A History of Chemistry, Lecture 7 - Synopsis



- The recognition that AIR is material is made possible with the invention of a technique to collect air.

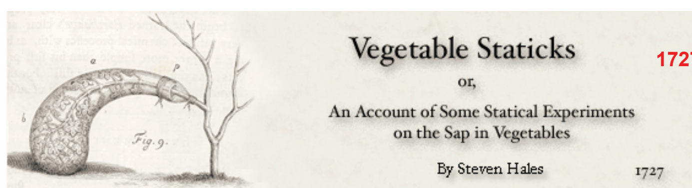
- Accordingly, we shall talk about Stephen Hales who invented the technique but asked the wrong question: "How Much" instead of "<u>what</u>".
- We shall tell about Joseph Black who frees the "fixed air" and weighs it. And about Cavendish who discovered so much and missed the meaning of his discoveries.
- We shall recount the O_2 story and the hailed Priestley, Scheele, & Lavoisier,…
- O_2 the only molecule on which a play was written.
- Finally, we shall discuss the compositional revolution of Lavoisier & The dawn of modern chemistry.

O_2



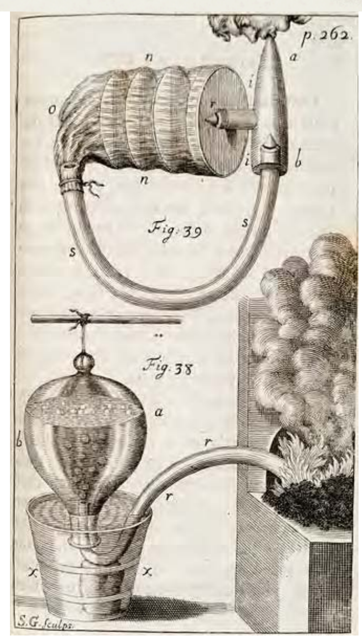
The inventor of the technique for Collecting Air is Stephen Hales:

- He was born in Kent (1677-1761). During his life he was very active (established the 1st colony in Georgia), and was interested in all branches of science.
- In 1727 he published his famous book on the determination the quantity of "fixed airs" in vegetables and solids.

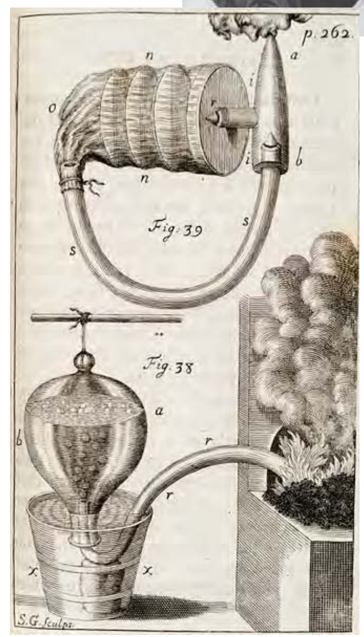


1727

- For this purpose he invented the trough in which he trapped gases that passed through water. The idea is wonderfully simple



• In his book, he states that his goal is to understand the action of God. And that the Creator's wisdom is revealed by numbers, & hence to understand the acts of the Creator we must "number, weigh and measure…as shown by Sir Isaac Newton"



• Like Newton with light, Hales wants to quantify the attraction between the particles of fixed AIR and the "sulphoureous particles" in bodies by measuring the weight of air per unit of weight of the body.

• He obtains the weight from the volume by postulating the same density for all airs.

• Clearly then, his AIR is a uniform entity that enters mechanically into other bodies. No chemical identity!

• Nevertheless, his work draws attention to air and he calls upon chemists: "…may we not adapt this [air],.. Which hitherto has been overlooked and rejected by the chymists?"

How Does Air "Enters" France, the Homeland of Lavoisier?

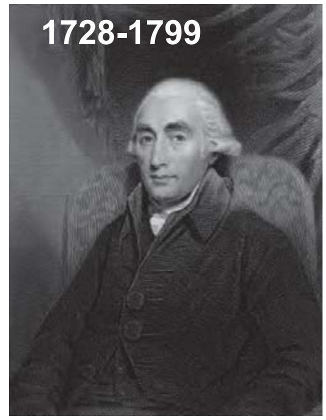
• 1735: conte de Bouffon (1707-1788), who supported Rouelle for the position in Jardines de Plantes, translated into French Hales' book.

• He emphasizes its novelty and the fact that it ought to be studied not only read: "It is a fruitful idea from which follows an infinity of discoveries on the nature of different bodies… Had it been thought possible that certain bodies, such as bladder stones…are more than two thirds air?"

• The new findings influence Boerhaave and Rouelle. And this also causes a renaissance of the 4-elements. For example, Rouelle distinguishes between the physical and chemical aspects of an element; the physical aspects are associated with the"free" element that serves as a matrix or means for causing chemical change (like the "free" FIRE), whereas the chemical aspect is associated with the "fixation" of the element in various bodies. Thus, in Rouelle's systems the AIR appears as a chemical element in bodies, e.g., in calx, alkali (remember K_2CO_3), as well as a free physical element that helps in evaporation and distillation.

Thus, AIR reaches French chemistry & in 1774, Lavoisier summarizes the evidence for the "chemical fixation of AIR".

Joseph Black is part of the AIR story **since he was the first one who distinguished the different types of AIRs in his research on Magnesia Alba($MgCO_3.xH_2O$) , which was a "journey into the magic of chemistry:, destined to release the the air that was fixed into this solid.**



• Black was born in Bordeaux, where his Irish father was a wine merchant. His Scottish mother also came from a family of wine growers and merchants.

• He studied in Glasgow and at age 22 he moved to Edinburgh to study medicine, and stayed there as a Professor, then moved to Glasgow. The chemistry buildings in Glasgow and Edinburgh are called after him.

• While in Glasgow he started his experiment with Magensia Alba, and noticed that Lime ($CaCO_3$) behaves the same. He then shifted to Lime.

Joseph Black and the Fixed Air

• Heating of Lime caused a loss of weight and the product (quick lime) did not effervesce in acid anymore. <u>This proved that the FIXED AIR left the Lime</u>. He noticed a 50% loss of weight and assumed: Lost weight = weight of the FIXED AIR. This is recognition of mass conservation!

Lime Stone = quick lime + fixed air

$$CaCO_3 = CaO + CO_2$$

• The original weight was restored with mild alkali:

Slacked quick lime + mild alkali = Lime Stone + caustic alkali

$$Ca(OH)_2 + K_2CO_3 = CaCO_3 + K_2O\ (KOH)$$

• This was the 1st demonstration that the presence/absence of a certain air is responsible for a specific chemical behavior, as Black generalizes:
"when we mix an acid with an alkali, … the [fixed] air is then set at liberty…; because the alkaline body attracts it more weakly than it attracts the acid, and because the acid and the [fixed] air cannot both be joined to the same body at the same time"

• This is an application of the "elective affinity" concept, and it also contains a seed of recognition that the "FIXED AIR" (CO_2) is itself an acid. Some years later Bergman notes this nature of "FIXED AIR" calling it "AERIAL ACID".

• Black's ideas come under attack (by Irish and German chemists), and is then defended by two French chemists in 1774, precisely when Lavoisier is asked to prepare the report on "chemical fixation of air".

6 Our Next Hero is Henry Cavendish (1731-1810), "*the wisest of the rich and the richest of the wise*" (Biot)

• **Cavendish was belonged to a noble family, the son of Lord Cavendish and the Duchess of Kent.**
He was born in Nice & educated in England. At age 18 he entered studies in Cambridge, but left without graduating. He started working alone in his home.

• **Cavendish was known as an eccentric recluse, who was also very shy. So much so, that he built back-stairs so he could enter his house without meeting his household lady.**

• **The only social events he participated in were the meetings of the Royal Society. But, even there, it was difficult to converse with him: when the conversation did not interest him, his conversant felt that he was "*speaking into a vacancy*", & when the conversation interested him, he would mutter unclearly.**

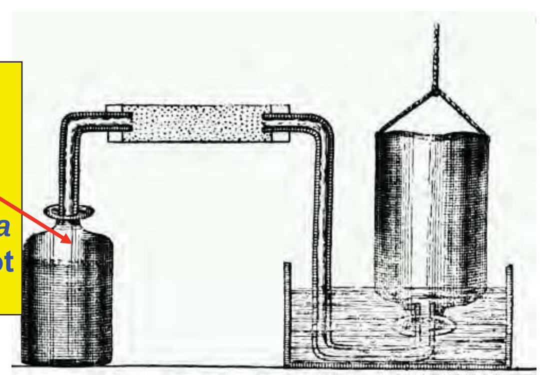
• **After his death, Maxwell found in his archives that he discovered Ohm's law, Coulomb's law, Dalton's partial pressures Law, etc.**

• **In his funeral Sir Humphrey Davy eulogized him: "*If I may be permitted to give my opinion, England has sustained no loss so great as that of Cavendish's death*"**

• **Starting 1766, he publishes papers on, "Experiments with Factitious Airs". He explains: By factitious air, I mean in general…air which is contained in other bodies… and is produced from thence by art [chemistry]" = fixed air**

• **In the 1st paper: production of "inflammable air" and "fixed air" & the "air produced by fermentation and putrefaction"**

• Inflammable air: Metal (Zn,Fe,Sn) in Vitriolic acid & spirit of common salt
• in oil of vitriol and *aqua fortis* the gases were not inflammable



• **His conclusions: (i) When metal dissolves in vitriolic acid the phlogiston embedded in the metal flies away as inflammable air. (ii) When the metal dissolves into oil of vitriol or *aqua fortis*, the metallic phlogiston combines with part of the acid and flies off as gas, but the embedded phlogiston in the gas is not inflammable anymore (NO, SO_2…)**

• **Only in 1783 he will show that combustion of inflammable air gives only water!**

• The phlogiston concept enters into pneumatic chemistry!

Carl Wilhelm Scheele (1742-1786) – The discoverer of oxygen, and the almost forgotten hero, who was resurrected by Historians and the play "Oxygen".

Statue
Köping
pharmacy

- Scheele was of Swedish-German descent. At age 14 he works as an apprentice to a phramacist in Malmö. At 28 he moves to Uppsala to work under Bergman.
- Then he moves to Köping where he buys a pharmacy from a widow. He marries the widow, and dies at 43 after 48 hours…
- Scheele is a Swedish hero, and is immortalized in Köping.

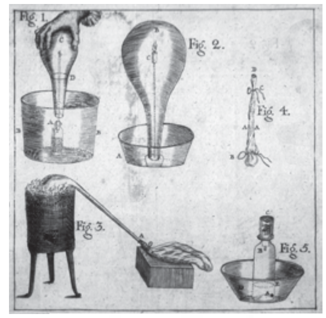
Scheele's love to chemistry is seen from theis except of a letter he wrote to his friend Gotlieb Gahn in 1774:

- "Oh, how happy I am! No care for eating or drinking or dwelling…But to watch new phenomenon this is all my care, and how glad is the inquirer when discovery rewards his diligence; then his heart rejoices"

- The letter was written 2 years after he discovered oxygen. His article was published only in 1777, and so he lost the priority to Priestley (actually 1st Drebble, 2nd Mayow)

8 Carl Wilhelm Scheele's discoveries

• A productive chemist, discovered: Mo(1778), Mn(1774), Ba(1774), W(1781), citric acid, lactic acid, glycerol, prussic acid (HCN in water), HF, H_2S, etc.
• In 1765 Hennig Brand made phosphorous from urine…
• In 1769 - Scheele finds a method to produce P without smell…Sweden leading producer of matches.



• Discovered Cl_2 : He obtained pyrolusite and identified lime and iron. When he treated it with HCl he obtained a green gas [most likely a biological type oxidation with Fe=O + 2HCl -> $Fe(OH_2)$ + Cl_2]

• The gas bleaches a litmus paper, flowers, fruit juices,… He calls it "the dephlogisticated spirit of marine sea".
• Cl_2 was rediscovered by Humphrey Davy, who calls it "chlorine".

• The increased use of phlogistic terminology increases the status of the theory

Scheele and the Discovery of O_2 (1772)

• O_2 was discovered by Scheele in 1772-3 in response to a question from Bergman: "why does my Saltpeter produce red vapors?" Scheele gave a quick explanation, and Bergman suggested to look also at the calx of Mn (MnO_2).
• Scheele heated the calx of Mn and collected the gas in Hales trough, showing that it supported "burning" and hence, calling it the "fire air" = "Luft Feuer" (a phlogistic term).

• He then produced 'fire air' in two methods, using: HgO, Ag_2CO_3, $Mg(NO_3)_2$, KNO_3: (a) he produced saltpeter (KNO_3) by treating aqua fortis with potash (K_2CO_3/KOH). He distilled the KNO_3 with oil of vitriol generating two gases (NO_2 and O_2). He absorbed the NO_2 into a solution of quick lime ($Ca(OH)_2$), and was left with the 'fire air' (O_2). (b) In the 2nd method he heated the calx or the salt strongly and getting 'fire air' and 'foul air' (e.g., $Ag_2CO_3 \rightarrow O_2 + CO_2 +$ Ag).
• He concluded that 'common air' includes 'fire air' and 'foul air', and believed that 'fire air' combined with phlogiston during combustion.
• Published only in 1777 - hence denied priority. Told Lavoisier…

Phlogiston strikes again... Suddenly a compositional theory that includes phlogiston as a material element...

Joseph Priestley (1734-1804)

Old age.

US home

The Priestly Medal.

His Birmingham's house is burnt by a mob

These Caricatures show that he was a public figure, and what he did and wrote affected the public.

1st -"Dr Phlogiston: The Priestly Politician or the Political Priest". He is stepping on the Bible ("Bible explained away") and burns documents that represent the British Freedom. From his pocket you can see a book, "Revolution Toasts".

In the 2nd, he calls to place George III's head on the plate:

• The caricatures shows the complex personality: On the one hand, he was a man or religion, but not of the Anglican Church. He did not believe in the Holy Trinity, and tried to advance a rational religion. These are a-vanguard notions and they were unpopular in England, to say the least.

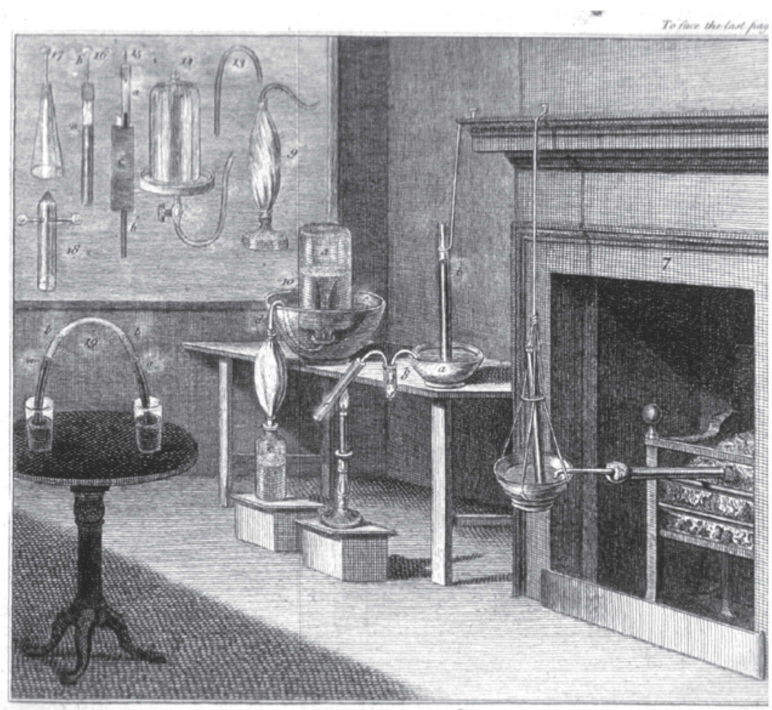
• On the other hand, he was a political activist who supported liberalism and freedom. He supported the French and American revolutions – something not well received in England.

These ideas cause an uproar against him, and a mob storms his estate and burns his house calling support in God & the King. He then decides to flee to the US.

• Priestly was a great supporter of women's rights (Bull. Hist. Chem. 2005, 30, 57)

• Additionally, Priestly was a man of wide-ranging knowledge: He spoke and wrote 10 different languages including Hebrew. He wrote on religion, philosophy, history, politics, and physics, e.g., history of electricity, introduction to electricity, and chemistry.

Priestley's Lab



• Hales trough, pipes… Mostly chemistry of gases.

• He invented soda water (CO_2+ H_2O) in 1772 when was a candidate to join Captain Cook (J.J. Schweppe made the money).

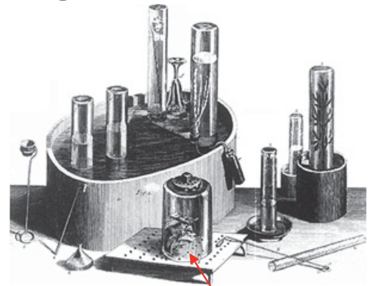
• His books show a qualitative approach to science. Facts are important, theories less, since a few theories can explain the same facts.

• Saw himself as: "An Investigator of the Wisdom of God in the Works and Laws of Nature" (Lectures on the Course of experimental Philosophy). In this sense he was Lavoisier's opposite.

• His approach is clarified by his philosophy of science: "We cannot solve one doubt without creating several more"

Joseph Priestley Discoveries: **Established Phlogiston**

- 1st paper in 1772: "*Observation of Different Kinds of Airs*"- already here he makes extensive use of the phlogistic idea to describe his findings.
- He remains loyal to the phlogiston theory till his last day; his 1803 book is :The Doctrine of Phlogiston Established".
- His technical improvement of the Hales trough is to use Hg instead of water, hence trapping NH_3, HCl, SO_2, etc.



Mouse

- During his experiments, he sees what others saw before him: A burning body in a closed vessel goes off after a while - Priestley explains that the phlogiston (the fiery element) escapes the burning body and saturates the air. He calls this saturated air "phlogisticated air" (later to be associated with N_2).
- He knows that this type of air is 'bad', since the mouse in the figure will soon die. Hence he invents a method to determine the quality of air.
- In this method he mixes nitrous air (NO) with common air over water. He observes that the volume of the gases shrunk, and the remaining gas was bad for burning and for mice. He concludes that the volume shrinkage measures the amount of the phlogistication of the air. In our terms what happened was: $NO + O_2 \rightarrow NO_2 \rightarrow HNO_3$, but Preistly does not know that; his mind his phlogistic.

[12] Priestley, the Method of 'Titration' of Phlogiston in Air

- He then applies the nitrous test to the air mixture that already shrunk. Now he observes no further shrinking in volume. In his view, this is a 'bad' air – maximally phlogisticated.
- 1774: he publishes his paper on O_2: He used the read calx of mercury (HgO), which upon heating gives off gas. This gas supports burning and makes mice and sparrows happier.

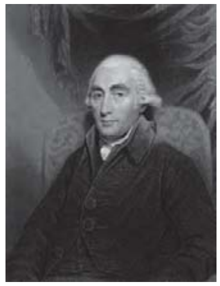
He writes on this new air: "Hitherto, only two mice and myself have had the privilege of breathing it"

$$2HgO \rightarrow 2Hg + O_2$$

- He then applies on this air the nitrous (NO) test and notes that the volume shrinks 4 times more than in common air. He calls it "dephlogisticated air".

- Priestley's work in the 1770s elevates the phlogiston to a rank of a real chemical theory. Till now phlogiston was merely another word for the inflammable principle of Paracelsus, and was applied only to the discussion of combustion; like formation of calx from metals, or of vitriolic acid from sulfur.
- Priestley's work and his measurement of volume shrinkage give phlogiston an elevated status as a material body.
- His writing skills, many publications, his origins in England - a European superpower, and his ability to measure it made phlogiston "an organizing quantity of chemical behavior"

Summary of Lecture 7

Phlogiston acquires a material status, and this will make it an important theory, but this is also the seed of destruction of the theory by Lavoisier

The person who brings the change is Antoine Laurent Lavoisier 1743-94

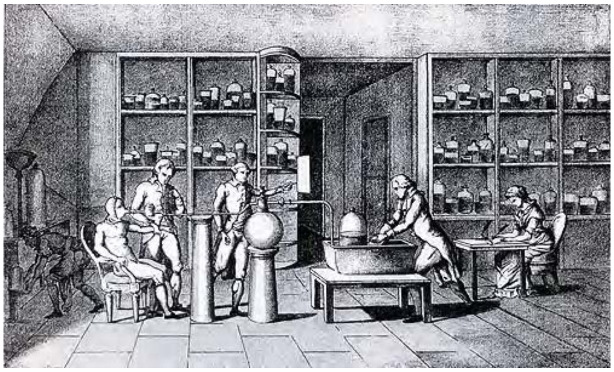
Here he is seen in his peak, with his beautiful wife, in a painting by the great painter David. Look how she is looking at David and Lavoisier is looking at her. He is in love…

- **Lavoisier was born to a family of Nobles in Paris.**
- **He was born in an enlightened age: An age of philosophers and great creative figures like Russo, Adam Smith, the Encyclopedists (especially Diderot).**
- **This is an age of great inventions, the vapor engine, mechanization of textile, crossing the English Channel with a balloon filled with H2.**
- **This was also an age of literature, poetry, etc.**

As fitting a son of such an age,

• He get his education during 1754-61 in the College Mazarin (to day Institute de France). He studies there chemistry, Botany, astronomy and mathematics.
•During 1761-3 he gets a law degree- something that will help him formulate a new language for chemistry.
•In 1764 he publishes his 1st paper in chemistry & in 1768- he becomes Member of the Academy, for a paper he wrote on Street Lighting and other contributions.
• in the same year he buys the Ferme Générale and his earnings amount to 20 M USD/y in to days money!
• Head of the board of Banque de France and director in many companies

• He then marries Marrie-Ann Pierrette Paulze, the daughter of his partner in the Ferme.
• When he married her Marie Ann was 13 or 14 years old.
• She gradually became more like a scientific colleague: She translated to French the work of Richard Kwiram "Essays on Phlogiston", and all the papers of Priestley.
• She drew his equipment, and engraved experimental scenes, and edited his memoires to the Academy. Below she is seen taking notes on a breathing experiment.
• In the play Oxygen it is hinted that she discovered oxygen.



- Another important figure in Lavoisier's life is Jean Paul Marat.
- Lavoisier met the young Mara, when the latter came to the Academy to submit some of his inventions.
- Lavoisier examined them and rejected them as they were poor.
- During the revolution Marat became an important figure, one of the heads of the "popular committees".
- The rejection of Marat's invention has cost Lavoisier his head, and he was executed in 1794: The facts that he owned the Ferme, and that he invented a special tax to enter Paris were certainly part of the story.

Marat

It is said that Lagrange eulogized him in the following words: "*It took them only an instance to cut off his head, but France will not produce another like it in a century*"

Apparatus designed by Lavoisier in 1773 (at left) for experiments to confirm that an "elastic fluid" (a gas) is released from a metal ore when the ore is heated is clearly only a slight modification of equipment in use at the time, such as that described by the English chemist Stephen Hales in "Vegetable Staticks," published in 1727 (at right). Lavoisier placed a sample of a lead ore called minium along with powdered charcoal on a pedestal inside a bell jar inverted in a water bath. After raising the water level inside the jar by suction through a siphon, he focused the Sun's rays on the sample through a large magnifying lens. He attempted to quantify the amount of gas produced from measurement of the change in height of the water column but was unsatisfied with the precision of his result. The drawing is Lavoisier's own, published in "Opuscules physiques et chymiques."

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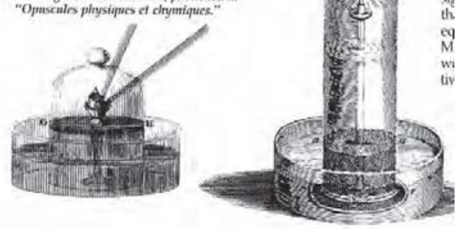
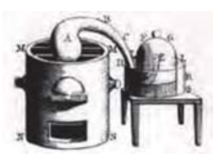


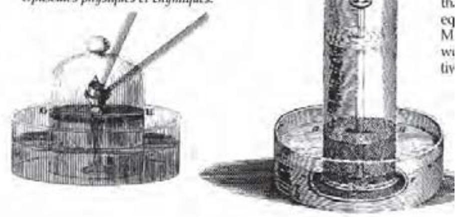


Lavoisier was a good experimentalist. Initially, he worked with Hales troughs, but soon enough he designed his own tools.

- Here are some tools he designed for fermentation studies (Fredrick Holmes, C&E News, 1994, Sept. 12th, p38). These can be found in the Parisian museum for technology. Very modern looking!

Lavoisier designed and used the equipment shown above right and in detail above and below right for fermentation experiments; this setup is displayed at the Museum of Technology of the Conservatory of Arts & Measurements in Paris.

Apparatus designed by Lavoisier in 1773 (at left) for experiments to confirm that an "elastic fluid" (a gas) is released from a metal ore when the ore is heated is clearly only a slight modification of equipment in use at the time, such as that described by the English chemist Stephen Hales in "Vegetable Staticks," published in 1727 (at right). Lavoisier placed a sample of a lead ore called minium along with powdered charcoal on a pedestal inside a bell jar inverted in a water bath. After raising the water level inside the jar by suction through a siphon, he focused the Sun's rays on the sample through a large magnifying lens. He attempted to quantify the amount of gas produced from measurement of the change in height of the water column but was unsatisfied with the precision of his result. The drawing is Lavoisier's own, published in "Opuscules physiques et chymiques."



Lavoisier designed and used the equipment shown above right and in detail above and below right for fermentation experiments; this setup is displayed at the Museum of Technology of the Conservatory of Arts & Measurements in Paris.

- His main contributions arise from a few factors:

1• Working in Closed vessels
2• Systematic use of balance sheet of matter
3• Broad knowledge of chemistry & a tendency to generalize.

The first two factors lead to the formation of Chemical Calculus, which will become the standard in chemistry and will pave the way for the Daltonian revolution.

The third factor helps him to generate the 1st Material Theory in chemistry

Early Application of the Notion of Conservation of Matter

• A wonderful example of the use of mass conservation law was the 1770 paper in which he tested the theory of 4 elements and particularly of their transformation from one to the other Thus, for example, upon heating water in a glass vessel up to complete evaporation there remains an earthy precipitate in the vessel. This was used as a proof for the transformation:
WATER + FIRE → EARTH + AIR

• Lavoisier boiled water in a CLOSED vessel for 100 days. He showed that the total weight did not change, namely the FIRE did not add any material into the flask. He then weighted the water inside the vessel and found a weight INCREASE, while weighing the flask showed a weight DECREASE.
• His conclusion was that the material form the flask dissolved into the water. He identified this material as Lime ($CaCO_3$), Potash (K_2CO_3) and some glassy material (silicates).

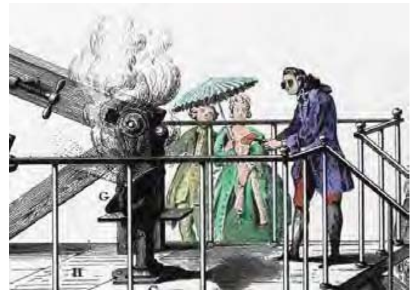
• We see the power of this book-keeping: on the one hand, it falsifies the theory of 4-elelments, and on the other, it creates a method of tracking changes in matter.

• A Beginning of Analytical Chemistry and a real dawn of a material approach to chemistry, as envisioned by Boyle.

Lavoisier began Investigation of Combustion

in 1772, since combustion, was considered the most important analytical tool of chymistry, and was believed to result in a decomposition to simpler bodies cause by release of phlogiston:

Metal + heat ⇒ Calx + Phlogiston↑



- You can see him in this picture using lenses to combust metals. The rising "smoke" looks like decomposition – and he concludes that these gases need to be tested.
- Till 1772, his mind is phlogistic. He is influenced from his great teacher Rouelle, and from Kirwan

- In 1772 he learns from Guyton de Morveau that metals gain weight in combustion. He concludes to himself that the theory of Phlogiston "has fallen into a labyrinth of difficulties":

How can something escape if the weight increases?

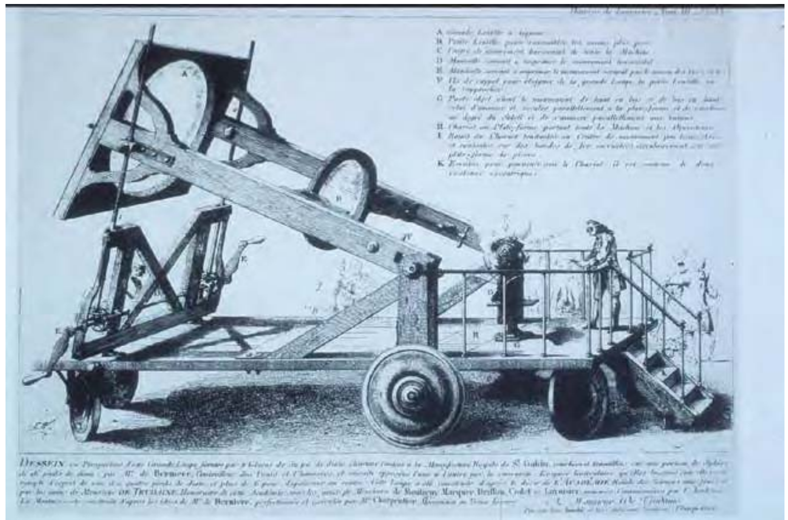
To answer his own question, he decides to redo the experiment with weight balance.

- As we shall see he indeed finds a weight increase in the calx. <u>He will conclude that combustion is a process of combination of the metal with parts of the air</u>.
- Thus the nature of combustion changes as follows:

Decomposition ⇒ Combination

This reversal in the nature of the chemical process defines a way to characterize the chemical transformation (the magic of chemistry), and provides a practical definition of a "simple body" that will eventually become the ATOM in Dalton's hands a few decades later.

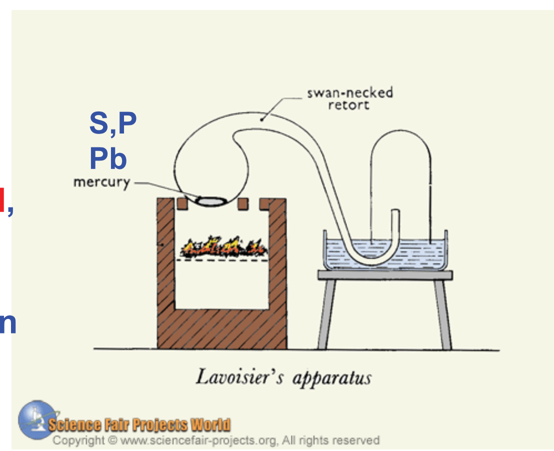
Personality Differences:
Combustion by Priestley and Lavoisier



Both use lenses, but look at the magnitudes of the operations!

Investigations of Combustion

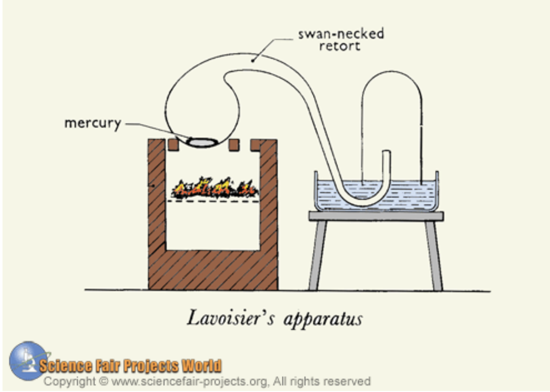
- The first experiments Lavoisier planned were done in 1772, when he investigated the combustion of S and P in a Hales trough. He found that the weight of the water solution increased, while at the same time the volume of the gas decreased.
- He then found a similar phenomenon with metals like Pb. The combustion leads to a heavier calx and a smaller volume of the air in the trough.



Lavoisier's apparatus

- He then does the reverse process. He takes "minium", the calx of Pb (PbO_2), and heats it with charcoal powder. He now finds an opposite phenomenon: the weight of the so formed metal is lighter than the calx, and the gas volume increases!

Lavoisier's Conclusions from the Investigations of Combustion:



• **The language of Lavoisier is still phlogististic. He calls the "air that left the calx" a fixed air using Rouelle's definition, and argues that the phlogiston (the fixed fire in charcoal) combined with the fixed air, and thereby restored it to its fluidic *aeriform*.**

• **Nevertheless Lavoisier understands the following features:**

Metal = simple	Calx = compounded	Air = material

• **1773: Lavoisier reads his paper and conclusions in the Academy and changes the nature of the key chemical process, combustion.**

During 1775-1778 Lavoisier Begins Systematic Investigations of Fixed Airs by Releasing them from Solids.

• **At this stage he is well aware of the studies of Scheele, Cavendish and Priestly, and he notes: "*The French alone seem not to take any part in these important inquiries*".**

• **His first publications in 1774 show still a Rouelle like thinking and Boyle type terminology, calling the "fixed air" in the calx, "*the fixed part of an elastic fluid…deprived of its inflammable principle*". He views the air as an element that when combined with the firey principle becomes free and is otherwise FIXED. Still very Rouelle/Boyle-like thinking.**

The Advantage of Chemical Calculus:

• In the same year, in 1774, he repeats Boyle's experiment with combustion of Pb, Sn in Hales trough. But his agenda and his knowledge about air are different than Boyle's, since he is looking for gases that are fixed in the calx and he knows how to trap and weigh gases. He weighs the retort before and after combustion and finds NO CHANGE in weight. Then he breaks the retort, notes how air goes whistling in, and he weighs the calx to find an increase of weight. He concludes:"*The increase in weight…[comes only] from the air contained in the flask*."

He explains Boyle's error - not to weigh the flask before and after.

• He does the reverse experiment; sometimes heating the calx by itself and other times heating the calx with charcoal. In both cases he uses mice, sparrows & candles to see the nature of the gas. In the cases he uses charcoal, he also notes that the charcoal was completely consumed.

• He reads his paper to the Academy in 1775, & notes: "*it follows that the air set free from reduction…is not simple; it is…the result of combination of the gas set free from the metal and that [which is] set free from the charcoal*"

The paper gets published only in 1778 and it shows that

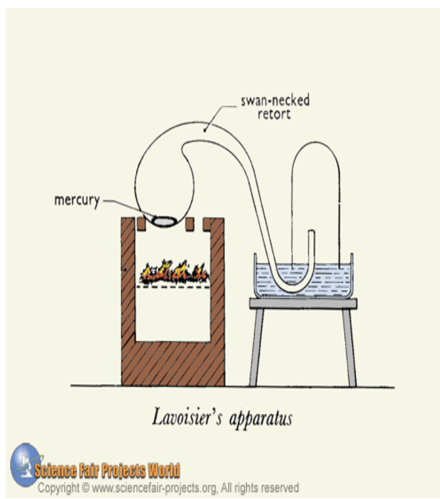
• from the time he read it to the Academy in 1775, till publications he has had a chance to refine and focus his views:

• He does experiments heating red calx (HgO):

• With charcoal he gets a gas, which he proves to be fixed air (CO_2) since it causes turbidity of a solution of quick lime in water ($Ca(OH)_2$). In so doing he proves that mercury is metal, since its liquid nature casts doubts on it status as a metal.

• Simply heating the calx he gets mercury (like Boyle and others). From the volume of the liberated gas, the weight differences of the original calx vs. the mercury formed. he determines the specific gravity (density) of the gas. He shows that the specific gravity is very close to that of common air.

• He shows that this air is breathable and can calcinate metals.



Lavoisier's apparatus

• While in 1775 he writes "*it is the air itself*", in the 1778 paper it is written differently: "*[the gas] emerges in an eminently respirable condition, more suitable [than air] to support ignition and combustion*"

Here is A Simple Experiment with RED Calx (HgO)

The Composition of Common Air, 1777-1780

- In a subsequent paper in 1777 (published 1780), he performs respiration studies to distinguish different AIRs:
- He heats for 12 days a certain volume of air in a flask containing **mercury**. He notes that red little droplets formed and are floating over the mercury, and at the same time the volume of the gas decreases; at the end by 1/6 of the original volume.
- The remaining air is not respire-able, does not cause turbidity in Quick Lime - so it is neither "respire-able air" nor "fixed air". He calls is "mephytic air", which has already been discovered by the pneumatic chemists before (N_2).
- The he performs the critical <u>analysis-synthesis cycle of proof of identity</u>: he heats the calx, he just generated, <u>in the same flask</u> and everything goes back to the original state, the mercury is regenerated, the air in the flask regains its original volume, and is again respire-able.

Beginning in 1773, Lavoisier conducted a lengthy study of the various operations—including respiration, shown here—that absorb or release an "air." Drawing is by Madame Lavoisier.

He confidently writes that he:
- Proved the composition of air: 5/6-mephitic, 1/6-respirable
- Calcination leaves behind only mephitic air
- By combining the two airs *"we can recompound air, similar to that of the atmosphere"*

The Definition of "Oxygen", 1777-1780

- In the same year 1777-8 he writes many papers on air. In the last one, "*General Considerations on the Nature of Acids, and of the Principles of Which They are Composed*", he makes a conceptual leap. He introduces a neo-Greek term "oxygen" which means "acid-former" and is wonderfully chemical and a compositional name. He explains that the vital air (respire-able air) enters the constitution of a number of acids: vitriol, phosphoric, nitric, etc, and then states:
"*Many additional experiments enable me to generalize… and to declare that this pure and highly respire-able air is the constitutive principle of acidity*".

- Note the term "constitutive principle"; it clearly shows that Lavoisier begins to think about chemical composition in terms of material bodies and not metaphysical bodies as before. He also speaks about the individuality of compounds - the chemical identity.
- All the more, this bold extrapolation enables him to link his combustion chemistry with the largest body of organized chemistry, the neutral salts.

- The signs of a great scientist: to see far, to weave conceptual worlds and unify knowledge.
- The introduction of Lavoisier in the 1778 papers sweeping and captivating: …. (Siegfried, p 177-178).

Solving the Material Puzzle of Aireal Composition (1783-1785)

- While oxygen was entered into mainstream chemistry, Lvoisier did not find yet any role, for inflammable air (H_2) and mephitic or phlogisticated air (N_2). This is a serious drawback since mephitic air is 5/6 of the entire body of air! Inflammable air was missed because his combustion was done over water…
- In 1783 Lavoisier learns about Cavendish experiments (published 1784). Cavendish mixed dephlogisticated air (O_2) and inflammable air (H_2) and reported that the only product is WATER. Cavendish is committed to phlogistic arguments and misses the meaning of his own findings, that water is not an element. Lavoisier does not! He understand that Cavendish has shown that water is compounded, not a simple body as in the 4-element theory!
- In 1784, Cavendish performs another brilliant experiment and performs a combustion of phlogisticated air (N_2) over water using an electric spark. He obtains nitrous acid. For Lavoisier, this is a proof that acids require oxygen. But more so, this characterization of the main components of AIR completes the puzzle & allows him to advance a material theory of AIR, whereby all the constituents can be followed by their weight/volume and features of identity (respiration, etc). No metaphysics…
- 1783-5: To consolidate his theory and topple the the rival phlogistic theory, he explains: "This body introduced by Stahl… has made science obscure… it is the *Deus Ex Machina* of metaphysicians, a body which explains everything and explains nothing."

During 1783-1785 – The number of memoires by Lavoisier is large

• To replace the phlogiston theory by his material approach, he takes experiments of others and gives them a materialist interpretation:

• For example: Torben Bergman devised a quantitative measure of the amount of Phlogiston in different metals. Silver dissolves in nitric acid (we know that it forms $AgNO_3$). This dissolved silver can be precipitated by other metals.

• Bergman measured the weight of precipitated silver by a fixed weight of these metals. He postulated that the precipitation-power of a metal measures its amount of phlogiston. Using his numbers Bergman organizes the metals on a <u>scale of phlogiston content</u>.

• Lavoisier uses Bergman's numbers and determines the equivalent amount of oxygen that combines with each of these metals (we know that they form $M_n(NO_3)_m$). To do that he uses the "equation": Oxygen = - Phlogiston

• This is an important victory since instead of weights of hypothetical entity, Lavoisier gives the chemist weights of "a real thing". Lavoisier writes about this advantage: "*what can be known by the balance and direct measurement is that all metallic calcinations…[undergo] augmentation of weight due to the addition of the oxygen principle…Once this principle is admitted, the principal difficulties of chemistry…evaporate. If everything can be explained without [phlogiston], it is…infinitely probable that [it] does not exist… It is within the principles of logic not to multiply bodies without necessity*" [Ockham's Razor]

These are the genes of our "positivistic" science:

In a situation where two theories have identical explanatory powers, the one which is preferred is the one that enables to measure "existing entities". In this case, the victor is the theory of "oxygen" and the ability to test it by weighing. It is the victor even though the phlogiston can explain the same chemistry.

Lavoisier's 'long march' does not cease here. May be by coincidence and may be a sheer luck… Guyton de Morveau arrives to Paris to learn the new pneumatic chemistry in order to include the gases in his new nomenclature of chemistry.

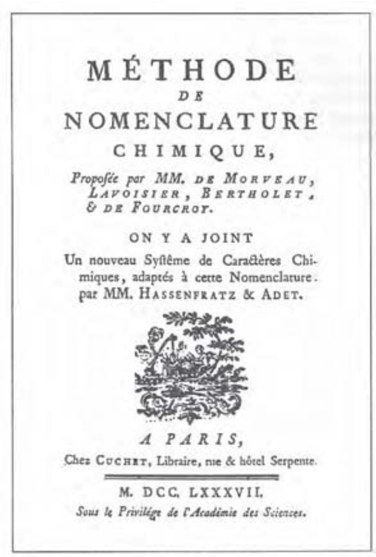
- In addition, we recall that de Morveau defined a "simple body", whereby he meant a body of a simplest composition allowed by the existing means of analysis.
- de Morveau is still a phlogistonist, and hence he is aware that expanding his nomenclature is not possible until it becomes clear <u>whether combustion leads to decomposition</u> to simple bodies (as Phlogistonists think) or <u>is it a synthetic procedure</u> that creates more complex compounds as the oxygen theory claims.

During de Morveau's sojourn in Paris, he falls for the "Oxygen Theory", and initiates with two additional convertees; Berthollet and Furcroy, and with the Maestro Lavoisier a book that will be published in 1787

"Methode de Nomenclature Chimique"

Berthollet

Furcroy


MÉTHODE
DE
NOMENCLATURE
CHIMIQUE,
Proposée par MM. DE MORVEAU, LAVOISIER, BERTHOLET, & DE FOURCROY.
ON Y A JOINT
Un nouveau Système de Caractères Chimiques, adaptés à cette Nomenclature. par MM. HASSENFRATZ & ADET.
A PARIS,
Chez CUCHET, Libraire, rue & hôtel Serpente.
M. DCC. LXXXVII.
Sous le Privilége de l'Académie des Sciences.

So the camp of the believers in the "Oxygen Theory" is growing and it includes two influential figures in France.

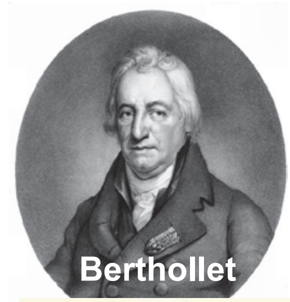
• Berthollet was a highly distinguished chemist, who later joins Napoleon in the campaign to Egypt. During his time in Egypt, Berthollet visits a 'natron lake' south of Cairo, in which Na_2CO_3 percipitates instead of $CaCO_3$, as happens in the laboratory:

$Na_2CO_3 + CaCl_2 \rightarrow CaCO_3 + 2NaCl$

• Berthollet write a paper "Statique Chimique" where he recognizes the mass law in equilibrium, many years before it is recognized in physical chemistry.

• Furcroy is an important Professor in the "College du Jardin du Roi" and a very popular lecturer.

• Later Furcroy will become "Director General" of Education, something like the minister of education in France.



After Lavoisier's execution, Berthellot and Furcroy will be the chief disseminators of the new theory.

Let me Return to the Essentials in Méthode de Nomenclature Chimique:

• The two important contributions in the book are those Lavoisier and Guyton:

• According to Lavoisier, language is an important instrument of thought, hence "*perfection of language was necessary to the perfection of knowledge*".

• He defines the difference between compounded and simple bodies: "*those substances we are not able to decompose…as a result of chemical analysis*".

• At the same time his definition is pragmatic and positivistic: "*…some day these substances, which are simple for us, will be decomposed in their turn*".

• In so doing, <u>Lavoisier defines for the chemist a practical agenda</u> for searching and defining simple bodies <u>in any given time</u>!

• Guyton, on the other hand, emphasizes the importance of simple bodies because: "*the denomination of bodies…which can be reduced to their elements, are properly expressed by the re-union of the names of those same [elements]*"

• This definition sets chemistry into a search for genealogy of substances.

• Together they classify 5 categories: (I) metals, (ii) earths, (iii) alkalies, (iv) acidifiable bases, (v) simple bodies. - A material/property based classification

• Later, Furcroy points out that the nomenclature constitutes a consolidation of Lavoisier's theory into a body of unified concepts and terms.

• The true consolidation occurs in 1789, when Lavoisier writes “ *Traité…*”, where he treats all chemistry in the new material approach. The book is highly influential

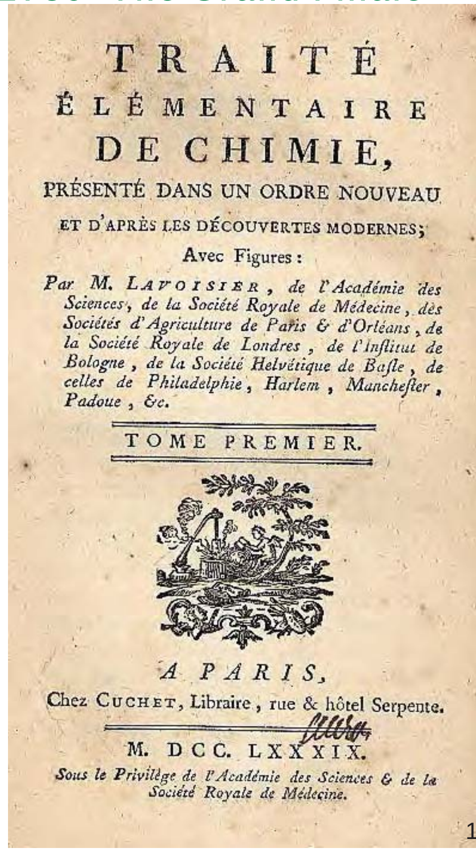
• In Part I, he discusses pneumatic chemistry, the nature of combustion; he defines ‘simple bodies’ and oxygen as the principle of acidity.

•These ideas and the ‘principle of conservation of weight’ constitute the theoretical foundation of the new chemistry (READ!!!).

• In Part II, he summarizes the body of knowledge on neutral salts and the notion that names are expressed as composition of the constituents acid and alkali. He thereby links cleverly his new chemistry with the main stream chemistry.

• As such, Lavoisier creates in Traité a powerful device for propagating the new chemistry. Even the opponents recognize this as “the chemical revolution”.

1789- The Grand Finalé



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.

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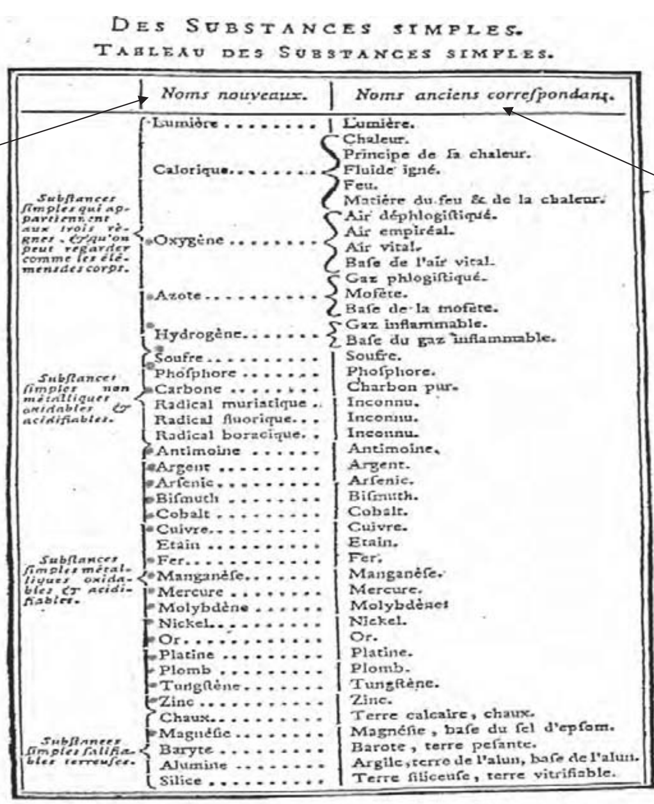
Sous le Privilège de l'Académie des Sciences & de la Société Royale de Médecine.

From Traité

New Names:

Ancient Names:



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. Mofète. Base de la mofète.
	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.
	Cobalt	Cobalt.
	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 THE ELEMENTS

28

The everlasting Achievements of Lavoisier:

• Using the principle of weight conservation in a manner that generated chemical calculus- the beginning of analytical chemistry, and the establishing the correct order of chemical phenomenon (decomposition, synthesis), and of ‘simple bodies’ and of ‘composition’ of compounded bodies.

• These ideas have been embraced by chemists and have eventually led to the "compositional revolution" whereby chemistry evolves into a science of material bodies as atoms and molecules.

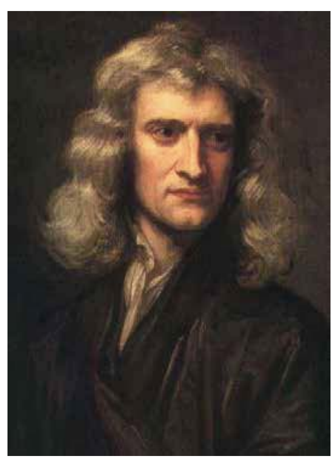
• The elimination of the metaphysical body phlogiston and its replacement by material bodies gave chemistry a positivistic agenda for research: chemistry must deal with tangible real bodies!

29

Newton & Lavoisier, and the Kuhnian-Poperian Relationship

• The introduction of mass in both cases has brought a new measure of "reality" and has formed the great divide between the new theory and the metaphysical older ones, despite the equal explanatory power.

• In the case of Lavoisier the mass gave the means to understand the ‘magic of chemistry’. This was expressed nicely by Kirwan, a staunch Phlogistonist:



"Phlogiston was rejected because the chemist’s choice to emphasize empirical evidence for [describing] reality".

• Kuhnian element: the new paradigm of Lavoisier generated a new agenda for research in terms of chemical calculus and constitution.

• Poperian element: Lavoisier falsified the phlogiston theory because there was no logical way to explain the increase of weight with the liberation of phlogiston, unless one assumed a negative weight!

• The Lavoisier’s story is a fantastic scientific drama.

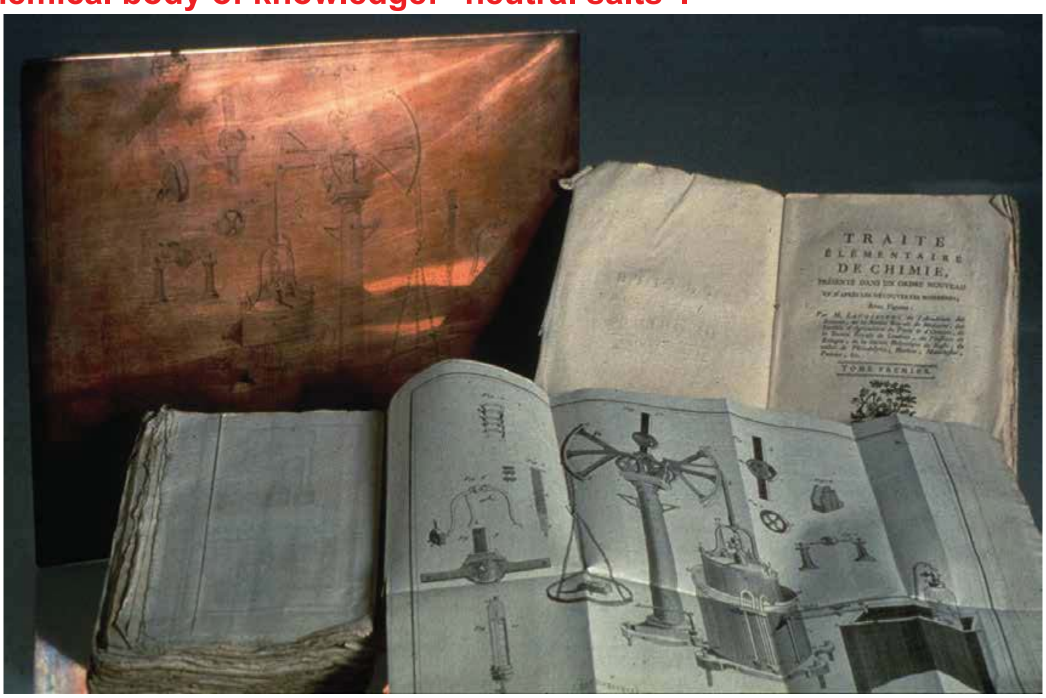
2

Background- 17C and Early 18C Status of Air

- Recall that AIR is one of 4-elements. Empedocles uses clepsydra to prove its existence.
- 17C- AIR is ousted of the chemical principles by the iatrochymists. It becomes a "physical being of no chemical essence". Things get more so with the mechanical philosophy:
- For example, Jean Rey 1630 - the increased of weight during heating of Lead is due to entrance of AIR particles into the pores of Lead, which were opened during the heating and closed after cooling, thus trapping the AIR.
- Boyle: His view of air is as a mixture of elastic particles and all kinds of "streams and smoakes, including inflammable particles". He shows that candles extinguished and sparrows died in closed containers undergoing evacuation - something in the air... He repeats the Jean Rey experiment, but now under refined conditions (closed containers and external heating by an alcohol lamp). He finds that (i) air entered into the broken retort, and (ii) the Pb weight increased. His conclusion is that some inflammable particles in the air penetrate through the walls of the container and got "fixed" into the metal.
- Hooke and Mayow experiment with KNO_3 , produce oxygen (*spiritus nitro-aerius*), are getting close to recognition of chemical identity, but fall short.
- According to Boyle, Drebble (1572-1633) conducts the1st experiment with $NaNO_3$: "Drebble conceived that it is not the whole body of the air, but a certain quintessence or spirituous parts of it, that makes it fit for respiration".
- van Helmunt originated the term gas (from chaos, but expressed in Flemish).
- Missing is a technique to collect gases!

Summary, Lecture 8

1778: Lavoisier makes a conceptual leap. He attaches to the respire-able air a general chemical role, "oxygen"- acid former. And he thereby links this air to the largest and most established chemical body of knowledge: "neutral salts".

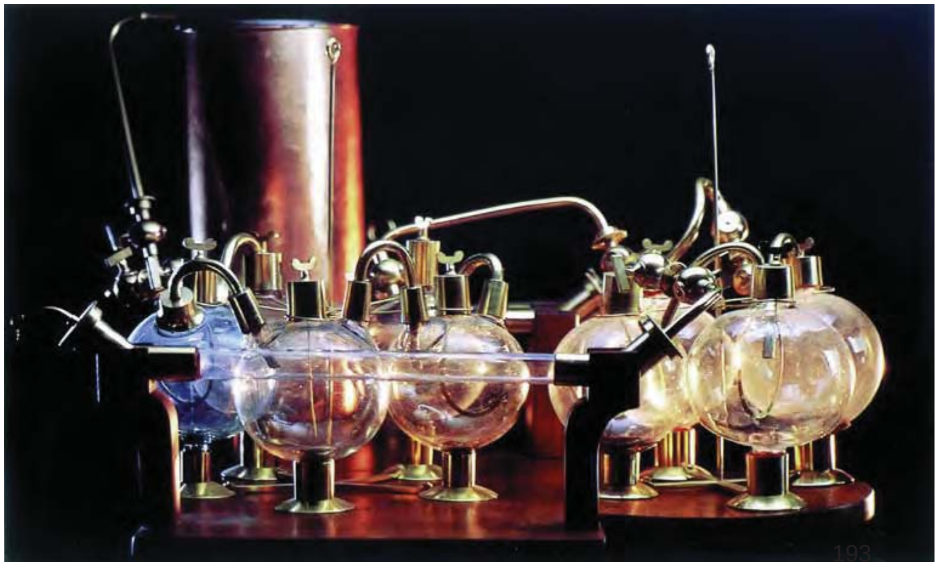


Summary-2, Lecture 8

• Furthermore, the working procedure, wighing matter as it changes, and doing so in in closed vessels, establishes the Law of Mass Conservation, and enables to follow the chemical reaction quantitatively.

• In so doing, Lavoisier transforms chemistry into a materialistic/ analytical science rather than the metaphysical science it was before.

• Finally, his definition of a ‘simple body’ provides chemists with a pragmatic and analytical agenda for research



Summary-3, Lecture 8

• For all these, the contribution of Lavoisier is fitting the title of “the compositional revolution”.

• We also talked about the great personal drama in the story: the successful scientist, the beautiful wife and scientific companion, and the tragic execution, and the symbolic re-execution when Germans enter Paris.

A History of Chemistry, Lecture 9

Synopsis : The Completion of the Compositional Revolution - The Atomic Hypothesis of Dalton

- In 1791 Lavoisier writes to his disciple Chaptal: "The revolution is complete"…
- It is doubtful however that Lavoisier actually understood the real nature of his own revolution. In his eyes, the revolution was the toppling of the Phlogiston theory. However, the real revolution was different:

- The implementation of the principle of conversation of matter in chemistry, along with the concept of "element" or "simple body" provided a practical research agenda and led to the birth of "Analytical chemistry" (first defined so by Bergman).

Early Outcomes of the Compositional Revolution

The improvement of the analytical techniques brought about ever more accurate quantitative information on chemistry, and this led to a recognition of "constant composition" of many chemical bodies, and hence to an incipient definition of "chemical identity".

- Nevertheless, other chemical substances seemed to have variable compositions, which posed a serious problem to the notion of "chemical identity".

- There is confusion in the air… until the Dalton hypothesis arrives and shades light on the results, solves the chemical identity and elucidates the chemical magic.

- We'll talk about the heroes involved in the process.

The Newtonian Dream - Chemical Calculus

• Before discussing the next heroes, let us say a few words about the background of the post-Lavoisier era, which is connected to the "Newtonian Dream".
• Ever since Newton has shown that the Universe functions according to mathematical rules, many chemists were guided by the "Newtonian Dream" to find the mathematical rules of chemistry.

• Venel, who wrote the chemistry chapter for the Encyclopedia of Didero, was the first to express this "Newtonian Dream"
• Then 30 years later, Lavoisier defines his own "Newtonian Dream" and writes: "*Perhaps some day the precision of data will… [enable the chemist]… to calculate… the phenomena of any chemical combination in the same manner as he calculates the movement of the celestial bodies*"

• Lavoisier's work on gases brought chemistry closer to the Newtonian dream.

The Newtonian Dream

• However, while the Lavoisier definition of an "element", which was based on the "limit of decomposition", led to many quantitative discoveries, many chemists where wondering, '*have we really reached the limit*' ?

• For example, Thomas Graham one of the leading British chemists writes in 1804: "…*Very possibly the bodies which we reckon simple, may be real compounds; but till this has actually been proved, we have no right to suppose it*" - Catch 22!!!

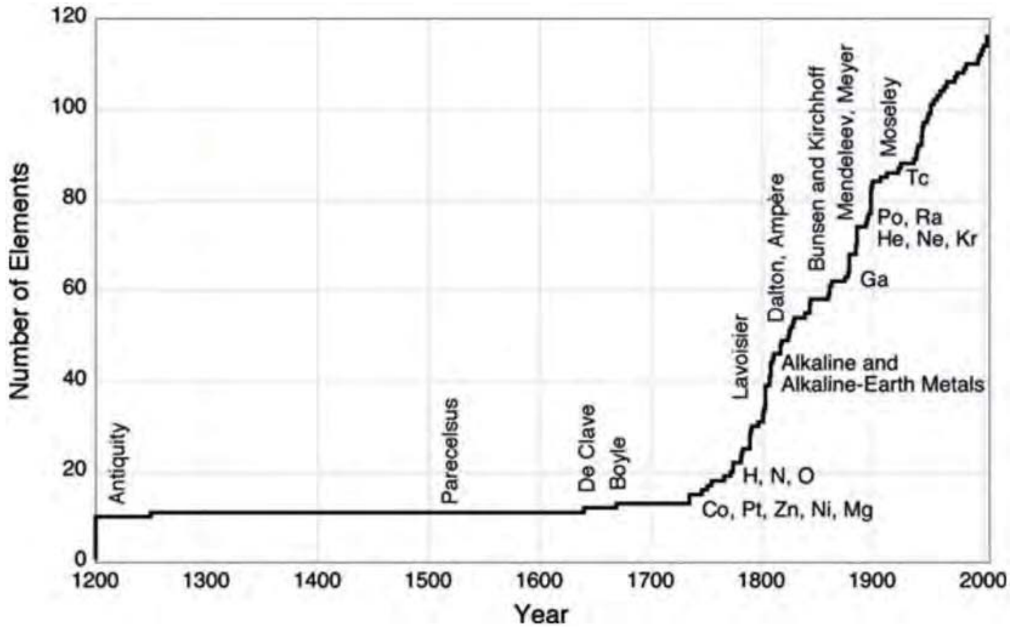
• Almost every chemist who writers at that period of time finds it necessary to make the distinction between the pragmatic and ideal/ philosophical definitions of the 'element':

• A Simple Body = Obtained at the Limit of Experimental Decomposition Process *vs* • The Philosophical Element = True Building Block of Nature

• All the more, the pragmatic search continues and new information flows.

3 Too Many Elements

- **Here you can see the explosion of information about "chemical elements" in the post-Lavoisier era:**



4 Too Many Elements

- **During the years, 1789-1810, 20 new metals are discovered! Chemist's hands tremble with nervousness: '*Till when*'? '*How many*'?**

The general feeling is that there are '*Too many*'. For example, Nicholas-Louis Vaquelin- writes in 1797 about his discovery of Cr:
"*In spite of the repugnance which I feel in admitting new simple bodies… I am nevertheless forced by the large number of new characteristics… to regard it as a metal… which has no analog*".

- **This large number causes chemists to yearn for the simple world of the "protyle" and 4-elements. However, as soon as the recognition sets in that this paradise is gone for ever, the next best is to find "order & rules" in the information.**

- **A major obstacle en route to a solution is the "Baconian Inductivism", that dominated chemical thinking: namely that the 'rules of Nature' have to emerge from empirical facts.**
'Hypothesis' is almost a 'dirty word' like speculation.

Too Many Elements

• Indeed, Lavoisier himself warns against the 'temptation' to let the imagination to dictate the conclusions, and writes: *"Imagination.. Which is ever wondering beyond the limits of truth… We must trust to nothing but facts… ".*

• A related obstacle to the finding of a solution to the Catch 22 is the "Positivism": "*Believe in what you can actually observe*". Again, Lavoisier himself warns against the chase after the 'the philosophical elements- atoms' : *"…it is extremely probable we know nothing at all about them"*, because they cannot be observed.

• Inductivism and positivism jointly are strongly rooted in chemistry and prevent the main stream chemists to come up with a hypothesis that will simplify "the complex new world" of chemical matter that begins to unravel.

Incipient Order in the End of the 18C and Beginning of 19C

• Nevertheless, within the ocean of facts, some preliminary order begins to emerge at the end of the 18C-beginning of the 19C, when quantitative data of "elective affinity" point to a quantitative relationship that will eventually be called, "the principle of equivalent weights", as formulated by Richter.

• Another emerging quantitative relationship is the idea of "Fixed/ definite composition" in chemical substances. This idea is first expressed already by Rouelle. But its present formulations is worked out only later by Proust, who is vehemently opposed by Berthollet the greatest French chemist of the time.

• The Proust-Berthollet dispute originated in the lack of accurate analytical techniques and in the lack of a clear definition of a chemical compound or the lack of a difference between a compound and a Mixt.

Incipient Order in the End of the 18C and Beginning of 19C

• **In summary of the background on which our heroes emerge: in 1803 there is a lot of information, there are two quantitative guiding principles, but there is also disclarity and disagreement because there is no theory that will create the necessary order.**

• **It is then that Dalton's hypothesis springs into this background and creates the long sought for order. These hypothesis was made despite the inductivism/ positivism dictum not to look for fictitious entities.**

Thus, the historian Siegfried writes on this hypothesis: "*So functional a rationale for the explicit laws of combination, that the whole dispute became moot*"…

• **Chemists accepted it because of its pragmatism and clarity of order.**

Now is the time to introduce our heroes

Our 1st Hero is Jeremias Benjamin Richter Who was Born in Germany (1762-1807), and Who Formulated The Law of Equivalent Weights:

• **In 1800 - the eve of his short life- he was made Professor in the Department of Mines & a chemist in the Royal Porcelain Factory in Berlin.**

• **In his background Richter was a mathematician who did his PhD Thesis under Kant on "Mathematics in Chemistry"**

• **After his PhD, Richter dedicated his life to the finding of regularities in the combining weights needed to create a "neutral compound" – defined as a point where there is no excesses of either one of the components.**

• **In 1792 he discovered that during a salt exchange process, there was a constant weight ratio of the salts required for the complete exchange. He accordingly wrote: "*…because neutral products were formed, [the reactants] must have amongst themselves a certain fixed ratio of mass*". He calls it "*the Law of Neutrality*",& finds that it applies also to reactions of alkali with acids.**

6 Jeremias Benjamin Richter (1762-1807)

• This idea was, in fact, implicit in works of Guyton de Morveau, Lavoisier and Bergman, but Richter was the first to articulate it in a clear and definite manner.

• In 1792-1794 he published his findings in 3 volumes, where he also coined the term "Stoichiometry" and defined it as:

"… the art of chemical measurement, which has to deal with the laws according to which substances unite to form chemical compounds".

• Richer was an avid mathematician and he tried to fit the data to mathematical and geometric series & instead of working pragmatically, as chemists do, he tried to fit data to his "*mathematical fantasies*" (Siegfried).

This does not work well with chemists. Hence, because of this and because of his cumbersome writing style, his work was completely ignored!

Fischer Saves The Law of Equivalent Weights from Oblivion

• In 1802 Ernst Gottfried Fischer, a chemist and then a Professor of Physics in Hale, used the equivalent weights of Richter and explained clearly their utility:

• For example, here is a table of equivalent weights: In column (I) there are weights of bases that combined with 1000 parts of sulfuric acid. In the second column (II) are weights of various acids that will combine with these standard weights of bases

Bases (I)	Acids (II)
Alumina 525	Fluoric 427
Magnesia 615	Carbonic 577
Ammonia 672	Muriatic (HCl) 712

• It is only with Fischer's work, that chemists begin to use these "combining equivalent weights" in design of their experiments to reach "neutrality". **But the actual meaning of these weights is not known.**

Berthollet and Proust – The Controversy of Definite/ indefinite Proportions

• The idea of definite proportions has been known already from Rouelle's days and may be even before that: In 1751 Rouelle's student, Venel, writes: *"[it is] an eternal truth [that] mixtes are composed of definite proportions …"*.
However, the technical ability in Rouelle's days was too lousy to established this rule…

• Nevertheless, it seems that sometimes, in order to re-awaken a good idea, one needs a great controversy.

• Indeed our next two heroes are two Frenchmen, Berthollet and Proust who were engaged in such a controversy:

Claude Louis Berthollet (1748-1822)

Joseph Louis Proust (1754-1826)

Berthollet and Proust

• We already met Berthollet through his work on the nomenclature book with Lavoisier et al. Berthollet studied dyes and bleachers (with Cl_2), he synthesized the "Salt of Berthollet" ($KClO_3$), and nonstoichiometric ceramics (from which we make superconductors to day).

• At the peak of his career Berthollet is one of the most important chemists in Europe, the President of the French Academy, and a confidant of Napoleon.

• The second Frenchman Proust was a Rouelle student, and the chief apothecary in the Saltpeter mines.

• in 1777 he is recruited by Charles IV of Spain and becomes a professor in Segovia, Salamanca and Madrid. He gains fame due to the clear articulation of the Law of Definite Proportions and the controversy with Berthollet.

Claude Louis Berthollet (1748-1822)

Joseph Louis Proust (1754-1826)

Berthollet- Indefinite Proportions

• A close friend of Napoleon the Consul, who in 1798 after the revolution starts a campaign to Egypt (*Bull. Hist. Chem.* 1999, 24, 61), and takes a few scientists as "*Committee on the Arts & Sciences*" headed by Berthollet, among whom are Laplace, Malus….

• Fourier will then edit 21 volumes "*Description de l'Egypte*".

• During the sojourn in Egypt Berthollet traveled to a "Natron Lake", where he saw huge sediments of Soda (Na_2CO_3) on its banks.

• After analysis of the lake water he realized that the following reaction takes place at the bottom of the lake: $CaCO_3 + 2NaCl \Leftrightarrow Na_2CO_3 + CaCl_2$. He knew from laboratory experiments that the reaction goes to completion to form $CaCO_3$, while here on the lake it was producing Na_2CO_3.

• He concluded that the results in the lake were driven by the huge quantity of NaCl, i.e., "*the action of mass could overcome the rules of elective affinities*" (Brock, Ch. 14).

• Clearly, this was the 1st recognition of reversibility. However, this idea will blossom and be articulated only 60 years or more later. At the times of Betholllet, this finding amounted to a statement that:
"*bodies combined in variable-indefinite proportions*".

• To prove his point, Berthollet used alloys and nonstoichiometric ceramics where we now know that there is nostoichiometric doping. He obviously finds indefinite proportions.

Proust- Fixed Proportions

• Proust was a firm believer in the notion of fixed proportion, & he sets out to prove it, by analyzing $CuCO_3.H_2O$, formed by salt exchange in a variety of ways. He showed that the weight ratios were fixed irrespective of the method of preparation of the salt. He published his findings in 1799 and wrote:

"*One hundred pounds of copper, dissolved in sulfuric or nitric acids are precipitated by carbonates of soda or potash, invariably 180 pounds of copper carbonate. If this quantity [is distilled] it gives 10 pounds of water, which appear to be essential to the color and composition of this carbonate as the carbonic acid itself…*" [Ann Chim 1799, 32, 26-54]

• He coined the term "The Law of Fixed Proportions"

10 Proust vs. Berthollet

• **Proust returned to France after the armies of Napoleon destroyed his laboratory in Madrid. There he continued to "fight" with Berthollet till 1808.**

• However, there was no clear victor in the controversy, since there were nonstoichiometric compounds, like FeO that crystallizes as $Fe_{0.95}O$ due to vacancies in the crystal.

• In addition, the accuracy of analysis was dubious, and primarily because of that Proust missed the "Law of Multiple Proportions"

Our Next Hero is John Dalton (1766-1844)- It is worthwhile to mention his biography in order to see that traditionally scientific revolutions start by outsiders who do not belong to the mainstream and oftentimes come also from the periphery and not from the central cities.

• **Dalton was born to a Quaker family in a small town in Cumbria (north England) - very far from the center. He was also an outsider by his Quaker religion.**

• **Quakers values education, and Dalton got a good one education. At 12 he was already teaching the kids of the village.**

• **In his teens he knew sufficient geometry to study Newton's *Principia*.**

• **His influential teacher was the Quaker Robinson who also introduced him to meteorology.**

John Dalton (1766-844)

- At 15 he left with his brother to Kendall & established a private school in which they taught, Greek, Latin, French and Math. There he also met the Quaker Philosopher John Gough who recognized Dalton's talent and taught him Math and philosophies of Newton, Boyle and Boerhaave.
- The capricious weather in Kendall rekindled his interest in meteorology and he began with observations (200,000 in his lifetime).
- In 1793 he published his first work "Meteorological Observations & Essays". The work contained the seeds of his atomic ideas. But as he was an outsider geographically and of different religion, his book was ignored.

John Dalton (1793 on) in Manchester

- Till 1793 Dalton was not able to enroll in a university due to his religion. In the same year he got a job as a tutor in the non-Anglican "New College" in Manchester, through recommendation of Gough.
- In 1800 the college went bankrupt and Dalton stayed in Manchester as a private teacher and consultant. He will remain in Manchester all his life.

- Manchester was an industrial city, and this caused a rise of the middle class, and hence the private teacher Dalton had quite a bit of work as a teacher. One of his students was Joule.
- Manchester had also a local Academy, and Dalton became a member in 1794. He read in front of the member his research on: "*Extraordinary facts relating to the vision of colours*". Dalton himself was color blind (could see yellow, crimson & blue) and the phenomenon is known since as "Daltonism"

John Dalton (1793 on) in Manchester

- **In 1800 - he becomes the secretary of the Academy and during 1817-1844 as the President till his death. Here you can see him presiding in a caricature, and greeting the audience: "*The weather is awkward; but the glass is rising. My best respects to all of you*".**

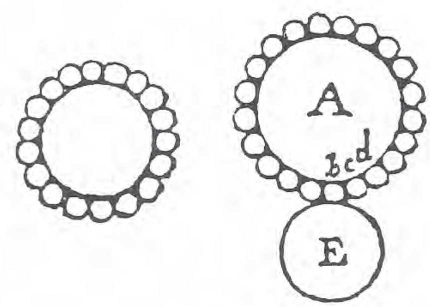
- **In 1801 he published his second book through the academy on English Grammar - showing the broadness of his knowledge.**

- **Via the same academy he will publish his époque-making book, "A new system of chemistry".**

John Dalton's Way to Atomism

- **Dalton was born into an "atomistic world". However, the atomism of Newton, Boyle and their contemporaries did not manage to create a new chemical order, since they did not explain the "magic of chemistry" and the secret of "the chemical identity".**
- **Nevertheless, the talk about atomism, the fall down of the phlogiston, and the Newtonian mechanistic theory, created a feeling that "the chemical identity" is materialistic, and this intensified the use of atomistic terms in thinking about the chemical objects under study.**

Bull. Hist. Chem. **13-14** (1992-93)



Figures from Newton's letter to Robert Boyle of 1678/9. The sphere surrounded by smaller particles illustrates Newton's concept of saline particles "encompassing the metallick ones as a coat or shell does a kernell ..." The same terminology appears in the corpus of Eirenaeus Philalethes, with which Newton was intimately acquainted. From the 1744 edition of Boyle's *Works*.

Dalton’s Way to Atomism (2)

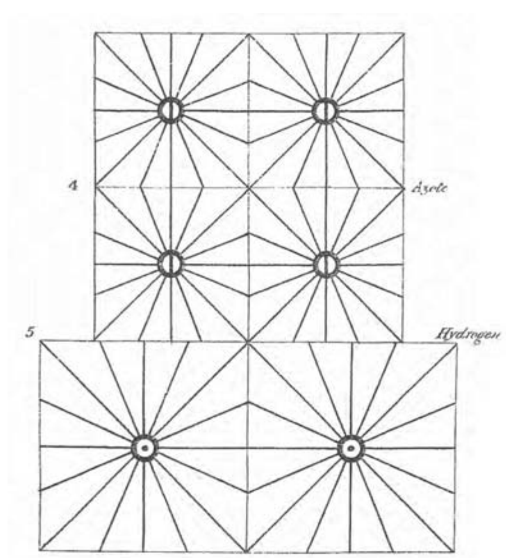
• In Dalton’s time, it was known that atmospheric air was made of a few gases, oxygen, hydrogen and azote (nitrogen).

• It was know also that there were water vapors in the air. The fact that these vapors condensed into dew and rain convinced Dalton that the air was a mixture of chemicals rather than a compounded body of them.

• Ever since his early exposure to meteorology through Robinson’s teaching, Dalton is interested in the condensation of water from the air.

• Dalton is wondering: since air is a mixture, why should this mixture being in constant movement will not separate out into strata (layers) like any gravimetric separation? The fact that the mixture is homogeneous bothers Dalton and he tries to understand this using an atomistic model

Dalton’s Model of the Air in the atmosphere



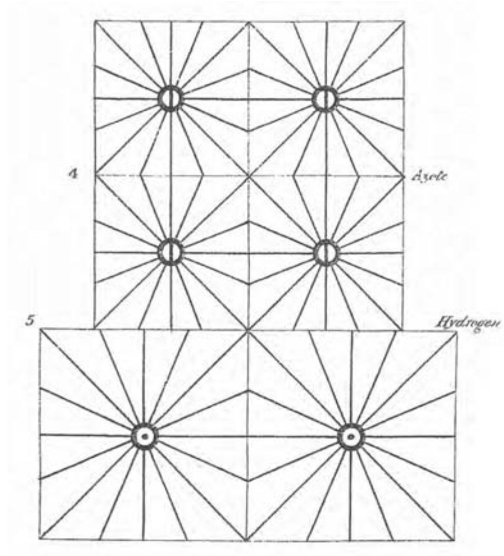
• In Dalton’s world the phlogiston died but was reborn (by Joseph Black) as “caloric”- an “element of heat”.

• Dalton uses the caloric as an envelope of heat that surrounds the atom and endows it with an effective volume. In so doing, Dalton uses atoms as little spheres and depicts their envelope of heat as rays.

• In the drawing you can see the visual model of nitrogen and hydrogen and their heat envelopes:
It is already apparent that Dalton is drawing “physical bodies” and gives his reader a sense of “reality”. You can also see the heat drawn as rays emanating from the atoms. Such “lines of field” will be used later by Faraday…

Dalton's Model of the Air in the atmosphere

- Using this drawing, Dalton clarifies that since the rays of heat do not meet, these bodies cannot maintain a mechanical equilibrium, but will interpenetrate freely and will thereby form a homogeneous mixture as in the atmosphere. <u>In this manner he solves his initial question</u>
- However, since he wants to use the "atoms" and think further about the properties of the air mixture, Dalton realizes that he needs atomic weights and volumes.

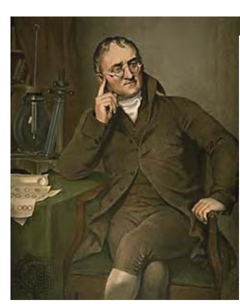


Rehearsal 1

Richter- law of equivalent weights in combination

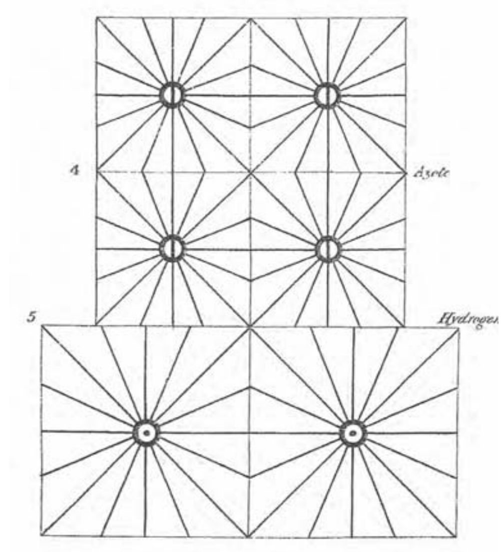
Proust- law of constant proportions
Bertholet- indefinite proportions

Who will save chemistry from further endless entanglement? Dalton is the savior



Rehearsal 2: Dalton's Model of the Air in the atmosphere

- Using this drawing, wherein atoms are physical object with heat radiation, Dalton clarifies to himself why the atoms in the atmosphere form a homogeneous mixture



- However, since he wants to use the "atoms" and think further about the properties of the air mixture, Dalton realizes that he needs atomic weights and volumes.

Dalton's Model of the Air in the atmosphere

- Here are the relative weights of atoms, which Dalton derived in different years.
- His derivation was based on compositional assumptions about substances. For example, using Lavoisier's analysis, water contains 85% Oxygen and 15% hydrogen by weight. Since hydrogen was the lightest atom, he used for hydrogen a relative weight of 1.

TABLE 4.1 *Some of Dalton's relative weights.*

	1803	1808	1810
Hydrogen	1	1	1
Azote	4.2	5	5
Carbon	4.3	5	5.4
Oxygen	5.5	7	7
Phosphorus	7.2	9	9
Sulphur	14.4	13	13
Iron		38	50
Zinc		56	56
Copper		56	56
Lead		95	95

- To find the relative atomic weight of oxygen he assumed that water is a simple combination "HO", which gave a relative weight of 5.5 (later modified to 7).
- Once he had these atomic weights, Dalton understands the immense meaning of what he did. He found the "game of LEGO" whereby the atoms combined to give substances - the secret of "chemical synthesis" and the "magic of chemistry".

[16] Some Important things about Dalton before looking at his theory

- Like King Saul, who sought for his father's asses and found a kingdom, so did Dalton: He attempted to understand the condensation of water vapors and in so doing he found the key to the "universal game of LEGO".
- Much as in any important event, here too, greatness means the recognition that what you found is more important than what you were looking for.

Dalton Goes Against the Mainstream

- You remember that the ruling scientific method was Baconian inductivism - let the theory be born from facts. The opposite way, starting with a hypothesis and do experiments to test it, what is known as the hypothetic-deductive approach, was considered forbidden especially in chemistry that just recovered from alchemy.
- Most normal scientists would obey the mainstream in their research. But not Dalton!
- As if in a miracle, Dalton did precisely the forbidden thing. He first hypothesized, and then showed that the hypothesis solved all the difficulties and elucidated thereby the "chemical magic".
- Even if these hypotheses did not resolve immediately all the problems, still their lucidity and enchanting simplicity provided a research agenda for all the chemists up to these days.
- Let us see the principles of the theory and its visionary horizons...

17

The Principles of the Atomic Hypothesis

- **In 1805, Dalton began to understand that the relative atomic weights he derived constitute a very efficient and simple rational for the "Law of Constant Composition".**

- **Moreover, he could see that these weights form a basis for another law: "The Law of Multiple Proportions", which resolves much of the controversy between Berthollet and Proust. It dawned on him that he holds in his hands the basis for "chemical calculus" & the rules of "chemical synthesis".**

- **In 1808 Dalton publishes the 1st volume of his book: "*New System of Chemical Philosophy*", wherein he discusses his hypothesis.**

17a

The Principles of the Atomic Hypothesis in Dalton's Book

- **The book contains the meteorological theory, and in the last 6 pages the principles of the atomic theory and its chemical uses.**

- **The second volume appears in 1810 and is dedicated to chemistry. The 3rd one appears in 1827.**

- **Dalton's hypothesis can be summarized as follows in a modern interpretation as the 1st quantum hypothesis:**

Dalton's Hypothsis

b

• The laws of atomic combination are based on the LEGO principle of atoms - homely and pleasant model...
• The algebraic principle of combination is simplicity: 1:1, 2:1, 1:2, 3:1, etc.

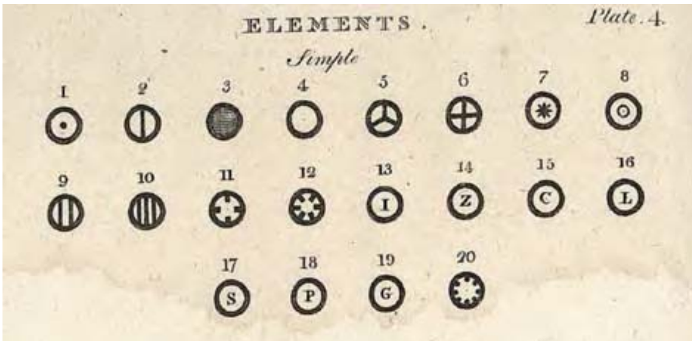
a

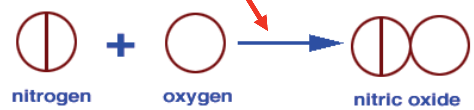
• The mass of matter is not continuous, it is divided into quanta, which are the weights of the atoms that constitute matter.
• Every type of atom has a characteristic weight.

The Following Drawings Illustrates the Powerful Visual Aspect of Dalton's Model:

• The elements are spheres with mass and are represented by symbols showing atomic identity.

•• The principle is very visual like a game of Lego that elucidates the chemical magic:

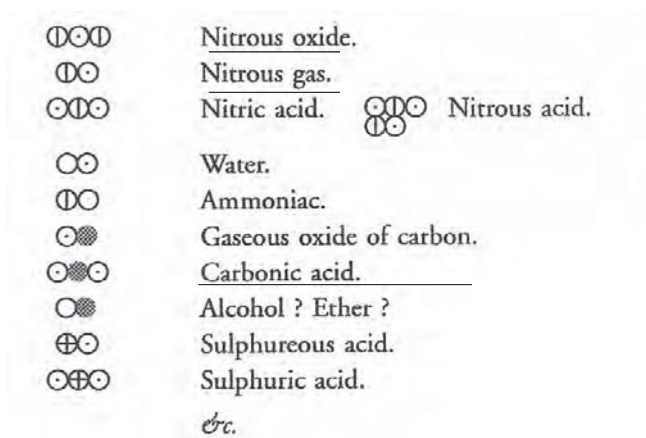




Dalton's Model Gives Clear Rationale to The Quantitative Rules

• Here are representations of several molecules from his notebook. These representations show clear "chemical identity" and the law of fixed proportions is apparent & clarifies thousands of data, related to elective affinities and equivalent weights.

• Having the equivalent weights, the assumption of simplicity in combination, enables Dalton to derive all atomic weights from a few simple compounds, water (HO), ammonia (NH), nitrous gas (NO), & carbon oxide (CO).



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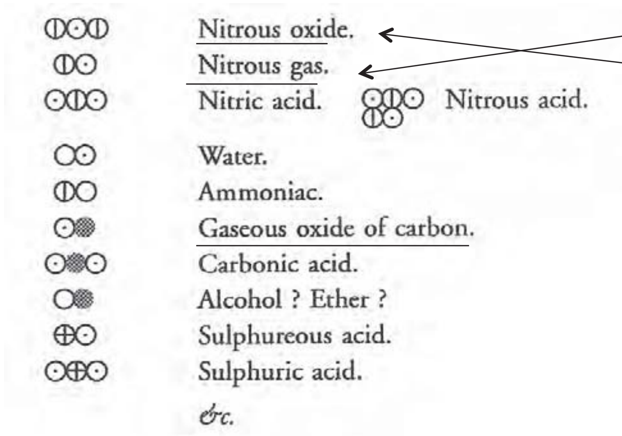
Dalton's Model Gives Clear Rationale to The Quantitative Rules



- **Looking at the nitrous gas (NO) and nitrous oxide (N_2O), makes it clear that <u>if</u> one could find evidence that nitrous oxide contains a double weight of nitrogen, this would be a perfect proof for The Law of Multiple Proportions. Dalton finds the proof but does not publish it. Others with greater technical skills will find and publish it later.**

- **Dalton gave them the long expected calculus with which it should be possible to convert chemistry into a quantitative science that is based on chemical identity- This achievement is the peak of the compositional revolution that started with Lavoisier.**

20

Dalton's Characteristic Confidence

- **Dalton himself understands the value of his contribution and in 1808, when he reads his paper in the Royal Society, he says:**

"The third chapter is on chemical synthesis; and tends to place the whole science of chemistry upon a new, and more simple basis that it has ever been before".

- **In 1810, when his second volume appears he again reads to the Royal Society and says:**

"I am confident, [it] will… contribute to establish a beautiful theory of chemical synthesis…, and which in due time, I am persuaded, [will] be made the basis of all chemical reasoning"

Fortissimo !

21

Dalton's Originality and Contribution to Chemistry

• One of the Attractive Features of Dalton's Model is the Visual Element: One picture is better that thousand words.
In 1830, one of his supporters, Thomas Thomson writes:
• *"It was a happy idea of representing the atoms and the constitution of bodies by symbols that gave Mr Dalton's opinion so much clearness. I was delighted with the new light which immediately struck my mind, and I saw at glance the immense importance of such a theory, when fully developed".*

• Another powerful element is his chemical calculus: Dalton did not invent the atomic hypothesis (Democritus...). However, by his quantal-weight hypothesis he invented a way for calculating the relative weights of the elementary particles of matter from experiments that were at his time doable in the laboratory.
• As such, Dalton succeeded for the 1st time in history to marry the atomic hypothesis with a tangible reality, and thereby, he created a bridge between experiment and hypothetical constituents of matter. He created then an intuitive explanation for the chemical magic and chemical identity.

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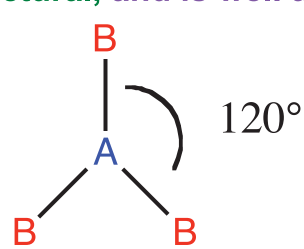
More on Dalton's Originality and Contribution to Chemistry

• An element of his theory that has been forgotten is the 2/3-D structure. His visual thinking led him to consider a structural model. He said that when B has affinity to A, then A will surround itself by as many B's until their repulsion will overcome the affinity. For example, when he considered AB_3, he draws a structure with 120°, AB_4 with 90°, etc. While we know that not everything here is correct, still we recognize that Dalton's thinking is material and architectural, and is well ahead of its time.



• At his time, the 19^{th} Century the chemical community was not yet ready to consider a structure for molecules. This, will arrive later with van't Hoff and Le Bell, and 150 years later by Gillespie (VSEPR model), but by then Chemists will completely forget that Dalton was the 1^{st} thinker about "structure".

22

Reaction of Chemists to Dalton's Hypothesis:

- One of the first supporters is Thomas Thomson who met Dalton in 1804 and invited him to talk in Scotland in 1807, and recommended his theory in his own book, "*System of Chemistry*".
- Another supporter was William Hyde Wollaston
- Already in 1808 Thomson and Wollaston bring evidence for the rule of multiple proportions in front of the Royal Society. Wallaston states clearly in his lecture:

"*… All the facts I observed are particular instances of the general observation of Mr Dalton that… the simple elements are disposed to unite atom to atom, singly, or [one atom] exceeds by a ratio to be expressed by some simple multiple of the number of its atoms*".

- Jöns Jakob Berzelius, the premier Swedish Chemist, has already been excited with Richter's law of equivalents, about which he said, "*I was impressed by the light I found…*". When he read Dalton's book, he wrote enthusiastically:

"*I realized that… it was necessary to determine with maximum accuracy atomic weights.., this was the most important task of chemical research and I devoted myself to do this entirely*".

22a

Reaction of Chemists to Dalton's Hypothesis:

- Berzelius undertook the task and developed the methods and the techniques for accurate determination of atomic weights. Within the years 1814-1827, Berzelius published tables of atomic weights; in 1818, 45 of the 49 atomic weights came from his group, 39 of them he determined personally.

- There were objections from Berthollet, but once Dalton showed the basis for the law of multiple proportions, the Berthollet doctrine of "indefinite proportions" evaporated into thin air. Ironically, during Berthollet's time as President of the Academy, he initiated the translation of Thomson's and Henry's books, which contained extensive reviews of Dalton's theory. This brought Daltonian theory to France.

23 Objections of Chemists to Dalton's Hypothesis:

- There were other objections on a more philosophical background, and we'll deal with those later. Nevertheless, at the beginning of the 19C almost all the chemists started to work in Dalton's paradigm and to express chemical composition in simple and whole numbers. They did so despite the philosophical inconveniences with the term 'atom', which no one could 'see'.
- As I said already, in 1818 all the techniques to determine atomic weights with good accuracy were available, including electrolysis with batteries, which were called then "Voltaic Piles".
- The real problem then, was: whether these were real atomic weights or some multiplications of the real weights. There was NO WAY to make this decision.
- Unfortunately, the negative attitude of Dalton to the experiments of Gay Lusac and to Avogadro's Hypothesis , as well as his disputes with Berzelius did not help and only intensified the inconvenience with Dalton's hypothesis.
- This state of affairs continued about 50 years, until Cannizzaro proposes a way out of the labyrinth.

- All these make the next topic ...

The Post Dalton Developments in Chemistry: A Bird's Eye View

A History of Chemistry, Lecture 10-cont'd

1• As we discussed, Dalton's ideas quickly gained a community of supporters. The wonderful simplicity and the visuality of his hypothesis provided an impetuous to seek simple combining relationships during chemical reactions, for example in volumes, weights, etc.

2• We shall discuss the important experiments of Gay Lusac, and the molecular Hypothesis of Avogadro, which advanced Dalton's hypothesis. This happened despite the objections of the owner of the hypothesis!

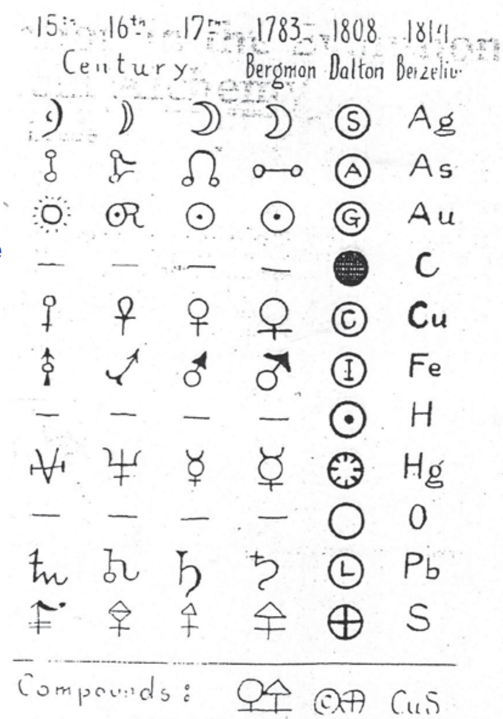
3• However, along with support there were also objections, sometimes very strong.

- We'll start with the objection and then discuss the ideas that advanced Dalton's model and matured it to its present day's status.

Jöns Jacob Berzelius (1778-1848)

- **One of the great chemists at all times was Jacob Berzelius. Except for his enormous practical contribution of techniques, new elements, and new compounds, Berzelius greater legacy is <u>the creation of a chemical language</u> based on letters and numbers that count the atoms.**
- **It is inconceivable to imagine chemistry without this language.**

Jacob Berzelius



Alchemical and Chemical Symbols. Berzelius introduced our present notation. Reproduced from, "Hackh's Chemical Dictionary," 3rd Edition. The McGraw-Hill Book Co., Inc., New York (1944).

Initially Berzelius **was a great supporter of Dalton's hypothesis, and applied novel techniques, e.g., electrolysis using Batteries invented in 1800 by Alexander Volta to determine atomic weights.**

- **By using electrolysis, he also developed a new theory of electric attraction (like ionic bonding to day), which he thought explains elective affinities.**
- **Dalton objects to the theory and to the usage of letters for the atoms. This caused a big rift between the two powerful personalities.**
- **So much so that Berzelius becomes a severe critique of Dalton's book, and writes about the book:**

"[It is] incorrect even in the mathematical part… In the chemical part, he [Dalton] allows himself lapses from the truth…"

Jacob Berzelius

There are also Philosophical Objections from other great chemists, e.g. Sir Humphrey Davy (1778-1829).

- **Humphrey Davy was a brilliant chemist, with charisma and huge personal appeal. He was a public figure as a lecturer and the President of the Royal Society.**
- **Here you can see him in a public lecture in the Royal Society hall in London (still there to day)…**
- **To have Davy on your wrong side was not too smart…**

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Sir Humphrey Davy's Objections

- **The major weakness in Dalton's model was the fact that no one could in fact observe atoms, which were figments of imagination, no matter how useful for organizing chemistry. This imaginary existence of atom aroused the positivism objection, which was rooted so deeply in chemistry.**
- **To this objection, one can add the fact that by that time there were more than 50 atoms. Davy commented that '*God would not design a world with so many atoms*'.**

- **This doubt intensified when Davy showed that some of these 50 elements were not really elements, but rather compounds. And this has cast doubts on all the atoms in the inventory.**

- **indeed, already in his speech during the award ceremony to Dalton, Davy did not mention the importance of atoms, and stated that Dalton is awarded for "*the development of the theory of definite proportions usually called the atomic theory of chemistry*".**

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Indeed most chemists avoided referring to atoms as physical entities, and this created a lot of confusion, so much so that every chemist had his own table of combining weights.

1837 Dumas

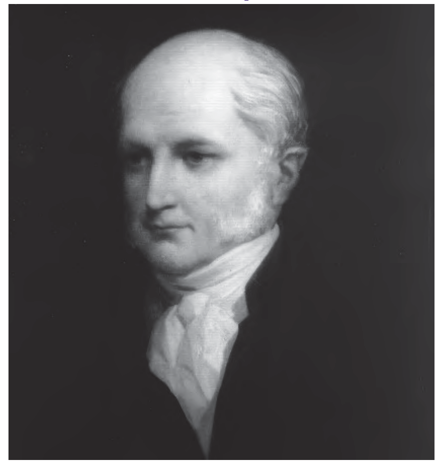
- **The confusion was so great that Dumas who measure the volume ratio of hydrogen and oxygen to give water, ended up describing water as composed of one atom of H and ½ atom of O.**
- in 1837 Dumas stated:

“ *If I were master I would efface the word atom from science*”

Davy invokes the Protyle

Coming back to Davy: in the same paper in which he showed that many “atoms” were in fact compounds, he also proposed to go back to the Protyle which he felt to be hydrogen – such that all matter is simply made from one element.

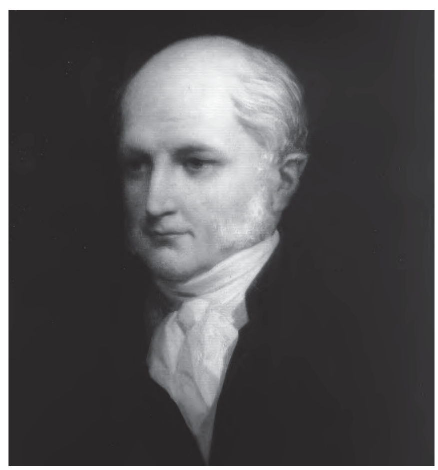
William Prout (1785-1850)



Davy's comment about protyle sends William Prout in this direction.

- Prout is a strong believer in Aristotle's' idea of the protyle, from which all the world is supposedly composed.
- In 1812, he arrives to London, and starts working in chemistry. He notes that the atomic weights seem to be related to one another almost by whole numbers.
- He compares the weights of equal volumes of different gases, sets the weight of H to 1, and calculates, the relative weights. He gets "whole numbers" , well, at least sort of…

In 1815-1816 he states: "*We may almost consider the protyle of the ancients to be realized in hydrogen…*"



- In retrospect, Prout's idea was a brilliant one. Later physicists like Gamow will adapt it to describe the synthesis of heavy nucleons in the universe.

At the same time, this idea had cast serious doubts on the atomic hypothesis.

- The return to Protyle, created confusion and doubts everywhere; all these plagued chemistry.

Chemistry was waiting for a 'savior' !

- The savior appeared in the form of new experiments which led to consolidation of Dalton's idea, even though he fought against them vehemently…

Joseph-Louis Gay Lusac (1718-1850) & A v Humboldt

- Gay Lusac was enchanted with the atomic hypothesis & the properties of gases, following the works of Boyle and Lavoisier. In 1805 he and Humboldt, the founder of the University of Berlin, collaborated to determine the proportions in the combination of hydrogen and oxygen.
- They found that O and H combined, under electric spark, to give water in the following volume ratio O:H = 1:2.
- Then Gay Lusac found in ammonia and in other compounds simple combining volume ratios, which he considers as evidence the existence of atoms, and notes that this is a rigorous method to determine atom ratios.

Gay Lusac vs. Dalton

- Obviously, Gay Lusac's findings led to the question, whether equal volumes contain the same number of atoms?

- Dalton opposed this idea categorically, and uses the gas "NO", which combines as follows:

	N	+	O	→	NO
Volumes Found:	1	:	1	:	2

Since *n*-atoms of N and *n*-of O should combine to give *n*-compounds of NO, this would have required a volume ratio 1:1:1. By contrast, the measured ratio was 1:1:2, this meant for Dalton that two volumes of NO involved as many particles as 1 volume of N and of O. Hence volume is not a fundamental property that counts atoms!

- Clearly what was missing from Dalton's hypothesis was the MOLECULE!

Amadeo Avogadro (1776-1856) provides the missing link.

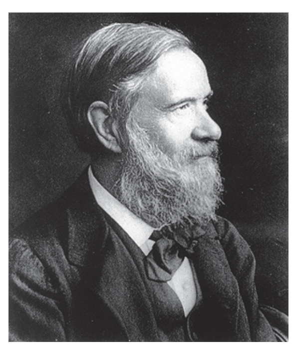
• Avogadro was a Professor of Physics in Tourine. In 1814 he published a paper in which he hypothesized that the elementary gases contain diatomic units, which he called "*Molécules elemantaires*", and he distinuished them from gases of different atoms which he called "**Molécules intégrantes**"

• The notion of diatomic molecules made from the same atom was **a bold hypothesis** since the rules of 'elective affinity' did not consider that identical atoms will have any affinity.

• Avogadro further added that: "*Equal volume of gases contain equal number of molécules elemantaires or molécules intégrantes*"

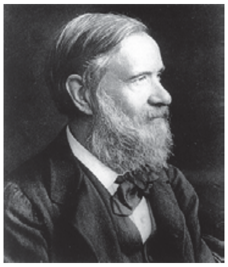
• No one pays attention to Avogadro, may be because he was a physicist, may be because he was far from the center, and may be because these were revolutionary ideas at the time. **Those who did pay attention completely objected to the idea** that two identical atoms can form a union, because of the central idea of elective affinity between different bodies. Also, there were gases like Hg vapor that were monoatomic etc…

Chemistry needed someone who will smoothen the difficulties and organize all the enormous amounts of quantitative data. This person was Stanislao Cannizzaro (1826-1910), who in the peak of his career was a Professor in Rome.



• In 1860- in the Karlsruhe Symposium of organic chemistry, orgnized by Kekule and Wurtz, Cannizzaro shows how the marriage of Avogadro's hypothesis to Dalton's atomic hypothesis removes all difficulties.

• He derives new consistent atomic weight based on a standard of H being 1.



He does so in the following manner:

- From the combining volumes $1(O_2):2(H_2)$ and the volume of water vapor obtained (2 volumes), [$O_2 + 2H_2 \rightarrow 2H_2O$] he determined the water formula as: H_2O.
- From the combining weights of (O_2): (H_2) he got an atomic weight of O as 16 relative to H being a standard of 1. This leads to further corrections of all the known atoms.

- Since equal volumes contain equal number of molecules, then the molecular weight is proportional to the density, M = kD. He gets k = 22.4 lit/mol, and this constant enables to determine more M values and corresponding atomic weights.

- • Subsequently he defines the quantity "mol" - <u>the gram weight identical to the relative atomic weights</u>. This leads to Avogadro's Number, as the number of molecules that would give the molecular (atomic weight) in gram units. Using Boyle's Law he determines the volume of "mol" as 22.4 lit/mol equal to the above k.
- He defines "Valency"; Valency = Atomic Weight (AW)/Combining Weight (CW)
- For example, for oxygen AO=16 and CW=8, hence: Valency (O) = 2.

Fast Development of Chemistry: Late 19C - The Periodic Table

- Cannizzaro's contribution closed a cycle: together with the language of Berzelius, the chemical formulae became simple and the chemical communication fast and efficient.
- The advent of revised atomic weights have led to another important idea: an arrangement of the elements according to some order. Many have contributed but the final construct, the Periodic Table, is associated more with with the name of Mendeleyev.

			Ti = 50	Zr = 90	? = 180
			V = 51	Nb = 94	Ta = 182
			Cr = 52	Mo = 96	W = 186
			Mn = 55	Rh = 104,4	Pt = 197,4
			Fe = 56	Ru = 104,4	Ir = 198
			Ni – Co = 59	Pd = 106,6	Os = 199
H = 1			Cu = 63,4	Ag = 108	Hg = 200
	Be = 9,4	Mg = 24	Zn = 65,2	Cd = 112	
	B = 11	Al = 27,4	? = 68	Ur = 116	Au = 197?
	C = 12	Si = 28	? = 70	Sn = 118	
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210?
	O = 16	S = 32	Se = 79,4	Te = 128?	
	F = 19	Cl = 35,5	Br = 80	J = 127	
Li = 7	Na = 23	K = 39	Rb = 85,4	Cs = 133	Tl = 204
		Ca = 40	Sr = 87,6	Ba = 137	Pb = 207
		? = 45	Ce = 92		
		?Er = 56	La = 94		
		?Yt = 60	Di = 95		
		?In = 75,6	Th = 118?		

Dimitry Ivanovich Mendeleyev (1837-1904)

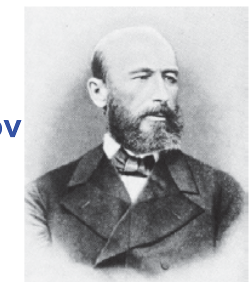
The notion of Valency Brings about The idea of "Structure"

- The idea of structure is associated a lot with Kekulé. But he is not the first. It seems that Berzelius with his idea of "radicals" – conserved groups that pass from compound to compound - was before.
- He was also not the only one, and the notion of structure seems to have been articulated by others:

August Kekulé 1829-1896

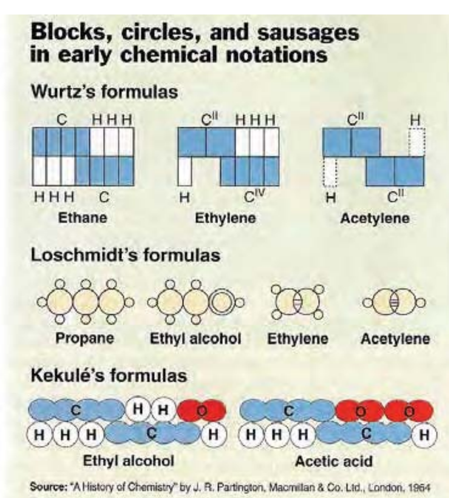
Joseph Loschmidt 1821-1895

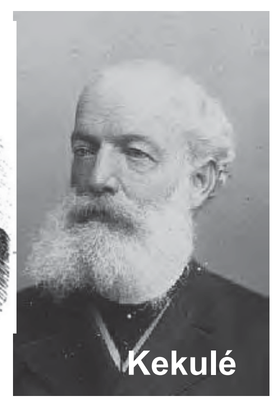
- Wurtz Charles 1817-1887
- Alexander Butlerov 1828-1886
- Ed Frankland 1825-1899

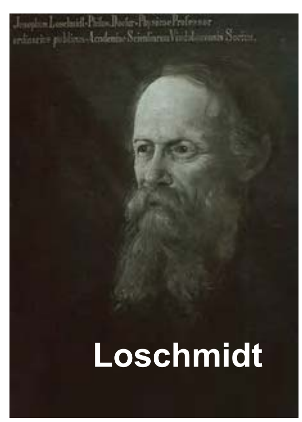


The "Structure" notion is initially abstract

- Except for Loschmidt's drawings which look almost modern, the initial ideas of structure were quite abstract and non-materialistic

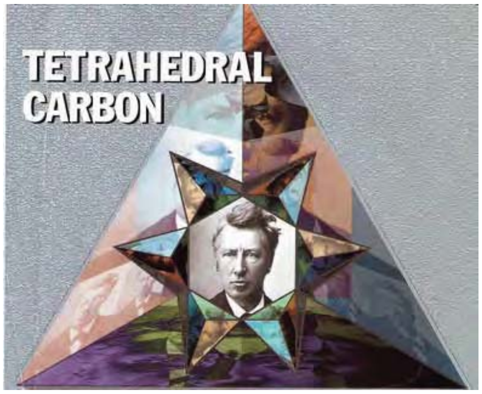






Very quickly Structure gains "Reality" by going 3D

Jacobus Henricus van' t Hoff 1852-1911



Van't Hoff's original tetrahedra. Reproduced with permission of Museum Boerhaave (Rijksmuseum voor de Geschiedenis der Natuurwetenschappen), Leiden, the Netherlands.

Joseph Achille Le Bell 1847-1930

Alfred Werner 1866-1919 does the same for coordination chemistry in 1893

With 3D and atomic weights, chemistry becomes fully materialistic.

Jacob Berzelius

The Development of the Notion of The Chemical Bond

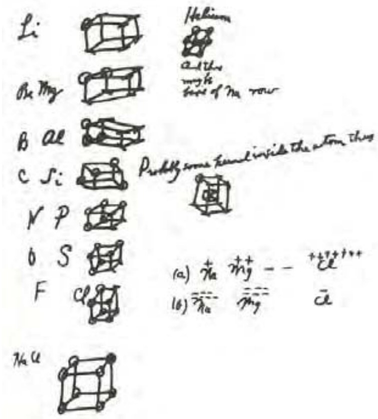
- **This starts even earlier than 'structure', when Berzelius who did a lot of electrolyses experiments, advances the Electric Attraction Theory of Chemical Affinity, which is a model of an ionic bonding.**
- **This theory goes into disrepute however, because organic chemistry has no ions…& it dominates chemistry,**

In the beginning of the 20th Century, many years after Berzelius, Thomson discovers the electron and then suggests a theory of chemical bonding in terms of electrostatic interactions between charged particles. He proposes ionic bonding even for H_2 - unaware that Berzelius failed before because organic chemistry is dominated by nonionic compounds …

J.J. Thomson (1856-1940)

& Then Comes Lewis and Hypothesizes the Chemical Bond

Lewis who was a postdoc of Nernst knows about ionic and nonionic compounds, and in a stroke of genius, he hypothesize an 'electron-pair' bond, which bonds the atoms, and which has 'covalent' and 'ionic' forms



In so doing, Lewis defines the quantum element, which is the 'glue' responsible for the entire structure of the chemical universe. Structure is a Lego of atoms bonded by electron pairs...

- Thus, Lewis starts the the 2nd revolution in chemistry: "the electronic structure revolution"

& The Entrance of Quantum Chemistry into Bonding

- **1926-1928: At least 10 years after Lewis, Quantum mechanics is developed by Schrödinger and his contemporaries.**
- **1927: Heitler and London the describe for the 1st time the bond in H_2 a la Lewis, without credit to Lewis.**
- **1928-31: Pauling develops VB theory, a la Lewis, without much crediting Lewis, and Mulliken develops MO theory.**

A quantitative dimension of the Lewis Theory and some more is made available to chemists; a new dawn for chemistry…