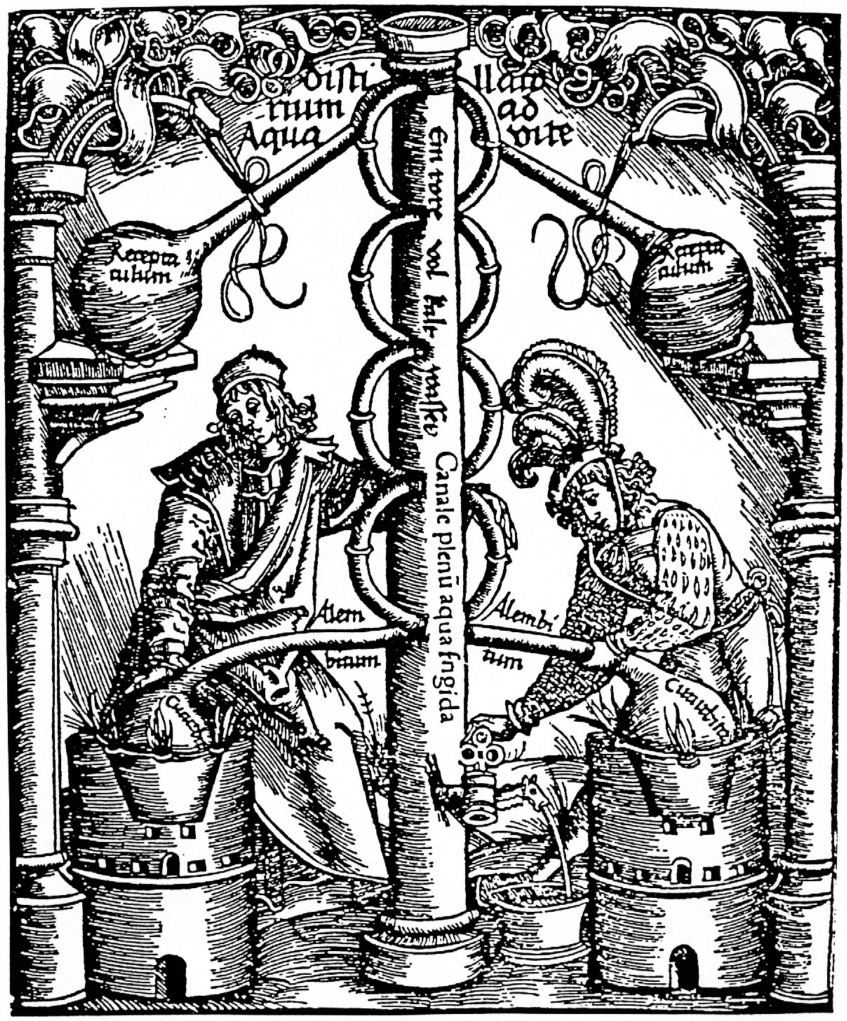
# Composition




## Background

- all modern sciences began as branches of a rational philosophy of nature known as “natural philosophy”
- only in mid 19th century did natural philosophers begin to become known as scientists
- in 17th century, nat’l philosophers interested in the properties and interconversions of substances became known as “chymists”, [from arabic ‘al chymia’, study of earths, as in alchymia]
- in 466 we review the areas of interest to chemists in the approx

order in which they became important historically
- the first area of general interest was composition; how and of what are common substances composed

-our modern view of composition links the physical properties of a substance, eg, water, to its elemental composition, as in $H_2O$, altho the properties of water are not reducible to the properties of hydrogen and oxygen. This is a very sophisticated theory of composition, which evolved out of a historical awareness of three different aspects of a substance's composition

i) ***purity***: how much of a substance 'A' needs to be that one substance 'A' to be classified as the substance 'A'

ii) ***chemical constitution:*** when is a substance composed of a single, simple element, and when of two or more simple elements, and in what proportions

iii) ***essential nature:*** how do chemical substances get their properties

## i) Purity

- pure = "free from anything of a different kind"
- for chemists, nothing is or can be totally pure

- consider "pure" bottled water
- how much Na, Ca, Cl, MG, $SO_4$???
- what is the meaning of "pure water, perfect taste"?
- at what level of purity does water become pure water? 70%, 95%, 99.9%, ??


- as we move to higher percentages, the su

bstance becomes purer. But 100% purity is unattainable, and the properties of a pure substance can only be extrapolated from substances of lower purity.
- historically, a substance was assigned properties once it had been freed of detectable amounts of known contaminants, but the physical properties of substances continued to change as more impurities were detected and removed

eg, s.g. of hydrogen:

- the concept of purity is a practical, “operational” one, ie, a substance is assumed pure if no things of a different nature could be detected in it

- even today, the best spectroscopic methods of detecting impurities can do no more than conclude impurity levels are, for example, below 0.1%, or below 150ppm, etc

**ii) chemical constitution**

- historically, many materials were believed to have been composed of other pure “simpler” substances

eg. acid + base salt

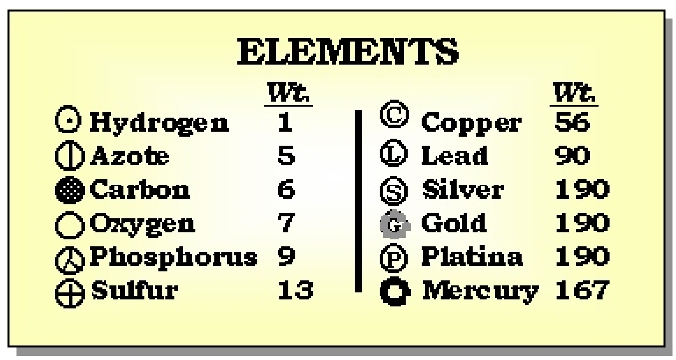
but what is a “simpler” substance ?; a quite complicated decision

Another example: What is “wood” made of? What is “wood”?

- complex substances were assumed to result from the combination of simpler substances; these simple ones might have also been derived from even simpler substances.
- “real” simple substances can’t be broken down any further.

Thus, simple can only be ***operationally*** defined until the 1800s. A substance is simple when it can't be made from anything simpler.
- operationally – simple as long as nobody knows how to break it down by known methods, or operations.
- thus, a substance is simple only until it could be analyzed into, or synthesized from, still simpler substances, ie, no philosophical criterion for simple, elemental substances.

- therefore, the concept of composition of a substance is an experimental one, that relies on things such as observation and experimentation; hence transient, until John Dalton equated atoms with the simplest units of chemical elements (1803)




**iii) essential nature**

- where do the properties of certain substances come from? Why is a substance the way it is? What confers the essential nature (the physical and chemical properties)to substances?

eg, let us return to salt formation

- where in a salt have the properties of the acid and the base gone? Are the constituents mixed together and blended in the compound? Or, transmuted into a new substance, ie, have all the properties of the acid / base became salt entirely? Can the salt constituents be converted back to acid and base components?

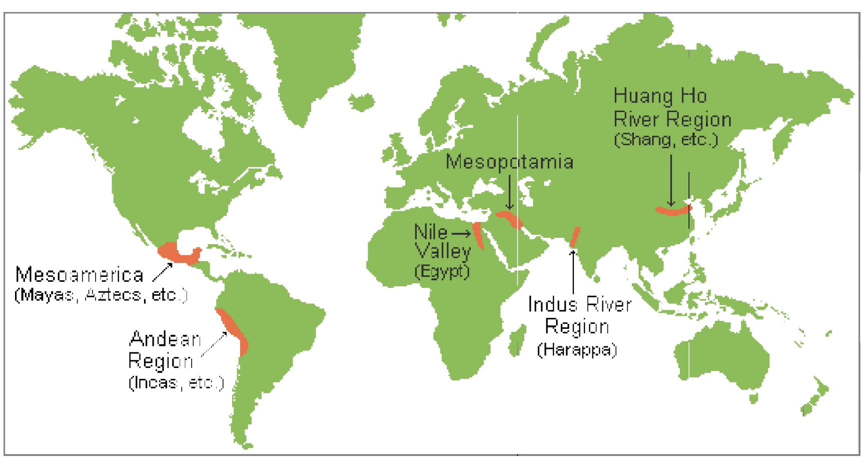
- thus, we must try to set aside our modern understanding (which is a very sophisticated explanation based on atoms and molecules) of composition while we look at its historical development.

## Early Metaphysical Ideas

- "metaphysics" - *concerned with first principles and ultimate grounds*; in natural philosophy often refers to postulated entities below the level of observation

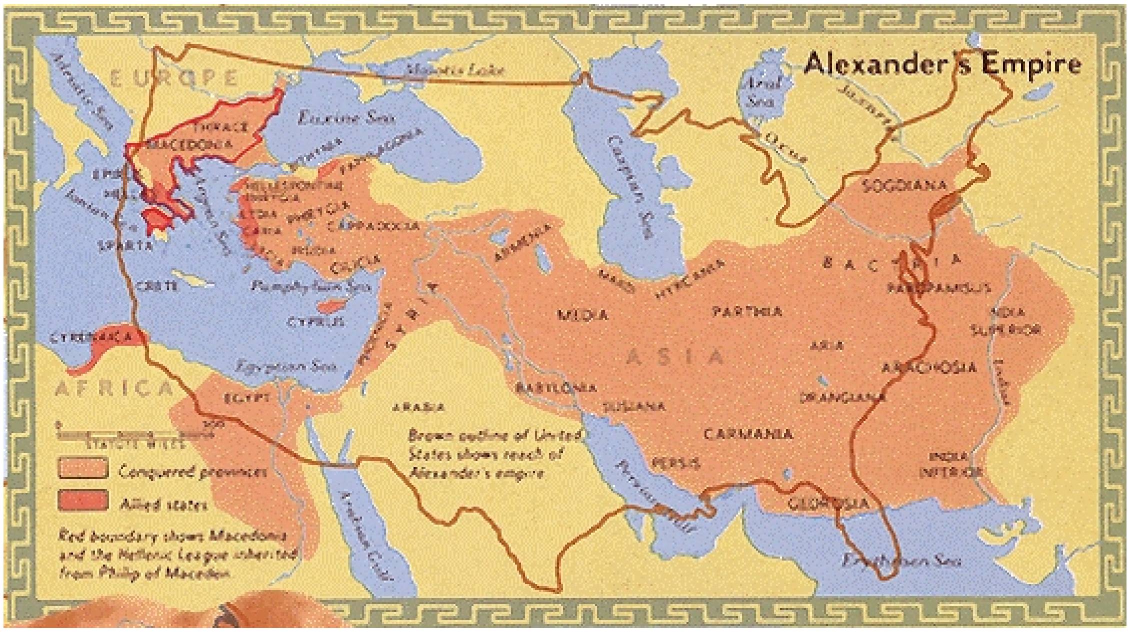
- first influential contributors to our modern scientific world view were the natural philosophers of classical Greece, ca 600-300 BCE
- they sought to explain material aspects of the natural world with ***rational, material, causal modes of explanation***

❖ historical aside - why the Greeks??




Early civilizations ca 3000 BCE

Alexander the Great's Empire, 300BCE




- perhaps rational explanations arose to reconcile world views of the Macedonian (Greek), Egyptian and Mesopotamian civilizations, interconnected by Alexander's conquests (??) ❖

- big three Greek philosophers, Socrates (d.399 BCE), Plato (d.347 BCE), Aristotle (d.322 BCE; Alexander's tutor)
- Aristotle major contributor to natural philosophy

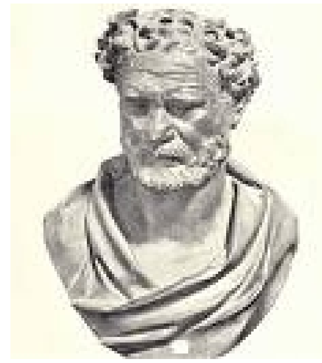
- Greek natural philosophers identified two basic requirements of theories meant to explain/understand material substances

☆ i) substances must have different, but stable properties, eg, water, rock, wood
but, ii) substances must have the ability to change properties under certain conditions

- rival philosophical schools proposed two different, competing theories

1. Atomic Hypothesis

- developed first by Leucippus and extended by his pupil **Democritus** (fl.450 BCE)



- all substances composed of ***one primary substance***, which existed in an infinite number of ***indivisible, differently-shaped atoms, moving in a void***

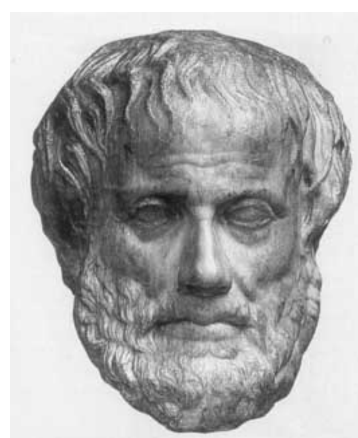
- atoms had different sizes and shapes and mixed together in different ways to form all substances found in the world (more in **atomism**, later)

- atoms gave substances their permanency, and their exchange and rearrangement was responsible for change

2. Multiple Elements

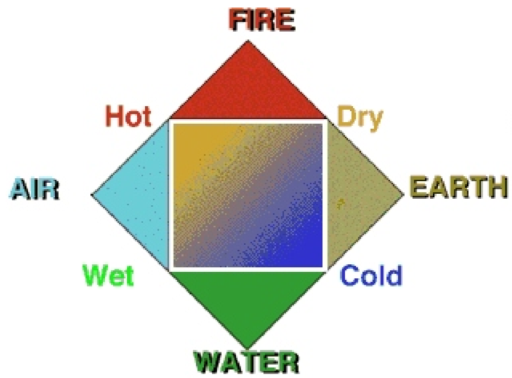
- various common substances were proposed as irreducible fundamental elements (eg, air, earth, water, fire; see later) by various Greek philosophers

- **Aristotle** (fl. 350 BCE) sought to unify their ideas by proposing that human perception and reasoning should decide the issue



- argued that most reliable human sense was ***touch***, and the four ***qualities*** sensible by touch were ***hot, cold, wet and dry***

- then argued that the 4 qualities could combine in 4 different pairings with one ***neutral, infinitely-divisible substance*** to form ***four primary elements - air, earth, fire and water***, as shown in the diagram




- when combined in a substance, the paired qualities were united to substance so homogeneously that the substance was ***infinitely divisible***
- under the influence of natural processes' eg' fire, fermentation, digestion, etc, or under the direction of a skilled operator, eg, an alchemist, any substance could be ***transmuted*** into any other by the correct adjustment of qualities

- Aristotle did no experiments (that was a task left to humble artisans) but supported his ideas by appropriate examples

eg, water ➟ air required addition of ______________

and, since on heating bone gave flame, water droplets and ash, he suggested bone = __earth + __ water + __ fire

❖ historical aside:
- the centuries following the Greek "golden age" saw the introduction in the Middle East of the world's major monotheistic religions (Judaism, Christianity and Islam). All shared the same foundational religious tenets (books of the old testament), and all incorporated the natural explanations of Aristotle's cosmology into their world view

- consequently Aristotelian views of physics, biology, astronomy and chemistry became part of religious orthodoxy
- Aristotelian cosmology was questioned first in astronomy, as an earth-centered universe was replaced by a sun-centred one in the 16th century ❖

- Aristotle's theory of 4 primary elements, infinitely divisible, combined in more complex substances, remained largely unchallenged until the 16th century

- there are still remnants of Aristotle's 4 elements in modern times: can you think of some??

## Alchemy

- from 300 BCE-1600AD, study of material substances was dominated by ***alchemy*** - the attempt to mimic nature by transmuting the base metals into gold, while simultaneously improving one's spiritual awareness
- this was a theoretically-sound process, consistent with both Aristotelian matter theory and religious thought
- despite failure to make gold, the alchemists accumulated a great deal of experimental knowledge, including properties of many specific substances, such as metals, acids, bases and salts
- altho alchemists accepted the Aristotelian theory of the elements, they increasingly adopted a chemical model in which it was assumed that

☆ chemical similarity = compositional similarity

- thus laboratory properties of substances began to replace metaphysical ones as unifying principles
eg, all substances that burned were assumed to contain a combustible component, and

- the component that contained most of the combustible property was ______________
- the three most commonly accepted property-bearing substances were:

| chemical property | constituent | in purest form |
|---|---|---|
| fluidity | liquid metal | mercury |
| flammability | combustible material | sulfur |
| saltiness | salty material | marine salt [NaCl] |

- the most famous alchemist was the Arabian, Jabir (aka Geber, fl.800); he proposed, using the classification scheme above, that

| | | | |
|---|---|---|---|
| metals = | sulfur | + | mercury |
| | (combustibility) | | (fluidity, malleability) |

- this belief fuelled all alchemy, because it was believed that all metals could be interconverted if the proportions of sulfur and mercury could be properly adjusted

- Theophrastus Bombastus von Hohenheim, who called himself **Paracelsus** (fl. 1530), an alchemist who used chemicals to treat illnesses (eg, mercury salts for syphilis),extended the alchemists' three compositional substances to all material substances

- he claimed all substances were composed of three elements he called the ***tria prima***, ie,

| | | |
|---|---|---|
| ***salt*** | conferred | solubility, incombustibility |
| ***sulfur*** | " | flammability |
| ***mercury*** | " | malleability, liquidity |

- the natural substances salt, sulfur and mercury were the purest versions of the tria prima

❖Historical aside: in the 15th century Johannes Gutenberg invented the printing press, which used interchangeable metallic type fonts to form typeset pages for printing. After 1500 hand-copied books and manuscripts were replaced by better quality, much cheaper and more widely distributed printed books. Soon knowledge became available to all who could read, and ideas could be disseminated much more widely and effectively ❖

- Paracelsus brought chemistry to the attention of physicians (who diagnosed illnesses and prescribed medicines) and apothecaries (who made and sold the medicines), and after 1600 they contributed the most to ideas of composition

## Simple and Compound Substances

- in 1615 the French apothecary **Jean Beguin** published the results of the following chemical transformations:

- Beguin proposed the “essential natures” of the simple substances antimony, sulfur, mercury and acid remained unchanged as they first combined to form the binary compounds and then exchanged partners to form new binary compounds in a “double decomposition” reaction

-in 1617 the Italian physician Angelo Sala extended Beguin’s ideas by including weight measurements. He reported

copper + vitriolic acid + water $\rightleftarrows$ copper sulfate

$$[\ Cu + H_2SO_4 + H_2O \rightleftarrows CuSO_4{\bullet}5H_2O\ ]$$

- he also reported that the starting materials combined in fixed weight proportions, and could be recovered from copper sulfate
- this was good experimental evidence for the idea of compound formation by the combination of simpler substances

- thus began the operational definition of compounds; compounds were to be viewed as unions of simpler substances which could be isolated, weighed and measured (even if the isolated simple substances could in theory be made up of non-isolatable Aristotelian elements or alchemical elements)

- these ideas were widely disseminated by the German physician **Georg Stahl** (1660-1734)

- Stahl emphasized that chemistry was an ***experimental science***, and one that should concern itself only with substances that could be characterized in the lab


Abb. 34. Georg Ernst Stahl 1660—1734.

- Stahl organized all chemical substances in a hierarchy of structure, ie,

| | |
|---|---|
| Principles | (Simplest chemical bodies) |
| Mixts | (2 or more principles) |
| Compounds | (2 or more mixts) |
| Aggregates | (2 or more compounds) |

- he suggested experimental operations could determine the constituents of all substances except principles

- Stahl concluded salt formation was a simple addition reaction, ie

acid + base ➜ salt

- this view was accepted until the middle of the 19$^{th}$ century (because the reaction was usually done in aqueous solution, water was not identified as one of the products)

- Stahl used the term ***affinity*** for the attractive property that held two units together in compound substances

## Affinity Tables

- Stahl's concept of affinity forces was used to explain single displacement reactions, such as

A—B + C ➜ A—C + B

if the affinity of A for C exceeded that of A for B

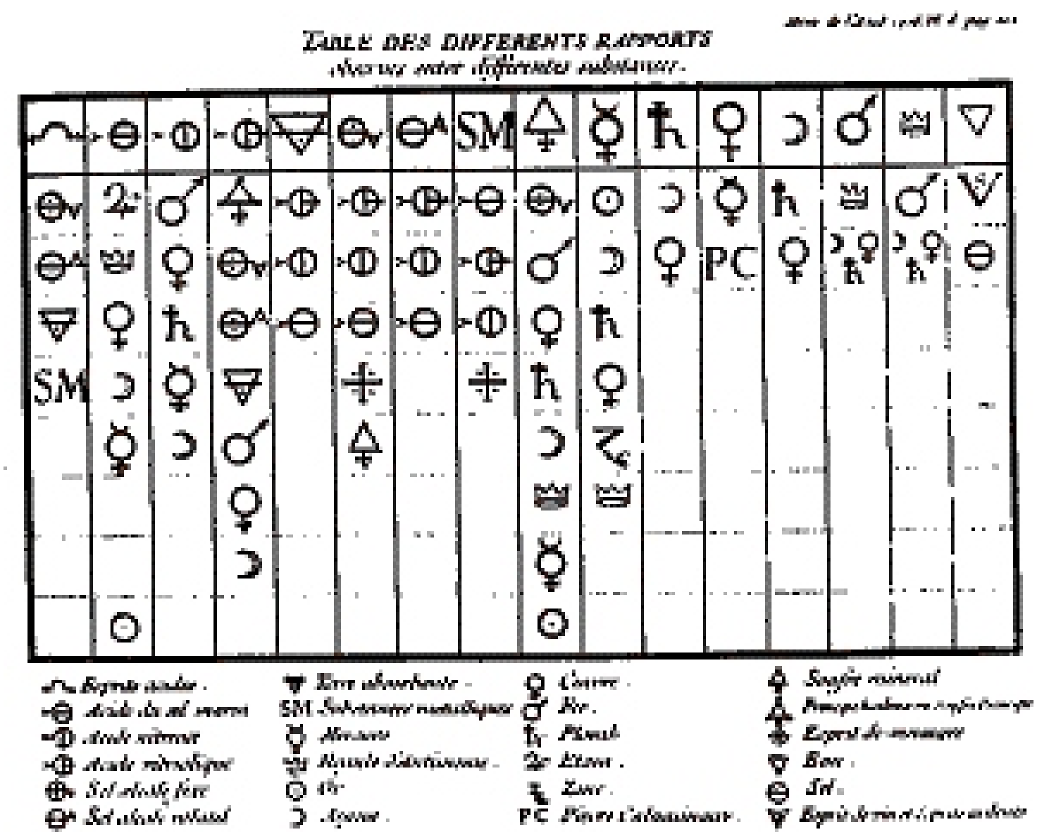
- this affinity concept was one of the <u>earliest unifying theories</u> in chemistry as it could be used to explain known reactions and predict some previously-unknown ones

Note: simple affinity sequences can explain single displacement reactions, but were not easily applied to double displacement reactions, eg, how to predict the reaction direction of

$$A—B \;+\; C—D \;\rightarrow\; A—C \;+\; B—D$$

such a reaction will give the products shown only if

- in 1718 the French apothecary Etienne Geoffroy published the first influential organizational scheme for reactions, a tabular summary of experimentall-determined affinity relationships he called a Table des Rapports, or Table of Affinities



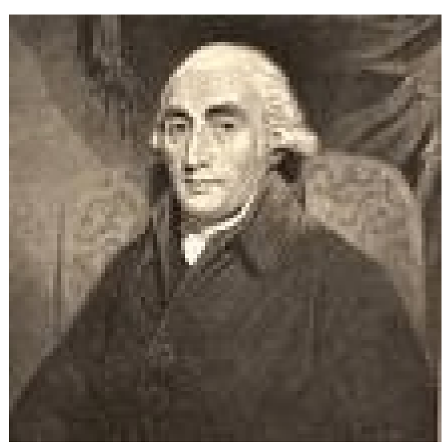
- Geoffroy arranged substances in columns beneath a title substance according to the strength of the affinity of each substance for the title substance
- in each column a substance in a column would displace one below it when forming a compound with the title substance

- eg, column 9 (mineral sulfur)
  sulfur combines most strongly with fixed alkali [sodium bases, eg, sodium carbonate], then with metals in the sequence iron, copper, lead, etc
  [ in modern terms if metallic iron is reacted with copper sulfide, iron sulfide will form and copper will be displaced ]

- the affinity table served both as a summary of known reactions and guide to future research (ie, to extend it); both Aristotelian and alchemical elements had been superceded by observable (and predictable) reactions on laboratory substances

- enlarging affinity tables became the major [490] research project of the 18th century, culminating in Tobern Bergman's massive table of 1775 (see later, Affinity)
- affinity concepts reinforced the theory of compound formation by the union and displacement of constituent, simpler sunbstances

## Joseph Black and the Chemical Balance



- in 1756 **the Scot Joseph Black** (1728-1799) reported his results on the decomposition of the alkaline earth magnesia [$MgCO_3$]

- he was a physician who was trying to find a way to decompose bladder stones, and used magnesia as a model compound

- Black decomposed magnesia by heating, ie,

magnesia ➜ calcined magnesia + "fixed air"
[ $MgCO_3$ MgO $CO_2$ ]

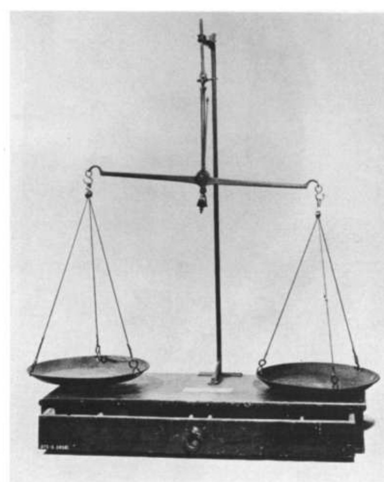
and he determined the ***weight changes*** of the reaction!!

- this is one of the most important discoveries in the history of chemistry for two reasons:

☆ 1. It was the first discovery of an "air" [gas] with distinctive properties different from common atmospheric air
- air ceased to be a fundamental element, and chemists everywhere started to search for other new airs, and found several

☆ 2. Black determined that on heating magnesia lost 58% of its weight [modern = 52%], and the weight loss was nearly the same as the weight of the product gas, which he named **fixed air**

- Black also recombined the product fixed air with the calcined magnesia to reform magnesia, ie, magnesia could be decomposed and then reconstituted from its component substances



Black's balance

- Black's discovery initiated a new age in chemistry because it
  - i) brought distinct gases into the known chemical substances
  - ii) showed simple chemical substances maintained their chemical integrity during combination and decomposition
  - iii) demonstrated that weight relationships were important features of chemical reactions

(was Black's discovery lucky, fortuitous, planned, serendipidous?)

## Lavoisier and the Conservation of Mass

- Black's discovery, and subsequent discoveries by British chemists (see later in oxidation/reduction) were the foundation of the revolutionary contributions of the French chemist **Antoine Lavoisier** (1743-1794); commonly viewed as the "father of modern chemistry"

- Lavoisier began his chemical researches in 1770 and studied every reaction with close attention to weight changes. In 1789 he published his famous chemistry text **Traite Elementaire de Chimie** (Elementary Treatise on Chemistry) in which he summed up his new chemical ideas. In that text he made the first definitive statement of the ***law of the conservation of mass***

☆☆ *We may lay it down as an incontestable axiom, that in all operations of art and nature, nothing is created; an equal quantity of matter exists both before and after the experiment*

- Lavoiser knew, from Black and others, that fixed air created an acid when dissolved in water, ie,

fixed air + water ➜ aqueous acid
[ $CO_2$ $H_2O$ $H_2CO_3$ ]

he concluded that fixed air must contain a principle of acidity

- the Englishman **Joseph Priestley** visited Paris in 1774 and dined with the Lavoisiers; he told Lavoisier that he had recently discovered a remarkable new air (which he termed “phlogisticated air”, see later) by heating the compound known as red precipitate

$$\text{red ppt} \rightarrow \text{mercury} + \text{a new air}$$
$$[\ HgO \qquad Hg \qquad \tfrac{1}{2} O_2\ ]$$

- a few days later, Lavoisier isolated the new air himself and found that it conferred acidic properties when combined with sulfur and phosphorus, ie,

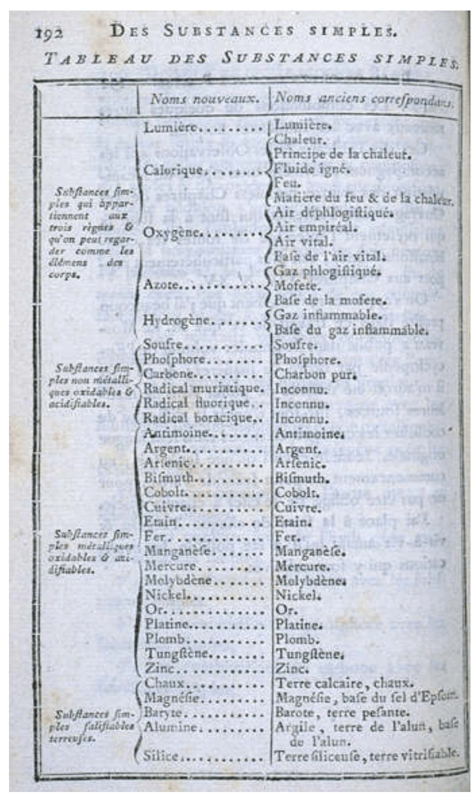
$$[\ S + O_2 \rightarrow \rightarrow SO_3 + \text{water} \rightarrow H_2SO_4\ ]$$
$$[\ P + O_2 \rightarrow P_4O_{10} + \text{water} \rightarrow H_3PO_4\ ]$$

- from these observations, Lavoisier concluded Priestley’s new gas was the source of acidic properties and gave it a new name **oxygen** (from Greek = “acid former”)

- in 1781 Lavoisier determined by analysis that fixed air was composed of carbon (28% by wt) and oxygen (72%) [see problem assignment #1], thus explaining why fixed air made water acidic

- Lavoisier never acknowledged Priestley’s contributions in print

- by making weight data a fundamental part of chemical reactions, Lavoisier was able to better categorize substances as simple (those that could not be decomposed into lighter constituents) or compound, and in the 1789 Traite published his list of ***55 simple chemical elements***



192 DES SUBSTANCES SIMPLES.

TABLEAU DES SUBSTANCES SIMPLES.

| | Noms nouveaux. | Noms anciens correſpondans. |
|---|---|---|
| Subſtances ſimples qui appartiennent aux trois règnes & qu'on peut regarder comme les élémens des corps. | Lumière | Lumière. |
| | Calorique | Chaleur. Principe de la chaleur. Fluide igné. Feu. Matière du feu & de la chaleur. |
| | Oxygène | Air déphlogiſtiqué. Air empiréal. Air vital. Baſe de l'air vital. |
| | Azote | Gaz phlogiſtiqué. Mofete. Baſe de la mofete. |
| | Hydrogène | Gaz inflammable. Baſe du gaz inflammable. |
| Subſtances ſimples non métalliques oxidables & acidifiables. | Soufre | Soufre. |
| | Phoſphore | Phoſphore. |
| | Carbone | Charbon pur. |
| | Radical muriatique. | Inconnu. |
| | Radical fluorique | Inconnu. |
| | Radical boracique | Inconnu. |
| Subſtances ſimples métalliques oxidables & acidifiables. | Antimoine | Antimoine. |
| | Argent | Argent. |
| | Arſenic | Arſenic. |
| | Biſmuth | Biſmuth. |
| | Cobolt | Cobolt. |
| | Cuivre | Cuivre. |
| | Etain | Etain. |
| | Fer | Fer. |
| | Manganèſe | Manganèſe. |
| | Mercure | Mercure. |
| | Molybdène | Molybdène. |
| | Nickel | Nickel. |
| | Or | Or. |
| | Platine | Platine. |
| | Plomb | Plomb. |
| | Tungſtène | Tungſtène. |
| | Zinc | Zinc. |
| Subſtances ſimples ſalifiables terreuſes. | Chaux | Terre calcaire, chaux. |
| | Magnéſie | Magnéſie, baſe du ſel d'Epſom. |
| | Baryte | Barote, terre peſante. |
| | Alumine | Argile, terre de l'alun, baſe de l'alun. |
| | Silice | Terre ſiliceuſe, terre vitrifiable. |

- Lavoisier's table of elements, based on observations legitimized by strict adherence to weight conservation and including several new gaseous elements, brought coherence to the study of chemical composition: - the fundamental chemical elements were those that could not be decomposed further, and they remained unchanged when they combined in fixed weight relationships under the control of affinity forces

## Fixed vs Variable Proportions

- study of combining weights in the latter half of the 18th century revealed that component substances nearly always combined in ***fixed weight proportions***

- but one of Lavoisier's colleagues, **Claude-Louis Berthollet** (1748-1822) proposed that study of reactions in solution, in which reagents and products remained in contact with each other, were not so easily explained
- Berthollet proposed that reactions in solution were generally reversible, and the relative amounts of reagents and products were dependent on ***both affinity forces and amounts of material***
- thus for the general reaction

$$A\text{–}B \;+\; C \;\rightleftarrows\; A\text{–}C \;+\; B$$

a greater amount of C causes a greater amount of B to form, even though affinity forces don't change
- Berthollet thus believed compounds formed with a range of compositions, eg, the oxides of tin

tin + oxygen ➜ tin oxide + oxygen ➜ tin dioxide
[$Sn$ $O_2$ $SnO$ $SnO_2$ ]

- Berthollet proposed tin could form a range oxides spanning the range from 12% O to 21% O, ie, combining proportions were variable in some compounds

- Berthollet's proposal was vehemently opposed by another French chemist, Joseph-Louis Proust, who insisted that all compounds were formed in fixed, invariable weight proportions
- Proust argued that a tin oxide found to contain 15% oxygen was, in fact, a mixture of SnO and $SnO_2$

- Proust's ideas were confirmed later in the $19^{th}$ century, but Berthollet's proved influential in developing ideas of equilibrium reactions (see later)

## Modern Beliefs

- we now understand that definite combining proportions result from:
  - i) valency requirements in covalent cmpds, or
  - ii) electrical neutrality in ionic cmpds

- ***but***, there are some crystalline solids known which do have variable proportions, which result from:
  - i) atoms being absent from crystalline sites
  - ii) anions being replaced by electrons
  - iii) some atoms being replaced by different ones
  - iv) foreign atoms present in a crystal

eg, titanium oxide = $TiO_{0.6}$ - $TiO_{1.35}$ and $TiO_{1.75}$ - $TiO_{1.90}$

- such compounds are known as "Berthollides"