will make a pure Salt shoot up, which mingle back into the Earth, by turning it all over. Then distill by graduated △ as *A. F.* forcing all the Spirits

An Explication of the Characters which are used in this Book.

☉ *Gold.*
☽ *Silver.*
♂ *Iron.*
☿ *Mercury.*
♃ *Jupiter.*
♀ *Venus.*
♄ *Lead.*
♁ *Antimony.*
✻ *Sal armoniac.*

A. F. *Aqua Fortis.*
A. R. *Aqua Regis.*
S. V. *Spirit of Wine.*
♎ *Sublimate.*
♍ *Precipitate.*
ȧȧȧ *Amalgama.*
▽ *Water.*
△ *Fire.*

Diderot's alchemical chart (1776)



An 18th century chemistry lab

(Deutsches Museum, Munich)

Joseph Priestly (1733-1804)

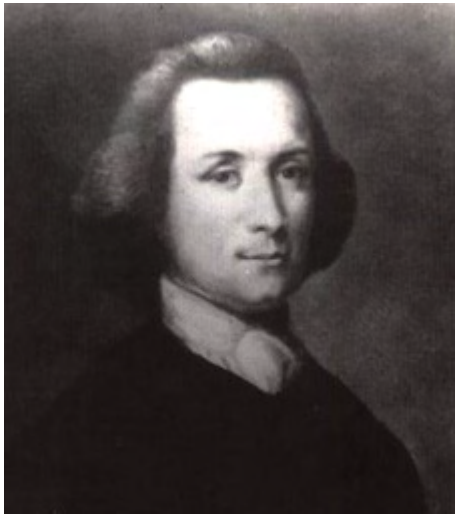
He was a polymath:

theologian, natural philosopher, educator, and political theorist, made significant contributions to electric phenomena, and published over 150 works.

He is usually credited with the discovery of oxygen gas, although Carl Wilhelm Scheele and Antoine Lavoisier also have such a claim.

He believed that a proper understanding of the natural world would promote human progress and eventually bring about the Christian Millennium.

Priestley was also the first to propose that electrical force followed an inverse-square law, similar to Newton's law of universal gravitation.

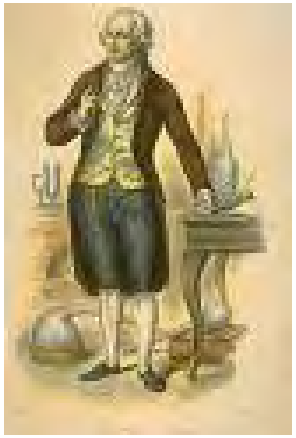


Antoine Lavoisier (1743-1794)

- He was a French nobleman prominent in the histories of chemistry, finance, biology, and economics.
- He stated the first version of the law of conservation of mass, recognized and

  named oxygen (1778) and hydrogen (1783)
- Overthrew the phlogiston theory,
- Introduced the *metric system*,
- Wrote the first extensive list of elements, and
- Helped to reform chemical nomenclature.
- Wrote the first modern textbook of chemistry.

Antoine Lavoisier…



- He was also an investor and administrator of the "Ferme Générale" a private tax collection company;
- Chairman of the board of the Discount Bank (later the Banque de France);
- A powerful member of a number of other aristocratic administrative councils.
- All of these political and economic activities enabled him to fund his scientific research.
- But because of his prominence in the pre-revolutionary government in France, he was beheaded in 1794 at the height of the French Revolution.

Antoine Lavoisier…

- **1774 J. Priestly produces "oxygen“:**

Heat

Calx of Hg---------gas? + X

- 1774 Priestly discusses this experiment with Lavoisier.
- 1774/75 Lavoisier repeats the experiment and identifies gas as "pure air".
- He publishes his findings but <u>does not give Priestley any credit.</u>

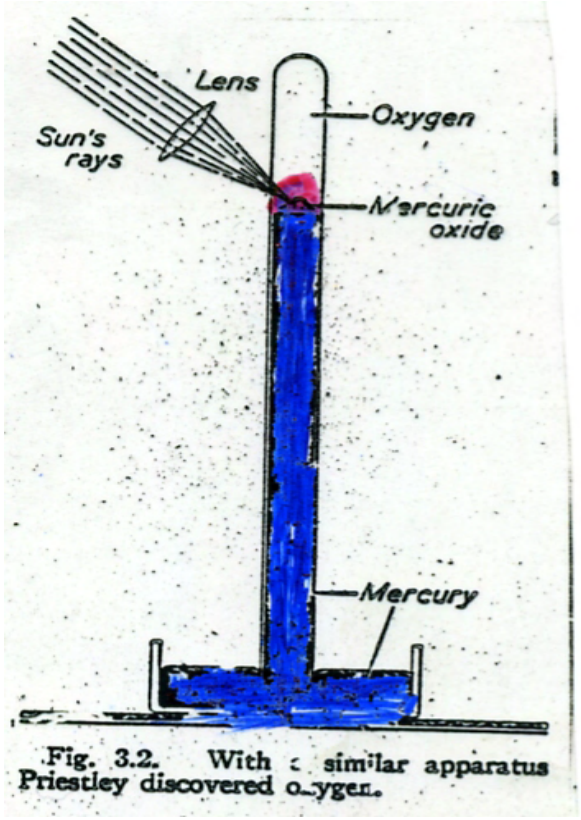


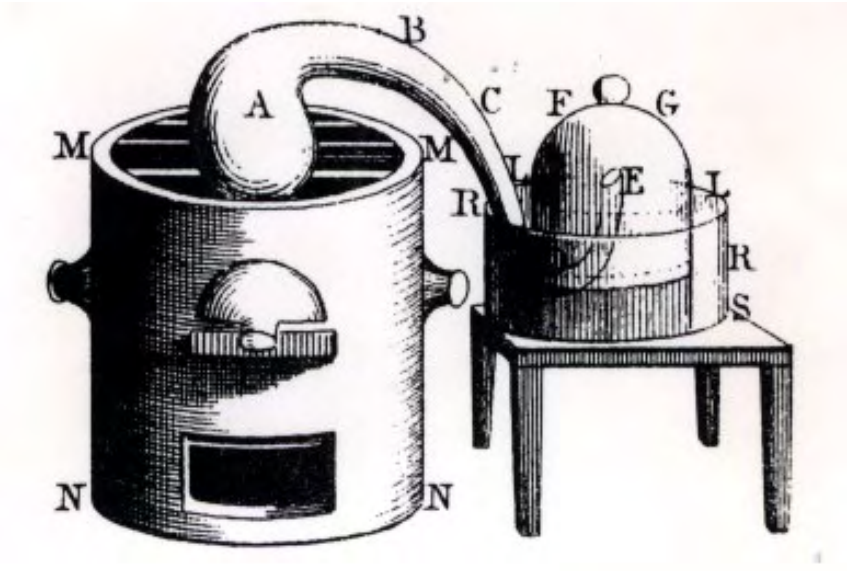
Fig. 3.2. With a similar apparatus Priestley discovered oxygen.

Lavoisier's famous experiment

Lavoisier heated mercury and air, using a bell-jar, for 12 days. Red mercuric calx (HgO) formed and the volume of air decreased from 50 to 42 cubic inches.

The remaining air was determined to be atmospheric mofette, and later renamed azote (nitrogen).

The red mercuric calx [HgO] was heated in a retort producing 8 in^3 of dephlogisticated air (Oxygen).



In modern terms:

$Hg(l) + O_2(g) \rightarrow HgO(s)$

and then stronger heating reverted the calx to the original substances (which the doctrine of phlogiston would predict to be impossible):

$HgO(s) \rightarrow Hg(l) + O_2(g)$

Lavoisier's famous experiment,,,

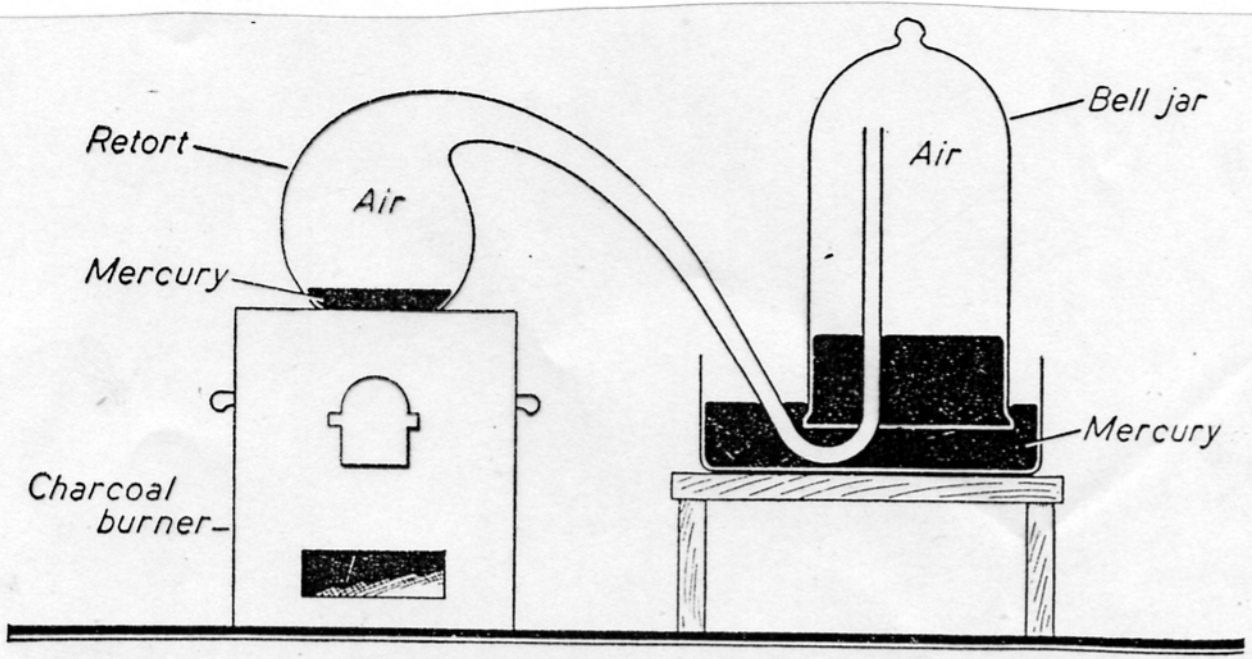


Fig. 3.4. A reproduction of a sketch made by Madame Lavoisier of the apparatus used by her husband in his famous experiments that led to the oxygen theory of combustion.

Lavoisier was acquainted with the following:

- **1781 Priestly explodes a mixture of "inflammable" gas (hydrogen) and "dephlogisticated" air (oxygen).**
- **In modern terms: 1 Volume of Oxygen and 2 volumes Hydrogen are involved.**
- **Priestly and Cavendish refuse to give up the phlogiston theory.**
- **“Inflammable air” (Hydrogen), they argued, was either phlogiston or water with an excess of phlogiston.**

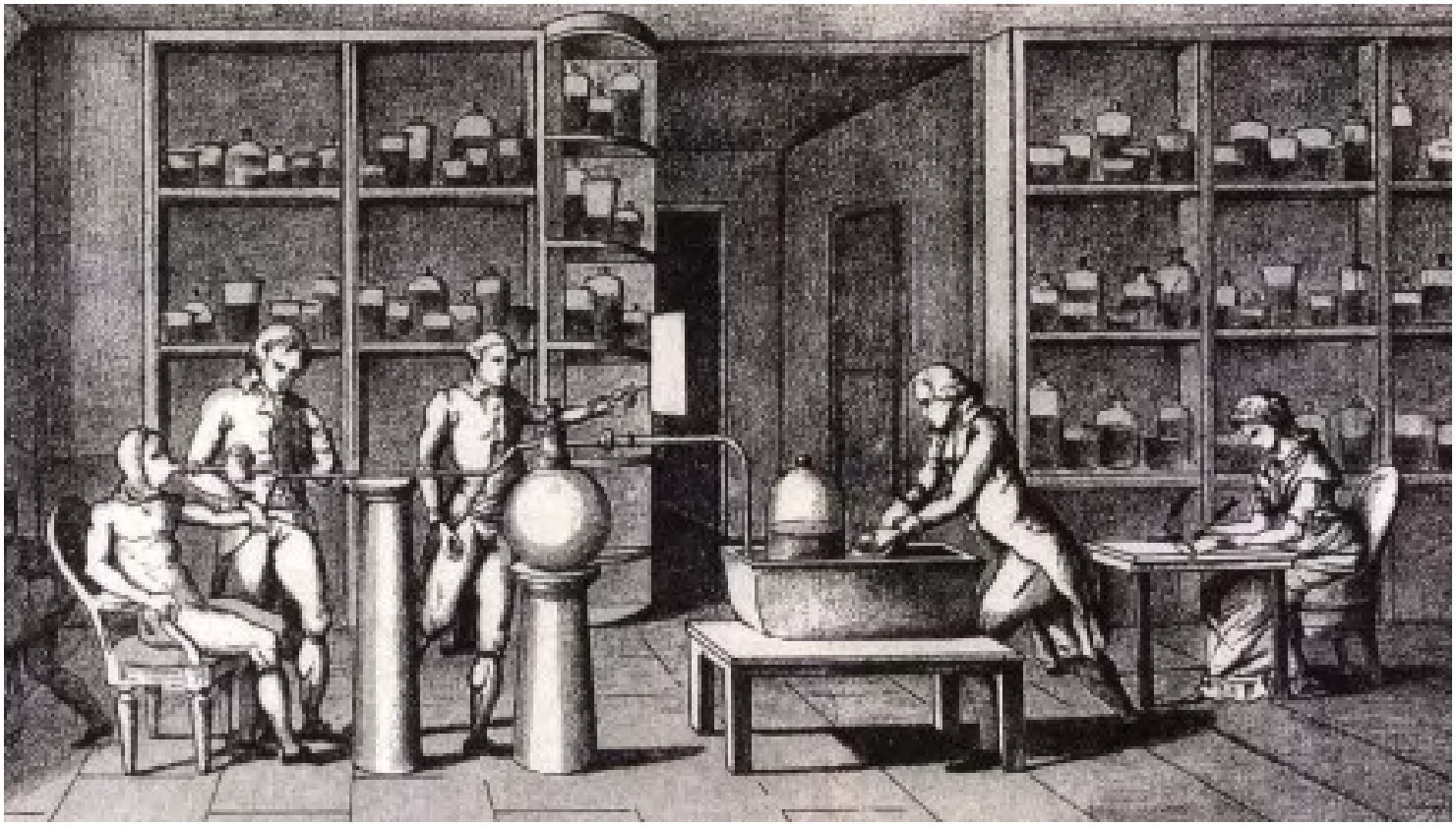
Lavoisier's experiments

- **Lavoisier thought that oxygen ("acid former"; in Germany still called "Sauerstoff") was always involved in the production of acids.**
- **The *operational definition* of an element:**

  The substances that chemists had not succeeded in breaking down into simpler bodies.

- **1776 Lavoisier re-examines the gas and concludes it is "actually a separable component of air".**
- **1776 Lavoisier experiments with respiration.**

Lavoisier conducts experiments in respiration



Who discovered oxygen?

1775 Lavoisie identifies "oxygen".

1775 Lavoisier guesses that water was a compound of two gases, what we today call oxygen and hydrogen.

Who discovered oxygen?

- **The following chemists produced oxygen at about the same time:**

  Carl Scheele, Joseph Priestly, Antoine Lavoisier.

Question:

"Who discovered oxygen?"

The New Chemistry

- **Water is not an element but a compound.**
- **Air is not an element but a mixture of gases.**
- **Combustion and calcination were now considered "reactions of 'bodies' with oxygen".**

Whenever we have Combustion we have:

X + Oxygen--->oxide of X -+ Heat

The new chemistry

- **The New Chemistry is based on:**

- **Conservation of Heat (caloric) in chemical reactions**

and

- **Conservation of mass in chemical reactions.**

- **Finally: Lavoisier understood that**

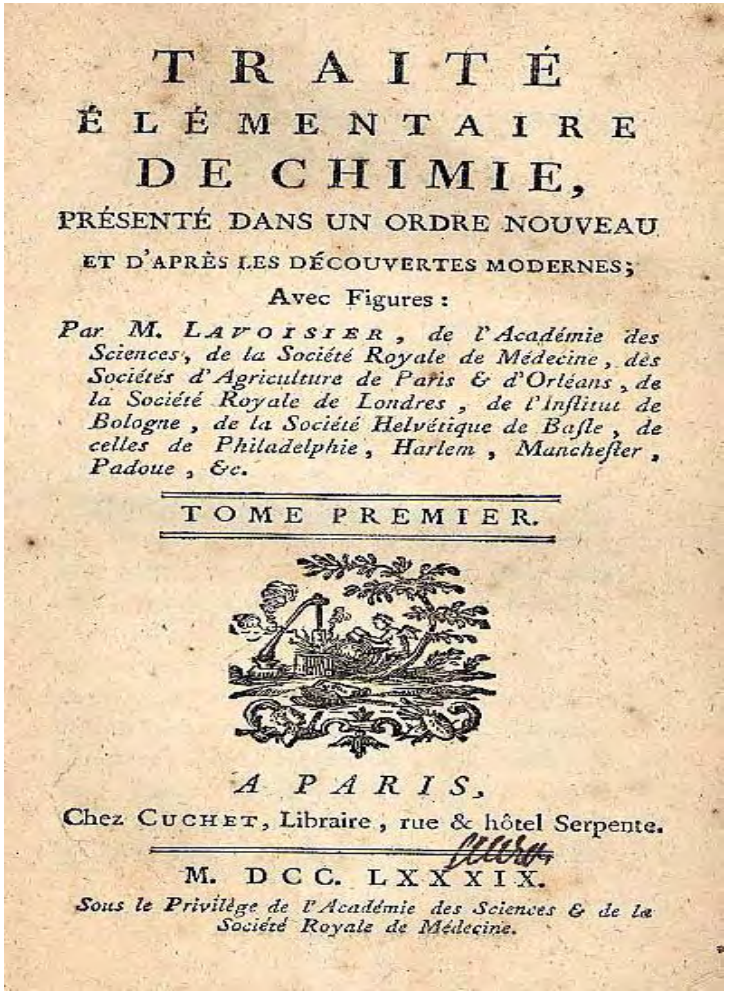
…a *new language of composition was required for chemistry that encompassed the new concepts and quantitative methods*.

The new chemistry

- **1783 Lavoisier publishes a paper:**

  “On the Nature of Water and on Experiments that appear to prove that this Substance is not properly speaking an Element, but can be decomposed and recombined”.

Just before his death in 1794 (by the guillotine) he publishes what is considered the first modern textbook of chemistry.



TRAITÉ
ÉLÉMENTAIRE
DE CHIMIE,
PRÉSENTÉ DANS UN ORDRE NOUVEAU
ET D'APRÈS LES DÉCOUVERTES MODERNES;
Avec Figures :

Par M. LAVOISIER, de l'Académie des Sciences, de la Société Royale de Médecine, des Sociétés d'Agriculture de Paris & d'Orléans, de la Société Royale de Londres, de l'Institut de Bologne, de la Société Helvétique de Basle, de celles de Philadelphie, Harlem, Manchester, Padoue, &c.

TOME PREMIER.

A PARIS,
Chez CUCHET, Libraire, rue & hôtel Serpente.

M. DCC. LXXXIX.

Sous le Privilège de l'Académie des Sciences & de la Société Royale de Médecine.

The new chemistry

Revolution in Chemistry

- Lavoisier's theory better explains known facts of chemistry than Phlogiston theory
- Earth, air, fire, water no longer regarded as elements:
- Earth: many elements or kinds of earth recognized.
- Fire resolved into heat, light, smoke.
- Air composed of O and N
- Water a compound of H and O

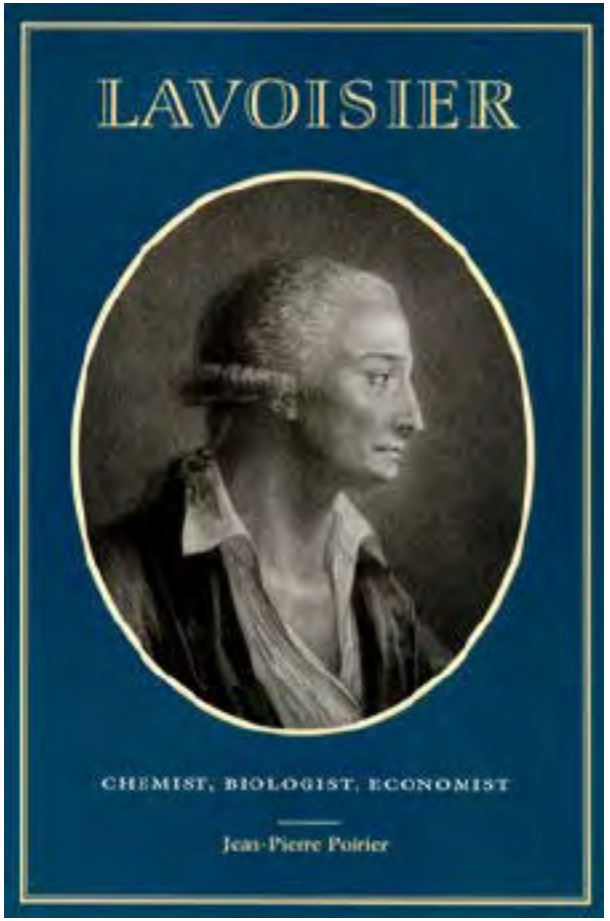


TABLE OF SIMPLE SUBSTANCES.

Simple ſubſtances belonging to all the kingdoms of nature, which may be conſidered as the elements of bodies.

New Names.	*Correſpondent old Names.*
Light	Light.
Caloric	Heat. Principle or element of heat. Fire. Igneous fluid. Matter of fire and of heat.
Oxygen	Dephlogiſticated air. Empyreal air. Vital air, or Baſe of vital air.
Azote	Phlogiſticated air or gas. Mephitis, or its baſe.
Hydrogen	Inflammable air or gas, or the baſe of inflammable air.

Oxydable and Acidifiable ſimple Subſtances not Metallic.

New Names.	*Correſpondent old names.*
Sulphur	The ſame names.
Phoſphorus	
Charcoal	
Muriatic radical	Still unknown.
Fluoric radical	
Boracic radical	

Oxydable and Acidifiable ſimple Metallic Bodies.

New Names.		*Correſpondent Old Names.*
Antimony	Regulus of	Antimony.
Arſenic		Arſenic.
Biſmuth		Biſmuth.
Cobalt		Cobalt.
Copper		Copper.
Gold		Gold.
Iron		Iron.
Lead		Lead.
Manganeſe		Manganeſe.
Mercury		Mercury.
Molybdena		Molybdena.
Nickel		Nickel.
Platina		Platina.
Silver		Silver.
Tin		Tin.
Tungſtein		Tungſtein.
Zinc		Zinc.

Salifiable ſimple Earthy Subſtances.

New Names.	*Correſpondent old Names.*
Lime	Chalk, calcareous earth. Quicklime.
Magneſia	Magneſia, baſe of Epſom ſalt Calcined or cauſtic magneſia
Barytes	Barytes, or heavy earth.
Argill	Clay, earth of alum.
Silex	Siliceous or vitrifiable earth.

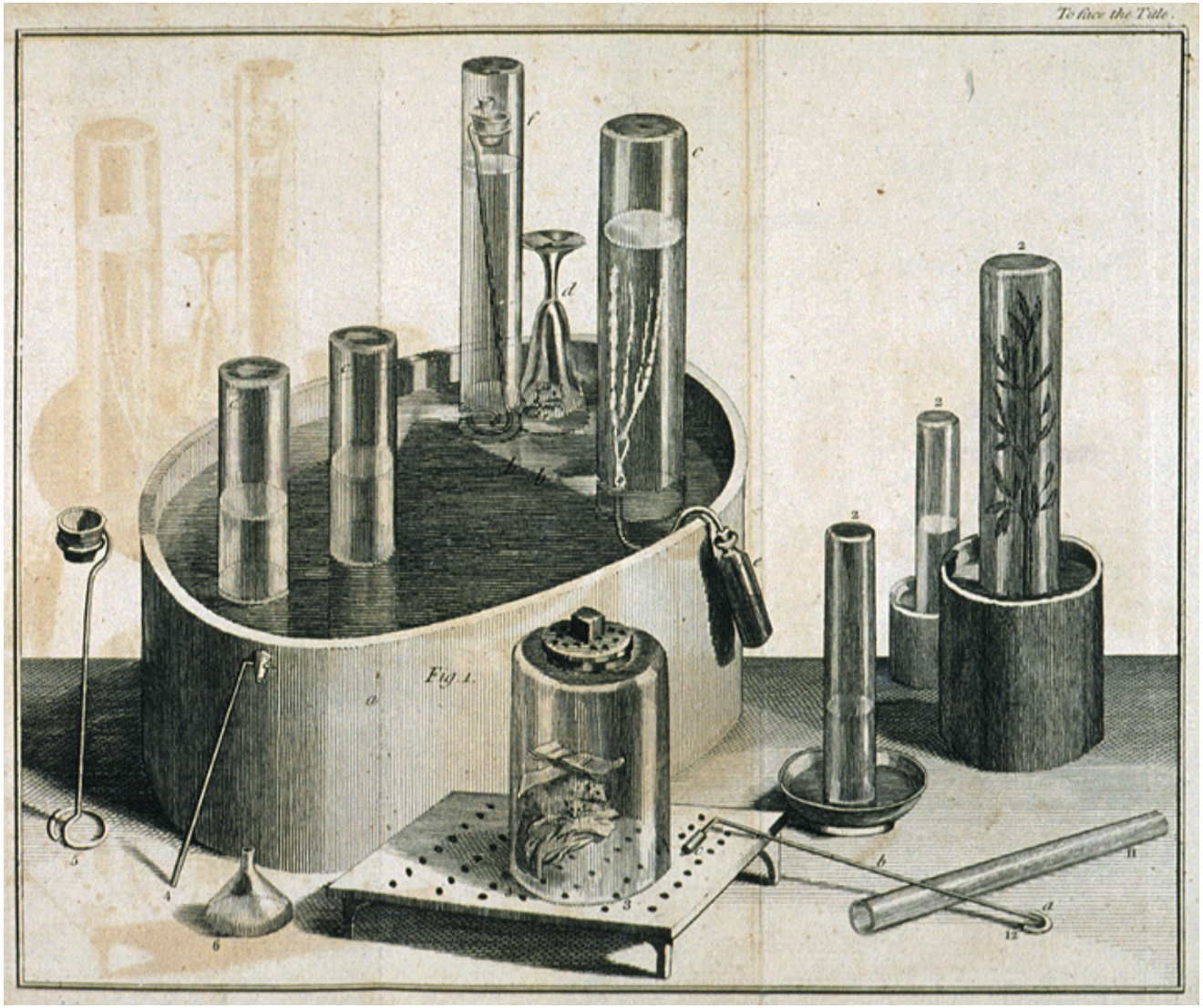
The new chemistry

Lavoisier shied away from using the term “atom” and regarded it a “metaphysical notion that would never accord with Nature”.

Reactions to produce "inflammable" gas (hydrogen), “fixed air” (carbon dioxide),“fire air” (oxygen), and “foul air” (nitrogen)

1. Hydrochloric acid + zinc →
   zinc chloride + hydrogen
   ($2HCl + Zn \rightarrow ZnCl_2 + H_2$)
2. Potassium chlorate + Heat →
   potassium Chloride + oxygen
   ($2K\,ClO_3 + Heat \rightarrow 2KCl + 3O_2$)
3. Calcium carbonate + heat →
   calcium oxide + carbon dioxide
   ($Ca\,CO_3 \rightarrow CaO + CO_2$)

How, do you think, was nitrogen produced?


f
c
d
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2
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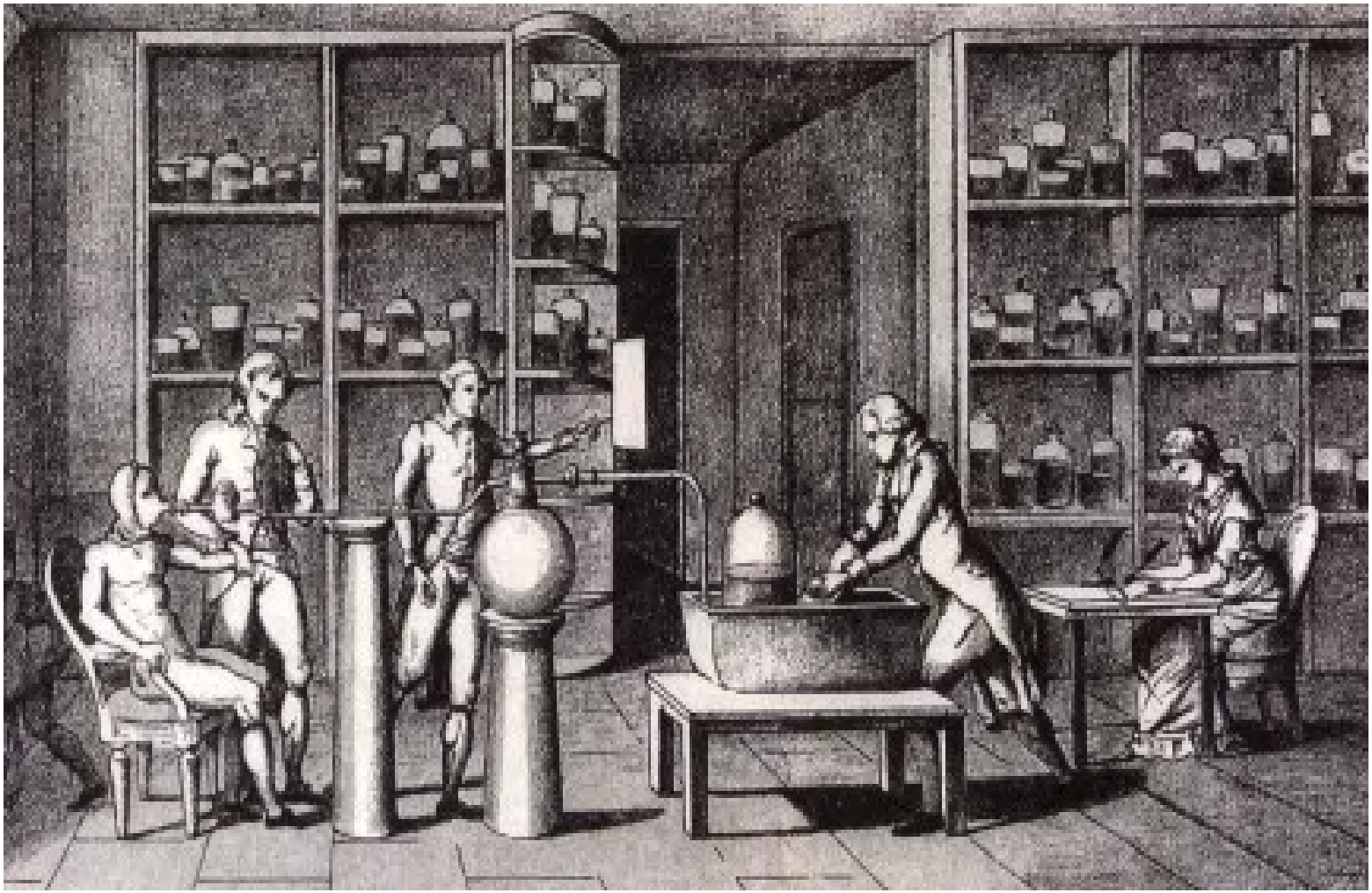
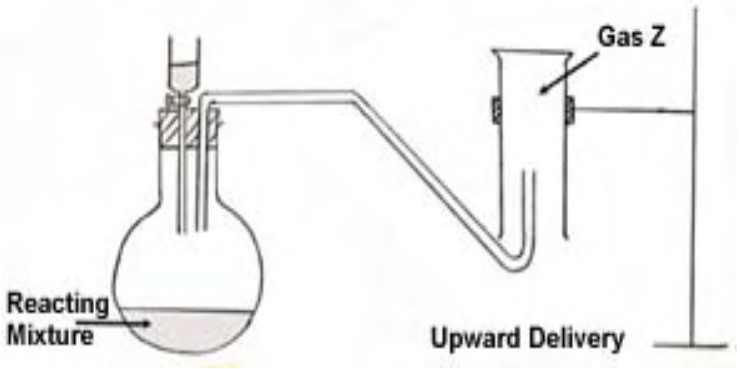
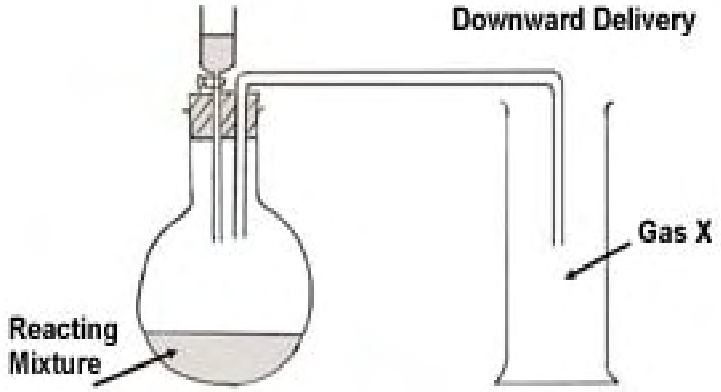
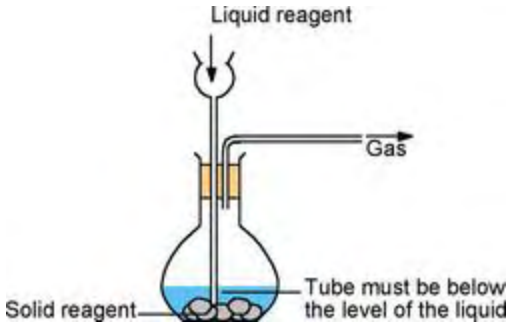
Fig. 1.
a
5
4
6
3
b
11
a
12

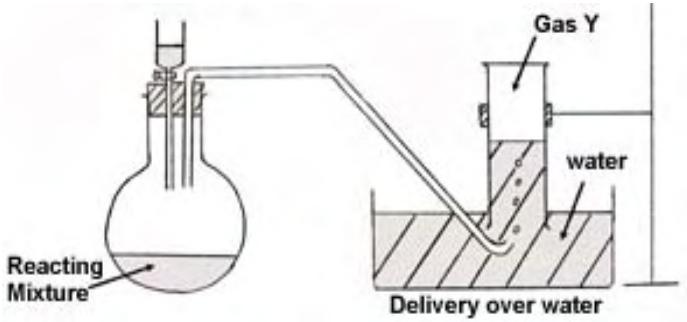


Collecting gases





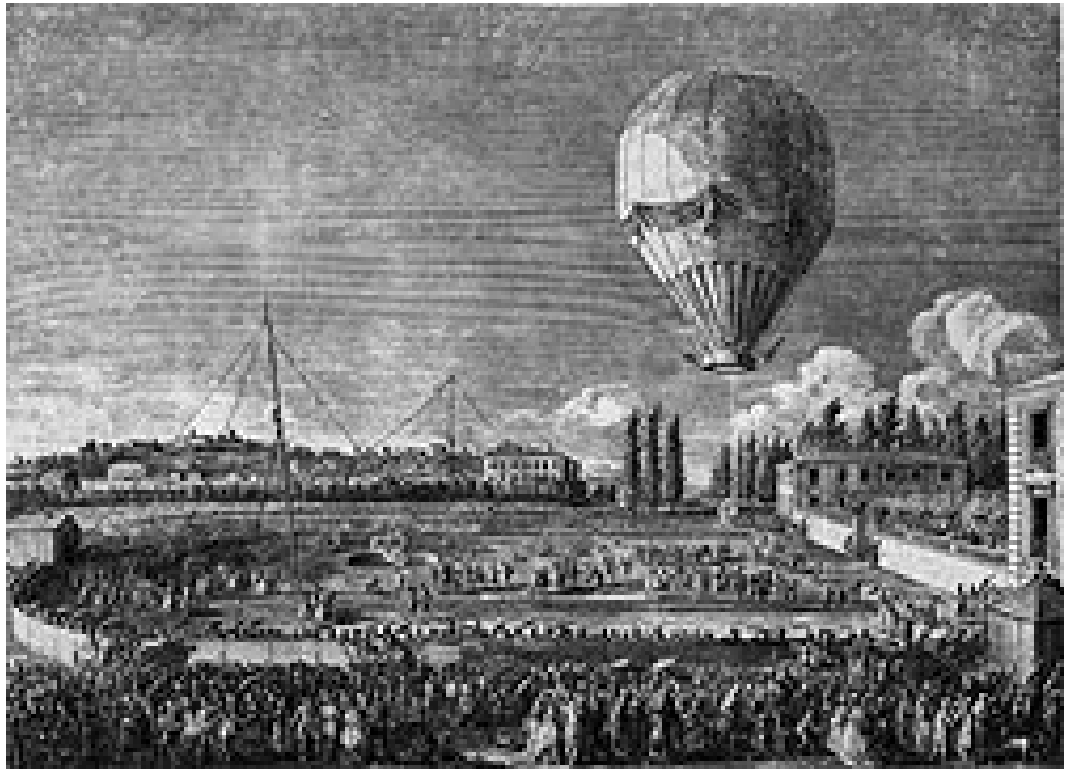




Montgolfier balloon flight in 1783

- **Prof. Thaddeus S. Lowe observing the battle from his balloon *Intrepid* during the Penisular Campaign of the American Civil War, May-August 1862**.

- **Illustration of the Montgolfier balloon flight in 1783**
  Picture courtesy of Clipart




ANTOINE
LAVOISIER
(1743-1794)

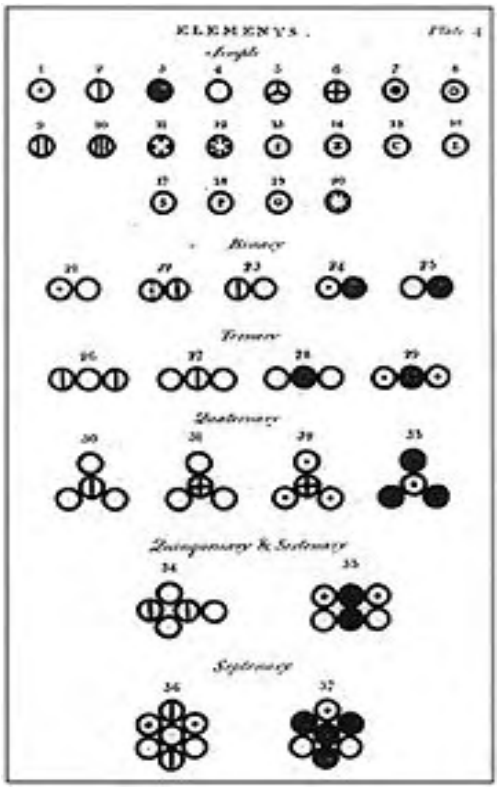
Anticipating the Atomic Theory of John Dalton

- Problem:

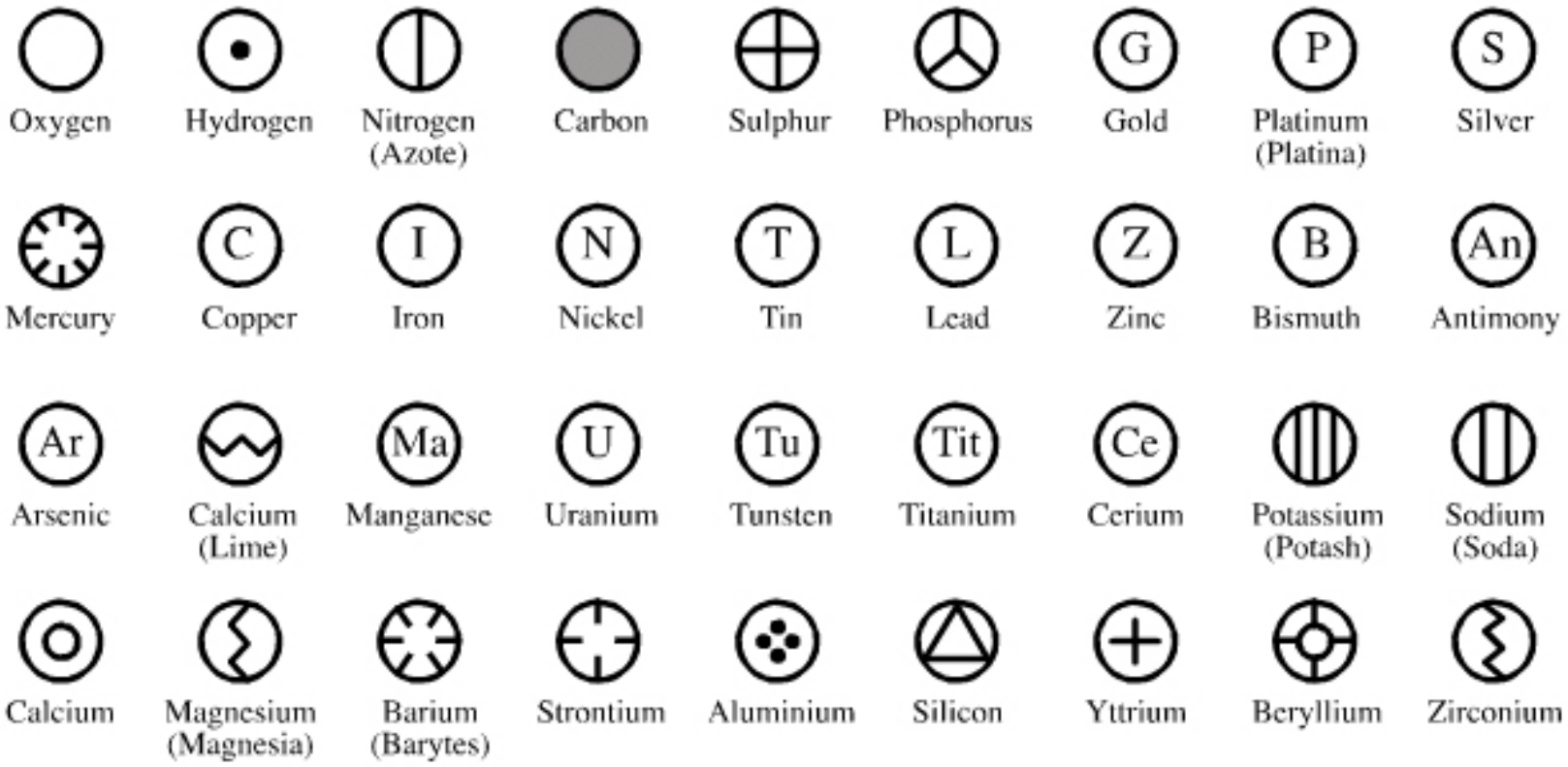
  How can the new idea of *element* be reunited with the older corpuscular tradition of Democritus, Boyle and Newton?

- This is the question that John Dalton tried to answer, in the first decade of the 19th century.

Next: The atomic theory of John Dalton



Next: The atomic theory of Dalton



Alchemy and Astrology

- We have a daily report of astrology in newspapers, that seems to guide the lives of some people.

  Why not have alchemical principles guide your understanding of science around you?

Your Horoscope for today:

Your horoscope for February 28 - March 5, 2008:

- The moon's light changes as she completes her monthly rounds. Just a thin slice is illuminated, with the points facing west indicating her waning position on March 5. This may prove to be a special day, not in terms of anything in the news, but in the sense that a special and magical time may be had.

- The moon travels through Aquarius as she hurries to meet up with her husband, the sun, on March 7. The moon occults Mercury, Venus, and Neptune on March 5. Similar to an eclipse, an occultation occurs when the moon passes directly in front of a planet, blocking its light from our view. An occultation magnifies the impact of the planets and signs involved.

Your Horoscope for today:

- Make it a special day, as the cosmos may be listening to any prayer and may hear our pleas. Along with a prayer, do something special. Blow someone's mind with an act of generosity and kindness that sends out ripples and waves of love, etc..etc…

Philosophical Relevance of Phlogiston Theory

Philosophical Relevance of Phlogiston Theory

- In Kuhnian terms, Stahl's Phlogiston Theory (PT) and Lavoisier's Oxidation Theory (OT) belong to different chemical paradigms. The former belongs to Iatrochemistry, the latter to so-called modern chemistry.

- They differ in fundamental ways about what counts as chemical phenomena; viz., the processes of combustion and calcination. The explanations they offer of what these processes are and their underlying mechanisms are dramatically different.

- Both theories accept that many substances are in fact compounds of others, PT retains the old doctrine of a limited number of basic 'elements' as the fundamental building blocks while OT allows a multiplicity of fundamental elements.

Philosophical Relevance of Phlogiston Theory

- In Kuhnian terms, PT and OT are incommensurable because their central concepts like 'element' and ‘phlogiston' and 'compound' do not overlap in meaning.
- In fact, they seem to mean completely different things in each theory.
- Furthermore, *observations* of the real world are in fact determined by the conceptual resources of each theory.
- For the proponent of PT, the release of Phlogiston is observed in combustion and calcination, and the measure of its actual negative weight or positive lightness in a substance is attainable by weighing that substance before and after combustion or calcination.

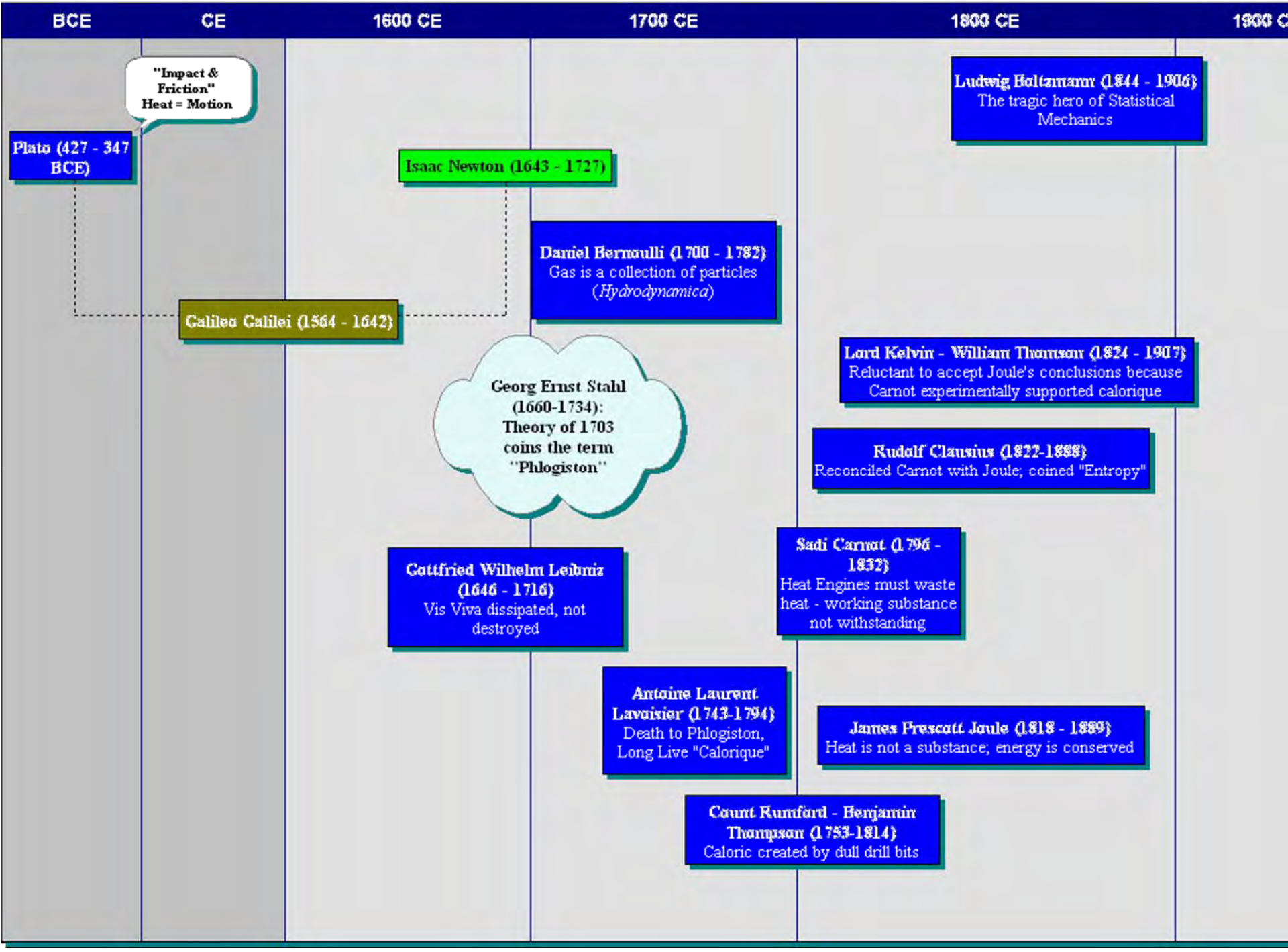
Philosophical Relevance of Phlogiston Theory

- If the very basic observations of each theory are themselves made possible only by already accepting the conceptual fundamentals of each theory, then nothing can count as a relevant observation which is neutral between the theories.

- This means that no observation from OT is sufficient to refute or falsify any theoretical claim within PT and vice versa.

Bad Philosophy of science

- Our world is made up of atoms, yet the atomic model of the universe is nonetheless considered a "theory." When scientists know beyond all reasonable doubt that a particular principle is the case, then it is dubbed a law.
- Laws address the fact that certain things happen, as well as how they happen.
- A theory, on the other hand, attempts to explain why things happen. By definition, an idea that is dubbed a theory has yet to be fully proven, and such is the case with the atomic theory of matter.
- After all, the atom cannot be seen, even with electron microscopes—yet its behavior can be studied in terms of its effects. Atomic theory explains a great deal about the universe, including the relationship between chemical elements, and therefore (as with Darwin's theory concerning biological evolution), it is generally accepted as fact.
- The particulars of this theory, including the means by which it evolved over the centuries, are as dramatic as any detective story. Nonetheless, much still remains to be explained about the atom—particularly with regard to the smallest items it contains.


BCE
CE
1600 CE
1700 CE
1800 CE
1900 C
"Impact & Friction" Heat = Motion
Plato (427 - 347 BCE)
Isaac Newton (1643 - 1727)
Ludwig Boltzmann (1844 - 1906) The tragic hero of Statistical Mechanics
Daniel Bernoulli (1700 - 1782) Gas is a collection of particles (Hydrodynamica)
Galileo Galilei (1564 - 1642)
Lord Kelvin - William Thomson (1824 - 1907) Reluctant to accept Joule's conclusions because Carnot experimentally supported calorique
Georg Ernst Stahl (1660-1734): Theory of 1703 coins the term "Phlogiston"
Rudolf Clausius (1822-1888) Reconciled Carnot with Joule; coined "Entropy"
Gottfried Wilhelm Leibniz (1646 - 1716) Vis Viva dissipated, not destroyed
Sadi Carnot (1796 - 1832) Heat Engines must waste heat - working substance not withstanding
Antoine Laurent Lavoisier (1743-1794) Death to Phlogiston, Long Live "Calorique"
James Prescott Joule (1818 - 1889) Heat is not a substance; energy is conserved
Count Rumford - Benjamin Thompson (1753-1814) Caloric created by dull drill bits