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Lecture 4: The latrochymistry Revolution & Ascent of Chymistry

Synopsis

Summary of Alchemy

• The Re-Definition of Alchemy & The Rise of latro-Chemistry in the 16 C

• Paracelsus and the great latrochymists.

• Was Alchemy Really Foolish? The Willow Tree Experiment

• The contributions of alchemy

Summary of Lecture 3: Alchemy

• Alchemy emerges from the tension between the magic of the chemical transformation and the religion that ascribes the power of transformation to god. Alchemy is UNIVERSAL!

2• before Alchemy there was Protochemstry that contained the technical knowledge to carry the transformation. As such, Alchemy is very important since it created an organized framework for the protochemical knowledge: Not only philosophy, but also a set of 'working codes', goals and paradigms, within which the Alchemist carries the work:

• The Alchemical process is a cosmic process motivated by a divine grace, and as such the codes of alchemical work are: (a)As above so below: So, what the alchemist does is to emulate the Godly harmony and perfection and improves the self at the same time.

(b) The duality and unification of matter and spirit.

• The material perfection is Gold, and the spiritual perfection is Immortality, and therefore these became the main goals of Alchemy, and the means of attaining these goals were: the Philosopher's stone and the Elixir.

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Summary of Lecture 3 -Continued: Alchemy

3• The theoretical framework of Alchemy included the 4/5 elements of the Greek philosophers and the '3 principles' of the Arab Alchemists:

• The 4 elements have become 'wombs' wherein materials are formed by heavenly fructification, e.g., the metals are formed by the influence of the Sun, and the other Stars.

• The three principles express the three aspects of the chemical transformation based on the experiences during the experiment: Sulfur: represent the inflammability of bodies

Mercury: represents the transforming power of different bodies (their 'plasticity')

Salt: represents the resistance of the body to fire

4• We discussed famous alchemists (Hermes Trismegistus, Maria Hebrea, Jabir, Avicenna, Razes, Albertus magnus, Raimond Lull, and Agripa.

• We discuss the fall-down of the alchemist from the level of the Magus-Demiurge to the lowest level of cheating and forfeiting seeking gold. The image of the Magus migrate to other sciences...

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The 15-16 Centuries constitute exciting times in Western culture:

• At the end of the 15C The New World is dicovered by Columbus, Vasco Da Gama, Magelan, Balboa.... New and great opportunities open up...

• The Renaissance era which begins is typified by challenging of accepted dogmas and by drastic changes in religion, science and art.

• Cupernicus pubishes his heliocenteric theory (1530), and Vaselius, his anatomical research.

• Michelangelo, Leonardo da Vinci, and their contemporaries revolutionize art and architecture.

• Chemistry is stuck behind trying to find Gold and follow recipes of masters on how to carry the chemical transmutation successfully.

15-16 C-Times of Change:

Just inspect the optimistic and radiant Primavera painting of Botticelli & compare it to the sad and depressing atmosphere in the quarters of the alchemist.



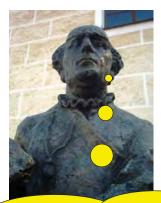
This is sufficient to comprehend the drastic difference between the State of Alchemy and the State of the World in those times.



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A Change is Needed. And this long sought change is brought about by Paracelsus the creator of latrochemistry

The rebellion of Paracelsus is in the spirits of the Renaissance



"Many have said of Alchemy, that it is for the making of gold ... For me such is not the aim, but to consider only what virtue and power may lie in medicines"

Statue in Berathausen- Austria. In Germany there is a U-Bahn station with his name. 76

Who is this reformer, and what is his real name?

• He was born in the border of Switzerland and Austria, and his real name was Philippe von Hohenheim -> Philipus Theophrastus Bombastus von Hohenheim -> Paracelsus.

• At age 16 he studied in Basel, and then in 1527, upon the recommendation of Erasmus of Rotterdam he became professor in Basel

• His self esteem is clear from his choice of the name Paracelsus , which means more than Celsus (the great Roman physician of the 1st Century)

(1493 - 1541)

 Already in his first lecture he burnt books of Galen and Avicenna, using S + Nitre, and expressed his hope that the authors are suffering the same fate wherever they are.

His character and success as a physician resulted in poor relationships with his colleagues. He had to leave Basel abruptly and live as a wonderer till his death.
The little portrait is most likely a realistic painting of how he looked like towards the end of his life.



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The contribution of Paracelsus to the shift from alchemy to iatrochemistry originates in a few reasons:



He believed that Life is a Chemical process, & hence healing must be chemical and substances need to be purified for medicinal use

• This Reorientation Causes scission of chemistry:

latrochemistry = Medicinal goals

Alchemy= Gold Seeking

The importance of latrochemistry is the entrance of Chemistry to center stage, as a science relevant to society!

• Paracelsus borrows from the Arab alchemists their principles, which he calls Tria Prima: Mercury, Sulfur, Salt. He uses them as both abstract and material...

• This duality shows that Paracelsus is still under the wings of alchemy. His approach is still cosmic and mystic, wherein the cosmus itself is an organism, made from the *tria prima* & motivated by <u>'a life-giving spirit</u>' and this unity is the God. He states that he has created a 'homonuculus" by mixing the *tria prima*. ••• Spirit and body are still united.

• The transition to chemistry will require an empirical approach, which characterizes his latrochemist followers in the 17C...



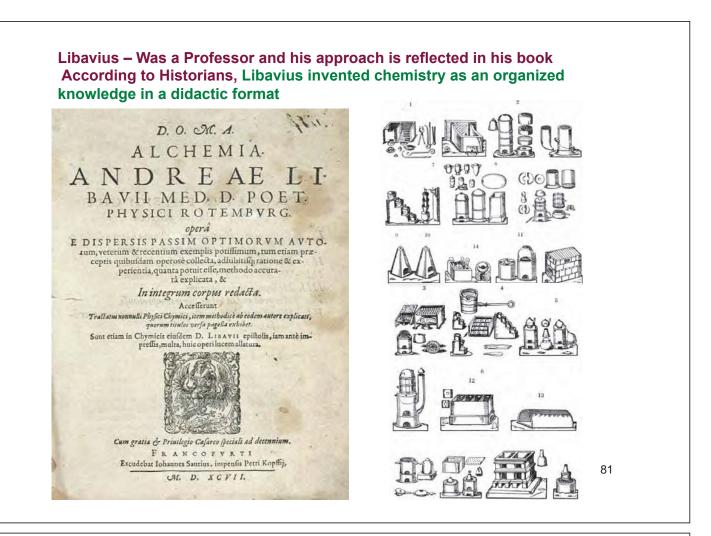
The iatrochemists were essentially Paracelians; they accepted the tria prima & added 2 more:

Tria Prima:	17 Century	Mercury, Sulfur, Salt,	Siegfried p		
	Jean Beguin	Phlegm (W), Earth (fatty)	60		

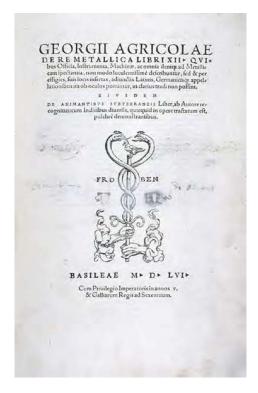
• This addition was rooted in the fact that the main analytical method used by the latrochemists was heating and burning: The heating (distillation) caused the materials to lose first liquids, which became "*Phlegm*". At the same time, the burning of materials left behind some solids, and part of the solids was not soluble in water, and hence became "*Earth*".

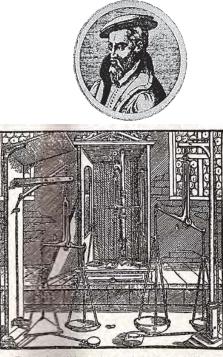
• The necessity to add these principles was the need to describe the entire experience during the latrochemical 'experiment'.

Let us see some of the latrochemists of the 16-17C



• Georg Agricola (1494-1555, Germany): *De Re Metallica-* Treatise of metallurgy- mainly observations





Fis. 17-Assay balances, from Agricola's De re metallica.

Books that follow Libavius borrow his style

• The 1st is the French latrochemist, Jean Beguin which wrote *Trocinium Chymicum* (chymistry for beginners); 1st Ed 1610, English Ed 1669. The book summarizes Libavius' book and popularizes chemistry.

Beguin is followed by 4 latrochemists who were all the King's Physicians (Luis XIII-XIV):

- William Davidson Guillaume Davisson (1593-1669)
- Nicholas LéFevre (1615-1669), Traicté de la Chymie
- Christoph Glaser (1615-1672), Traité de la Chymie

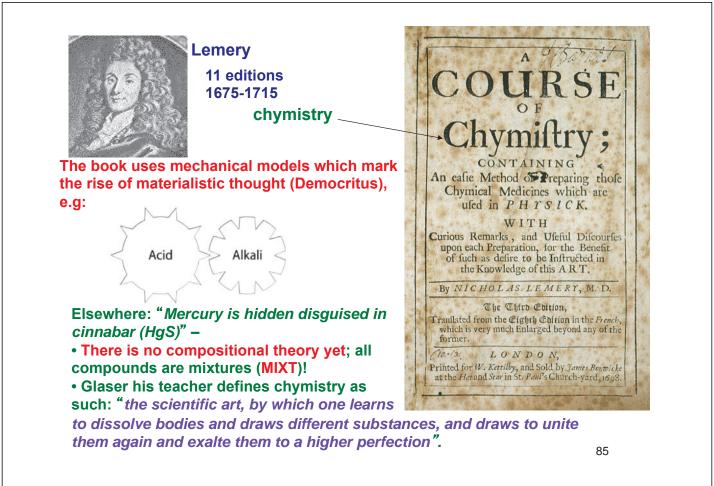
• Nicholas Lemery (1645-1715), Course de la Chymie

•They wrote books for private public lectures they used to give in the Jardin du Roi. All these books were written in a modern fashion a la Libavius with classifiction of materials and techniques.

• The most influential book was by Nicholas Lemery which was published in 11 editions.

• They were all Paracelians and LéFevre called Paracelsus: "Our German Trismegistus".

Nicolas Le Fevre	Complet Poder
	Compleat Body
	OF TATILATION TO THE
	CHYMISTRY
	Wherein is contained whatfoever is neceffary for the attaining to the Curious Knowledge of this Art; Comprehending in General the whole Practice thereof: and Teaching the most exact Preparation of Animals, Ve- getables and Minerals, fo as to preferve their Effential Vertues,
The rise in status	Laid open in two Books, and Dedicated to the Ufe of all APOTHECARIES, &c.
due to iatrochemistry	By Nicafus le Febure, Royal Profefior in Chymiftry to His Majefty of England, and Apothecary in Ordinary to His Honourable Houfhold. Fellow of the Royal Society.
	Rendred into English, by P. D. C. Efig one of the Gentlemen of His Majeflies Privy-Chamber.
	PART. I.
	Corrected and amended; with the ADDITIONS of the late FRENCH Copy.
	Landon, Printed for O. Palleyn Junior, and are to be fold by John Wright at the Sign of the Globe in Little-Bristoin, 1670.



Other Great iatrochemists:

• Johann Rudolph Glauber (1604-1670, Germany).

• Glauber is still a Paracelsian, but his approach is highly empiric and his great skill is technical, e.g., he prepares the acid of marine salt (HCI) - by heating NaCl in potter's clay (high T), instead of Jabir's method using vitriol (H_2SO_4).

1st to recognize that salt is made from two opposing entities: "acid" and "alkali".
1st to do metathesis reactions between different salts to get new salts & the same salt may be made in different ways. This leads to recognition of purity and individuality of substances: "each salt has its own type and [...properties], no matter how it may have been prepared" (Paul Walden - historian).



Na₂SO₄ is called Glauber Salt

The greatest latrochemists is Von (van) Helmunt whose work shows that Alchemy was not really foolish.



Jan Baptista von Helmunt (1577-1644, Belgium) - A latro-Chemist

As we already said, even though the 17C latrochemistry is empirical, its foundations are still alchemical and the 'constituents' of matter are: The *tria prima* of Paracelsus: Mercury, Sulfur, Salt, & the two additions by Beguin: Phlegm (W), Earth (fatty solid)

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The Famous Experiment by von (van) Helmunt is The Willow Tree Experiment



Van Helmunt read the writings of Paracelsus and others and tried to perform "a test of the hypothesis" by characterizing the essential constituent of all matter

 His novel approach was to test the hypothesis <u>quantitatively</u>, using weighing

• The Willow Tree Experiment... conclusion: the only element is WATER (the primordial element)

• This is a rigorous science in the spirit of von Helmunt's times and his theoretical framework! He "missed" photosynthesis, but in his time there was no way to weigh gases or recognize their materiality ... A perfect experiment for that time

• Of course, weighing was not necessary to prove that the tree grows by watering. But the weighing showed: (i) The importance of measurement; and (ii) The power of numbers, which will lead later to the compositional revolution ⁸⁸

More on von (van) Helmunt



• The 1st to discover gases (which is a distortion of the word 'chaos' in Flemish).

He is interested in the "spiritual essence" of body, and analyzes the smoke that is left after burning them. When he burnt 60 pounds of coal what was left behind was only 1 pound of ashes, the rest goes in smoke. He recognized that this smoke is different than water vapors, since it does not condense and calls it 'chaos' - gas.
He notices that this gas suppresses burning, it is evolved in the action of vinegar on lime stone and shells, & during fermentation: The conclusion that the same gas evolves in different processes - very important recognition for the development of chemistry. We'll see this again in Boyle's work.

• So van Helmunt is the 1st discoverer of CO₂ and other gases; SO₂,CO, Cl₂, and CH₄.

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More on Helmunt



• Von Helmunt is the 1st to notice that when a metal dissolves in acid it does not really disappear it can be re-created from the same solution:

• Thus, when he introduced Fe into a solution of copper in vitriol (H_2SO_4), the metallic copper precipitated. Hence, the process of dissolution of copper is not a transmutation, because copper can be reformed by adding another metal to the solution! <u>Mechanistic approach</u>...

• Van Helmunt discovered the acid nature of stomach juices. He proposed that "acids" are the power of digestion. His idea that acids serve as the power of physiology became a universal theory expounded by his students Sylvius and Techenius (invented indicators).

These acid-base relations initiated the notion of "neutral salts", which formed the first 'compositional thinking' in the 18th Century.
In his attempts to prove that all is WATER, he generates from sand "water glass" (Na₂SiO₃) & converted it back to sand-same weight... 1st principle of mass conservation.

More on Helmunt



• Despite his greatness, van Helmunt is still an Alchemist and he expresses his conclusions in an alchemical manner that combines religion, philosophy (Protyle...) and empiricism:

" The spirit of the Lord hovered on the waters, and from water every object takes its origins... Water as such is empty: It is a general medium which precedes all differentiation; all bodies are fruits of water..." (Siegfried, Ch. 1)

"Water" is a womb where bodies are formed – a la alchemy!

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In Summary of latrochemistry, let me explain again how the three principles become 5. Recall that already Jean Beguin, one of Paracelsus followers from the 17th C, feels the need to add to the *Tria prima; Mercury, Sulfur, Salt, also Phlegm (W), Earth (Fatty solid)*

• Recall, the major analytical technique of latrohemistry was combusion/heating (distillation): Heating led to emergence of liquid, while combustion left solids. Some of these did not dissolve in water (unlike salts which dissolved), and hence the *tria prima* were insufficient to describe the scope of the iatrochemical experiment, one needed the phlegm and earth.

• As such, it is important to recognize that despite of the fact that latrohemists were empiricists, their world view, language and conceptual articulation of their experimentation reflected the duality of spirit and matter, and were still alchemical in nature, albeit in the good sense of the word.

Read from
Lemery,
Siegfried p
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A Summary on the State of Knowledge of Alchemy and **latrochymistry** • it is important to note that the doctrines of 4-elements/5-principles did not lead to any experiment whereby a body was analyzed to its constituents, not even van Helmunt experiment, which at best was "synthesis" not analysis. • In fact, the Alchemical/latrochymical analysis was "decomposition of a body" into adjectives" that describe integrated experiences related to the Principles like flammability (Sulfur), liquidity (Phlegm), etc • A material body was called "mixt" and its gualities were a mixture of the qualities of the supposed elements/principles. "Composition" is a continuum of the blending, e.g., adding Phlegm to Earth makes the body continuously more' liquidy'. • A latrochemical explanation of a "composition" rested on analysis by fire and was an ad hoc explanation of what was observed without any attempt to use a cycle of analysis-synthesis as proof of composition. • "AIR" disappeared from chemical consideration, and when mentioned it is a "cosmic influence" trickled from heavens into the earth. • van Helmunt is an exception, but still his "gas" does not have a material essence.

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Despite the latrochemical reformation, Alchemy did not die out. The "Last" Alchemists" *Thompson, The Lure and Romance of Alchemy James Price (b 1752) (suicide 1783) Semler ('salt of life'); Klaproth (1789) the salt of life is Na₂SO₄/MgSO₄ 1931: Heinrich Kirschaldgen (Düsselfdorf) * This tendency is still with us and it orginates in the "magic of chemistry": Polywater Cold Fusion The tendency for the unusual is very strong in our science because its essence is the transformation; the

transformation of matter, the transformation of the soul....

Summary: The Contribution of Alchemy

1-2• In the 16/17C latrochemistry replaced the alchemy. However, latrochemistry only changed the goals (not Gold rush) & in fact, it retained all its conceptual/theoretical frame on the nature of 'bodies'. Interestingly, the philosophical elements of alchemy exist to these days in astrology, and even in psychology. This shows that the human race tends to preserve its myths, which eventually infiltrate its thinking and design its future worlds. 3• What did Alchemy left us?

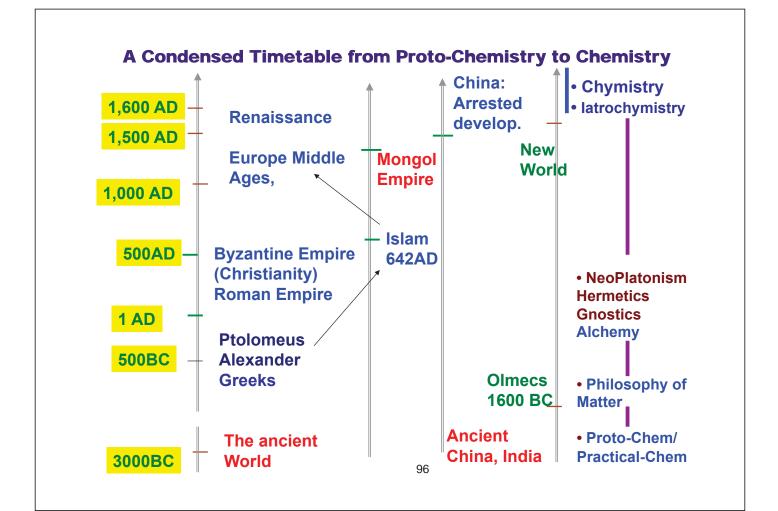
* Mythology and history of chemistry

* A legacy of techniques and many new compounds that were born out of the concepts of alchemy that the ultimate goal of the transformation of matter is the attainment of "perfection"

4• The central concept of alchemy as is embodied by the logo of the Ouroboros, teaches us that the transformation is periodic & eternal and that we must learn to tune with the harmony of nature instead of pushing it off balance.
5• Green chemistry is a manifestation of the ouroboric concept of alchemy. Organic agriculture is so too.



6• Chemistry continues to deplore Alchemy; But, a science that ignores its history and mythology ceases to be a fundamental intellectual arena of human activity...



A reminder:

The latrochemists, headed by Paracelsus, reoriented Christian-Western alchemy from gold-seeking to medical needs, and have therefore caused a major flourishing of chemistry and upgraded the status of chemists.
Great Practical chemistry was done by Glauber and van Helmunt. Look at the beautiful tools of alchemists and latrochemist:





• Still though latrochemists were thinking and working within a cosmic theory of matter; 'as above is below'. Thus, despite their use of materialistic language their building blocks are actually metaphysical. Air disappeared from matter and became a metaphysical spiritual entity.

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The Second Reformation en-route to Modern Chemistry - Atomistic Thinking

A History of Chemistry, Lecture 5

 The 2nd Reformation (17C - begin of **18C): Rise of the corpuscular**/ mechanistic philosophy, which lead to alternative Chemical Theories: **Elective affinity; Phlogiston.** • As we shall see in the next weeks, these changes bring about the 3rd **Reformation which forms the** "compositional"- material chemistry & defines the "chemical identity". Let me emphasize that I do not think that the separation of spirit and matter is necessarily right or the last word in science. On the contrary... Still this separation was a must for the formation of the science of chemistry in the productive form we know to day.

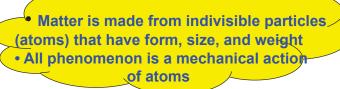


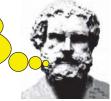
 latrochemistry defined a practical agenda for research, but did not provide a coherent organizing conceptual for organizing chemical knowledge In parallel to latrochemistry, the field undergoes another reformation, during the 16-18C; instead of the abstract elements/ principles, a corpuscular philosophy starts to be established, but although it makes changes, it still falls short of providing the organizing principle for chemistry. Almost 100 years will have pass to usher the compositional revolution and to define the "chemical identity". The stumbling stone is the Chemical magic: • When bodies mix, the properties blend, but when they react their properties disappear! This magic was also the root cause of the difficulty to form a chemical theory that will include this magic. Still, since the corpuscular approach ceased to be metaphysical, it served as a stepping stone for modern chemistry. 99

• Let's tell the story of some of these heroes.

Atomism

• Let us go back in time & recall that alongside the abstract theory 4-elements/3(5) principles there was an atomistic theory of Democritus and his school. Here he expresses his theory clearly and succinctly:





• Recall: the elements/principles theory was continuous allowing infinite number of combination to form a mixt, whereas the theory of Democritus was "quantized" - matter is not continuous!

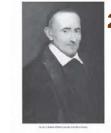
• Atomism was rejected because it lacked the spiritual content and did not describe the integrated experience (beauty, hot-cold, etc). It was also anti-religious since the days of Epicurus, and hence atomism was vehemently rejected by the Church. This attitude changes in the 17C...

In the 17C there's awakening of the Corpuscular/Mechanistic Philosophy that reaches its peak with Newton in his book *Principia*. Here are some of the dominant figures:









5



Bruno

Descarts

s Gal

Gallileo

Pierre Cassendi



Newton









Sir Francis Bacon (1561-1626) *Novum Organum* - 1620 (The New Method)



He is the frontrunner of the separation from the Aristotelian scholastic approach.
The Rule of facts and deduction: "Further progress in knowledge... can only be looked for... when a large number of experiments are collected and brought together into a natural history".

• This is the hypotheticodeductive approach to science that still rules much of chemistry....



1. Bacon criticizes alchemists and Paracelians, whose deductions are based "on a narrow and obscure foundations of only a few experiments... A notable example of this is to be found in the alchemists and their teachings... It is true that alchemists have some achievements, but these came by chance, not from any art or theory... The alchemist nurses eternal hope, and when the thing does not succeed, he thinks he has not properly understood the words of his art or of its authors..."



2• Bacon's atomism is a bit strange. On the one hand, his atoms fill space, and are not real bodies but internal and undefined structures that are typified by the properties of the bulk. On the other hand, he sometimes believe they are real observable bodies: "the microscope is only useful for looking at small things, and if Democritus had seen such an instrument, he would perhaps jumped for joy"

3• Other than being the 1st important atomist after Democritus, his hypothetico-deductive approach to science Influences Boyle & Hooke, who will establish of the Royal Society of Sciences in 1662.

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Robert Boyle (1621-1691)

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Boyle was the son of the Earl of Cork, born in Waterford in Ireland. When his father died he moved to Dorset, and used his wealth exclusively for science.

Boyle Is considered to be the dominant figure in the transformation of alchemy to chemistry.
It is common to ascribe to him a full disengagement from alchemy. But recently, there are new publications showing that both he and Newton were avid alchemists.

• We have to remember though that people are not one-dimensional & and certainly not a person like Boyle – Hence he could have been engaged in alchemy and at the same time going against it!

Boyle is considered to be the father

of **pneumatic chemistry** in which he used the vacuum pump invented by von Guericke to derive the first rule of physical chemistry, Boyle's law.

Robert Boyle is also one of the pioneers of the corpuscular approach and the mechanistic philosophy in chemistry.

• In 1661 he publishes his book, "The Skeptical Chymist", which is written as a dialogue between Carneades (Boyle's voice) & the Aristotelians & Paracelians and he criticizes their approach to chemistry:

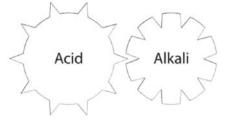
The 4-elements & 5-Principles are one and the same things, and according to the theory, "these are the ingredients of which all those called MIXT bodies are ... compounded and into which they ... are resolved."
But experiments show, according to Boyle, that the bodies emerging from a heated compound are neither elementary nor identical for different compounds.
A chemical composition must be proven by a cycle of analysis-synthesis! - This is the guiding principle in modern chemistry.



THE CEPTICAL CHYMIST BY CHYMICO - PHYSICAL Doubes & Paradoxes, Training is Paradoxes, Commany range MCASS Commany range MCASS

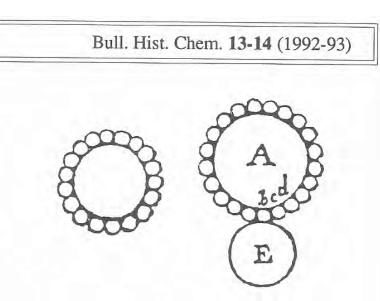
Boyle's Principles of Atomism are the following:

- All compounded materials are composed from the same corpuscles that however differ in their shapes and packing:
- "Any body owed its properties to the arrangement of these particles... Stable arrangements are more frequent"
- e.g. Fe is hard due to the packing & movement of its particle (unlike what Aristotle would say: it is hard because of its property of 'hardness').
- Boyle also thought that a chemical process is a change of packing & motion of the constituent particles.



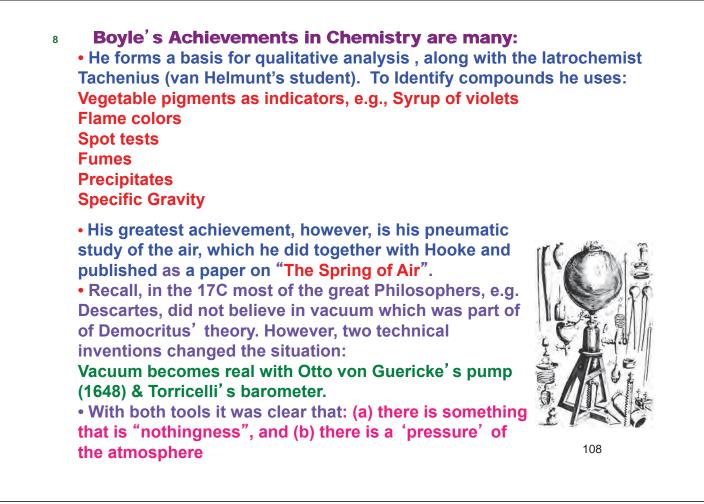
- **4.** A Reminder of Boyle's mechanical ideas is Lemery's acid-base corpuscles (1715)
- Lock & Key in Biochemistry of enzymes!

5• While this is advanced thinking there is nothing new beyond Democritus. All the more, Boyle's theory allows transformation of anything to anything. It lacks a definition of "chemical identity" and hence, it couldn't form an intellectual basis for chemistry. Nevertheless, the seeds of the corpuscular theory have already been planted... A Reminder = of the mechanical theory in the corresponden ce of Newton and Boyle: Description of a Salt



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*.

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This is the instrument with which Boyle and Hooke derived Boyle's Law, PV = K



An Disense on this and between the and this band Design of the second order of the red second convertised or the red second convertised or the red second convertised or the rest second or the second or the REFE at REFE CONVERSION Invertised Convertised Acceleration where rest of the second or the rest of the second of the Boyle and Hooke pumped out the air from a glass vessel, hooked to a barometer & found



strokes that every pump stroke decreased the level of mercury (h), & hence pressure & volume are linked...

Air

Hg

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Then he did the "J-tube" experiment, in which he showed that the air left in the J-shaped Torriceli tube shrinks as more Hg is added to the open and long arm.
By measuring the heights of the air part and the Hg column, he showed an inverse relationship, between pressure and volume, and thereby derived the Law PV = K. This is the 1st Rule in "Physical Chemistry"!

Boyle Had Achievements in Air Chemistry & in Combustion:

1• The ticking-clock experiment - fainter ticking with more pumping, but transmission of light or magneticity were not affected.

2• Since Combustion is considered as the main analytical method, Boyle tests the role of Air: With increased pumping: (i) combustion stops, (ii) sulfur fumes but does not burn, (iii) gun powder (C,S, saltpeter) still burns even with 'complete' vacuum => particles of air and saltpeter are good for combustion
3•Weighing Experiments during combustion of metals in sealed glasses. Boyle finds that the weight of the metal increased - He suggests that the metal gained real corpuscles in the air which can pass even through glass. Breaking the glass air enters in in a whistle, but he is still not a believer in the air's materiality

4• Boyle formulates a theory of air; it is composed of three particles: (i) real air particles that are elastic and fluid, (ii) exhalations from the earth, vegetables, animals, (iii) exhalation from celestial bodies and the sun (particles of light, etc). => combustion is due to (ii) & (iii); i.e. still no recognition in air as matter.

5• His partners Hooke and Mayow suggested that the air consisted also of inflammable corpuscles that are common to the air and the Saltpeter.

6• Boyle, Hooke and Mayow understand the role of air in combustion but cannot identify oxygen since the means of collecting gases were still nonexistent.

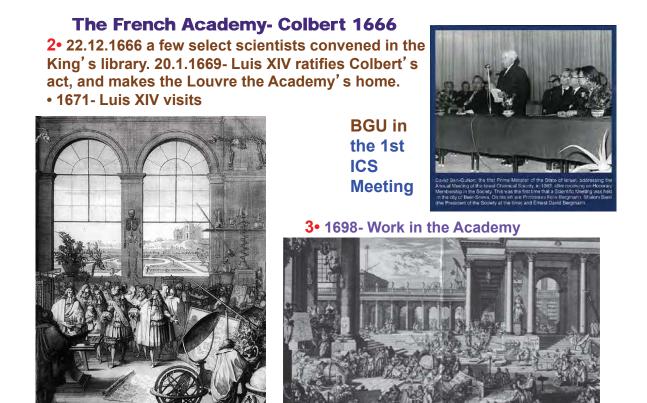
More Reformations en-route to Modern Chemistry -Atomistic Thinking

1 • The atomistic-corpuscular approach and Boyle's dictum of establishing chemical identity by means of a cycle of analysis-synthesis seeded the 3rd Reformation.

2. The reformation associated mostly with the French Chemists, and we shall talk about the following topic:
Neutral Salts (made from acids and alkali), and how they bring about he ascent of "compositional" & "chemical identity" concepts.

3• Since the contribution of the French chemists to modern chemistry is associated with the establishment of the Academy in Paris, we shall start by saying a few words about the Academy.

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obtained as an oily liquid by extracting the ashes of burning plants. • Also known was alkali of *tartar*, that was produced from deposits in wine barrels. Later known that both are K_2CO_3 (Na_2CO_3).

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The terms salt was coined 1st time in Europe in 16C and 13

was called so to describe the soluble material extracted from the solid residue after "analysis of a body by fire".

• Paracelsus defined 'salt' as one of the tria prima, whereby the "principle" describes the body's resistance to fire, its solubility, and saline taste.

• By the end of the 17C known acids are: * HCI (spirit of salt), HNO₃ (spirit of Niter or aqua fortis), H₂SO₄ (spirit of Sulfur or vitriolic acid). By the way, the different names for H_2SO_4 mark the common notion that these are different acids: * one from burning of S, * the other from

"killing and nullification" (recall: the chemical magic).

cooking vitriols, which are salts, e.g. $FeSO_4$ in some acid.

 in the midst of 17C, Glauber was the first to recognize the mutual destruction of acid and alkali -which he called

definition: While Rouelle's definition is clear compositionally, it

3. Before proceeding, note a few aspects of Rouelle's

contains terms that are a bit opaque regarding the alkali. Let's therefore talk about salts and their constituents...

History of Neutral Salts

a nice history of chemistry:

1. 1744 Rouelle: "I call a neutral salt every salt formed by the union of whatever acid,..., with a fixed or a volatile akali, an absorbant earth, a metallic substance or an oil". [Mémoires of the Paris Academy]

The mémoires of the academy are important and give us

2• This definition of a chemical identity causes in 1782 to the formation of a compositional nomenclature of neutral salts by Guyton de Morveau: from 18 acids and 24 alkalis (bases) => 324 "names" of salts.

2a• As soon as language becomes precise, this leads to a more precise scientific research. This is part of the background that prepares, what historians call, the "compositional revolution".





BERNARD GUTTON-MOR

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Reactions of Acid-base & Neutral Salts

• In 1668 Pierre Borel, a French chemist suggests to define the reaction of acids and alkali as follows: "*if a body effervesced by addition of acid, it was an alkali and vice versa*". Of course, this refers to the formation of CO_2 from K_2CO_3 . Note that Borel is not aware that gas is a material entity, but nevertheless there is a recognition that the "*end*" of the process was the end of effervescence, which Borel calls the "*bowl action of the earthy alkali*" with the acid.

• Note that the Mythical idea of the bowl action of the "earthy (fatty)" principle leads to useful scientific models. Recall that van Helmunt described acid-alkali reactions as a model of animal digestion.

• Boyle used vegetable pigments (especially syrup of violets) to determine "end point" of reactions, and relied on color changes as means to identify acids and bases.

• Boyle objected to Borel's definition and showed that Cu dissolves in aqua fortis but also in alkaline urine! This means that Cu is not alkaline even if it leads to effervescence with acids, because at the same time, Cu dissolves in the alkaline urea.

• We clearly see here embryonic chemistry!

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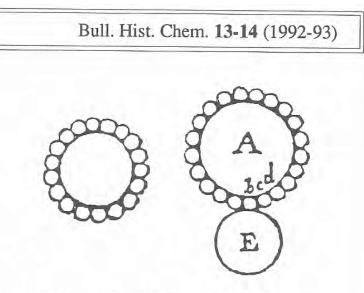
• The conversion of the term 'alkali' to "base" has mythical origin. The Greeks already referred to the 'elements' as 'matrices' i.e. "cosmic wombs" wherein things are formed. Paracelsus describes the action of the cosmic womb in the deeps of the earth (recall, the drawing of the 4 elements as wombs)



• Initially, 'alkali' slowly transforms to 'matrix', because many alkalis come from 'earthy' sources, like quick lime (CaO) & limestone (CaCO₃), etc.

• In 1713, Louis Lemery (son of Nicholas Lemery) describes a reaction between saltpeter (KNO₃) & vitriolic acid (H_2SO_4) that forms *aqua fortis* (HNO₃) & a precipitate. He writes that the saltpeter parts off with its acidity, while the vitriolic acid: "remains at the bottom of the crucible with the matrix of saltpeter".

Namely, both acids are held inside alkaline matrices, and the reaction is simply exchanging place in the 'matrix' – one acid out & one goes in. $KNO_3 + H_2SO_4 \rightarrow HNO_3 \uparrow + K_2SO_4 \downarrow$: Here is a reminder how Newton and Boyle and their contemporaries described a salt as an acid encapsulated by metallic particles.



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*.

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• Later in 1717, the same Lemery writes on aqua fortis : " that in its natural state it is found in several sorts of terrestrial saline sulfureous materials which serve as its base or matrix".

This is the 1st time the term **base** appears. Lemery uses alternately the terms "matrix" and "bases" as a "container" of the acid. Note that he refers to these containers as "sulfureous" – Here the association is to the Paracelian term of the sulfur principle that represents inflammability. Recall that nitrates are typically inflammable.

• In 1735, Jean Baptiste Hamel describes the reaction between NH_4CI (sal ammoniac) & vitriolic acid and writes about H_2SO_4 doing to NH_4CI :

"It removes by superiority of force the alkali which was its base...and takes it for its own, and the marine acid [HCI] thus freed & passes off in distillation"

Namely, the H_2SO_4 kidnaps the ammonia from HCI ('the alkali which was its base') and releases the HCI to the air.

• Thus in a span of a few years the cosmic term "matrix" vanishes in favor of the practical term "base".

The cycle "analysis-synthesis"

1. By Boyle, a Proof of Chemical Identity must be done in a cycle of analysis-synthesis. Let's see how chemists apply this dictum: One of the first to do so is Wilhelm Homberg (1652-1713), born in Jakarta and then becomes a member of the French Academy.
2. In 1703, he synthesizes the 'spirit of sulfur' by burning sulfur and then he synthesizes the 'spirit of vitriol' by cooking green vitriol (FeSO₄) in *aqua fortis* (HNO₃).

3• He concludes that the two "spirits" are identical: "*ils sont parfaitment la même chose*", adding: "because everything that can be made by the spirit of vitriol can be made also by the spirit of sulphur and vice versa".

4• He then continues :

"Also, the vitriols [e.g., CuSO₄] could be recompounded with either of these acids with a selected metal to give the true vitriol of the metal".

5• He then uses the 'base' of tartar (K_2CO_3) and shows that the "two spirits" (acids) gave the same crystals (K_2SO_4).

6• This is a proof of chemical identity by means of the analysis-synthesis cycle.

And More on "analysis-synthesis" tool for chemical identity

• In 1718 Etienne-François Geoffroy generates the 'spirit of sulfur' by burning sulfur. Then he "resynthesizes" sulfur by cooking the spirit of sulfur with charcoal (C) and the oil of tartar (K_2CO_3), he gets the liver of sulfur (K_2S_n) to which he adds dilute vinegar & leads to precipitation of sulfur powder ("magistry of sulphur").

The secretary of the Academy writes in the mémoires: "one is never so sure of having decomposed a mixt into its true principles as when with the same principles one can recompose it".



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2• There is thus clearly a prevailing recognition in the cycle of analysis-synthesis as the means to establish chemical identity.

3• Still, it may seem strange to note that the Secretary considers sulfur as a mixt (compounded). But recall that we are still under the partial rule of the "principles theory", wherein S is made here from: EARTH (oil of tartar), SALT (spirit of sulfur) and a FATTY material (charcoal).
• Nevertheless, the logic of the experiment is a proof of identity.

•The Term Salt - from a 'Principle' to Chemical Identity

Known natural salts 18C: vitriols, alum [AIK(SO₄)₂; AINH₄(SO₄)₂], saltpeter (KNO₃), marine salt (NaCl). Borax (Na₂B₄O₇) was defined by Lemery as a salt in 1703 because of its failure to react with either acids or alkalis. Hence:
in the early 18C, the functional definition of salt is a product of the reaction of acid-alkali, & this identity has to be proven by generating the same products from salts originating from different sources:

• Lemery who investigates vitriols writes about its goal: "I wish to know... that neutral vitriol that is formed in the bowels of the earth [is identical] with the same materials and in the same manner that we fashion in our laboratory".

• Therefore, Lemery takes Fe and dissolves it in vitriolic acid (getting FeSO₄). He then shows that the product does not react to magnets (discovered in 1600 by Gilbert). Subsequently, he heats the product until a sulfureous smell comes out and a residue is formed ('FeO'). After heating the residue further, he obtains a body that reacts to magnet (Fe). He repeats the same process with "Natural English vitriol" (FeSO₄) and gets the same results. He then writes:

"The last operation certainly proves to us that the common vitriol is not different from that we make..."

This is a generalization of the chemical identity for salts. 12

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En Route to Chemical Identity: Early Recognition of the Principle of Conservation of Mass

1• Homberg and then Geoffroy make attempts to weigh the reactants and products in reactions between acids and alkalis. In all cases they do not find a weight balance and they discuss it in terms of impurities and all kinds of other errors.

2• It is clear that they are fully cognizant of the **Principle of Conservation of Weight.** The reason is probably religous since "nothing can be lost in the world of God"

However, none of them is cognizant that "AIR" or gases are material bodies, since they still have no means of collecting and quantifying gases.

3• The gas becomes "material" when the technique of collecting gases becomes available. Then the principle of mass conservation causes the "compositional" revolution.

But everything is already in the air and in the background...

Lecture 6 & Summary of Lecture 5:

• 2nd Reformation Alchemy to Chemistry: The ascent of the corpuscular theory. Rejection by the Church: (i) Atheistic (Epicurus), (ii) atoms that cannot be subdivided - anti religion ["there's nothing in God's world that is unachievable"!], (iii) vacuum is objectionable. ... Casendi's influence...

• The main influence on the transition to chemistry:

- (a) Bacon: first experimental facts than theory a positivistic deductive approach Chemistry accepts the rule of deductive-positivism.
- (b) Boyle: (I) shakes the "4 elements", (ii) a proof of chemical identity requires a cycle of analysis-synthesis, (iii) establishes with Hooke the Royal Society of Science (1662), (iv) formulation of Boyle's Law (enabled by the vacuum pump - Guericke, and the Torricelli Tube).

• The French Academy (ours is similar) and its mémoires. Its chemistry follows the Bacon-Boyle's dictums.

• Neutral salts: the family of compounds for which there is a clear recognition of "chemical identity", and use of the analysis-synthesis cycle to define identity.

• The mythical origins of the names "salt, acid, base" and their 'transmutation' from mythical to material terms - <u>the alchemy of language.</u>

•1744- Rouelle's compositional statement on the composition of salts.

- Homberg, Joeffroy, Louis Lemery and others perform a proof of identity in a Boyle cycle. Homberg and Joeffroy clearly know of "mass conservation"
- Further progress in Chemistry will come from Neutral salts, but a theory is needed!

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Bablverwandtichaften.

Ein Roman

Goethe.

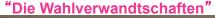
Erfler Theil

¹⁹ The 1st Practical Theoretical Principle of Composition is the Theory of Elective Affinities: Meaning Chemical Selectivity of mutual attractions

2• The term 'Elective Affinity' appears for the 1st time in Lemery's book in the 17C, as a selective attraction between acids and certain alkalis and is explained in terms of the mechanical philosophy.
3• During the 18C the idea evolves to a practical theory by Geoffroy. This is one of our main topics in today's lecture.

Very influential theory: In 1809 it becomes a title of a roman by Goethe, and includes a discussion of social relations in chemical terms by Eduard and Charlotte –
it is still in sociology, Max Weber

• 19C chemistry is highly important



20 Geoffroy 1718- an interesting table similar to Mendeleev' s: "Tables des différens rapports observé en chymie entre différens substances"

• He states that the Goal is to enable chemists to decide what reaction transpires and "to predict what should result when they mix different bodies".

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• each column IS a title, e.g. 1st entitled "esprit acids": • The top compounds are Na₂CO₃, K₂CO₃, called; "sal alcali fixe & volatile", which combine best in the column with any acid, i.e., having the highest affinity towards acids.

• other columns: refer to the same preference with respect to specific acids, e.g., 2nd col. HCI (acid du sel marin), 3rd acid nitreux (HNO₃)...

5

• Note:2 entries in a column represent a chemical reaction, e.g. in col. 2, the title is HCI. Hence Sn, at the top, will replace Hg, which is 5th, from its combination 12 with HCI: Sn + HgCl₂ \rightarrow SnCl₂ + Hg

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 Ursula Klein credits Geoffroy as the 1st to generalize: "the basic concept of modern chemistry - that of the chemical compounds, and its related notions of chemical analysis, chemical synthesis and chemical affinity"

Geoffroy



Rouelle



 This is the background for Rouelle's 1744 definition of a neutral salt.

 Indeed the area of neutral salts become in 1750 onwards the most secure empirical basis of knowledge in chemistry, thus laying the foundations for a new "compositional nomenclature" en route to 126 the compositional revolution

The idea of 'Elective Affinities' and its representation by Goeffroy in a table,

enables the systematization of the chemistry of salts.

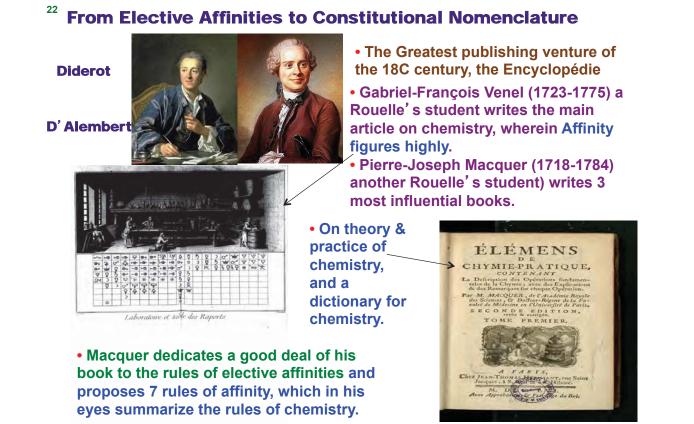
• This systematization has many followers all over Europe

• Gradually the amount of information that gets organized under the wings of this theory increases and becomes the driving force of an organized science of chemistry.



• Let us mention some evidence for this systematization of chemistry.

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Macquer's Rules 3 and 4 of Affinity are Noteworthy:

Rule 3: "when bodies unite they lose part of their properties, and the compounded body acquires part of their properties"



This is some recognition that chemistry is not a mixture of bodies – "The Magic of Chemistry"

Rule 4: The simpler the body the greater is its affinity and the more difficult it is to decompose it to its constituents

This rules forms a background for a future definition of "an element" which will be done later by Lavoisier.

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23 Extended table of Affinities en route to Constitutional Nomenclature

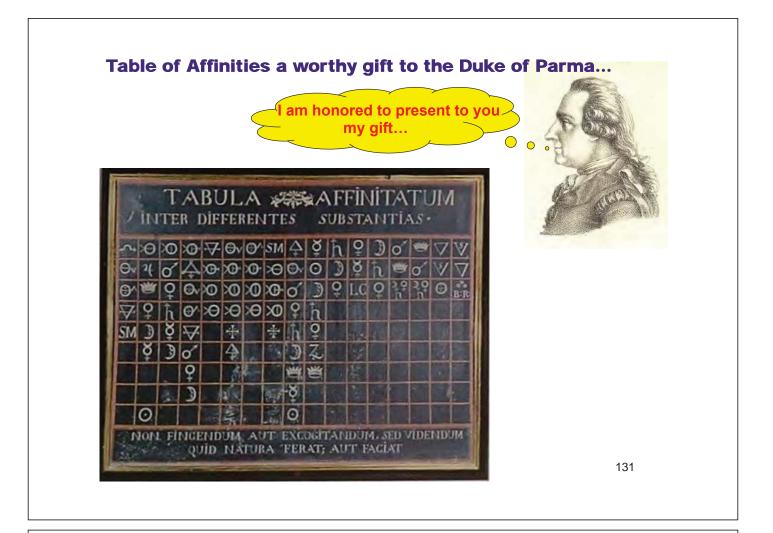


• One of Geoffroy's most productive followers was the Swedish Torben Bergman (1735-1784) from Uppsala: Originally a mathematician and a physicists, but turned chemist of minerals, and the teacher of Scheele.

• 1775: "A Dissertation on Elective Attractions".

1775-1783: The Table contains a few thousands of chemical reactions, classified according to substance types (acids, bases, metals, etc) and reaction conditions (dry-by fire & wet-in solution).
He estimates 30,000 more experiments are needed to complete all the possible combinations.

Torben is influenced by Linneaus (1737) who used genus and species to systematize the biological nomenclature. Bergman uses in addition to alchemical symbols also letters A,B,C, to classify.
 With the great explosion of knowledge it is not possible anymore to be content with the old, descriptive, names like "the liver of sulfur" (K₂S_n) or "aqua regia", etc. A systematic method is needed!



25 The 1st Step towards Constitutional Nomenclature and a Chemical Language was done by Louis-Bernard Gyuton de Morveau (1737-1816)



- A lawyer, an attorney general of Dijon & a chemist.
- As a politician he votes for the execution of Louis 16
- He serves in the "committee of public safety" after the revolution.
- He invented gun powder.
- He established the Balloonist Regiment, who use flying balloons full of H_2 to fight from the air.
- He established the Ecole Polytechnique, etc

Gyuton de Morveau



is in strong connection with Bergman. He tries to measure affinity by measuring the force needed to lift metal plates floating on Hg – Classical Newtonian!
In 1782 he undertakes to write a chemical dictionary for the Encyclopédie Méthodique & Neutral salts is a good field to start. His general principle: "the denomination of a chemical compound is ... precise only to the extent that it recalls its component parts by names conforming to their nature".

• The components of neutral salts were the acids & bases which formed the salt. Hence, he proposes a la Linneaus: the name of the acid is the *genus* of the salt, the base will define the *species*.

• Salt name: generic name + base suffix, e.g., vitriol de plomb (PbSO₄), muriate de calcaire (CaCl₂), etc. 474 names, which require to know only the acids and bases

• An important contribution of de Morveau is the definition of a "simple body", which is an operative definition of "a chemical element": "*it is not yet possible to separate to their principles*".

• The notion 'simple body' is around for many years but at a sub-conscious level. Guyton is the 1st to define it as a 'simple body', and as such he brings it to a conscious level, thus making it an intellectual tool.

25b

25a



• Indeed, the concept of 'a simple body' and the constitutional nomenclature of Gyuton de Morveau join to form a new basis for the chemical knowledge.

Concepts generate new worlds...

A new world for chemistry will be unveiled soon by Lavoisier.

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²⁶ To understand Lavoisier we need to learn about Phlogiston

• Phlogiston theory was developed in the 17C, and in the second half of the 18C it affected the thinking of the French chemists, especially Rouelle and his students Macquer & Venel.

• The importance of this theory derives not from its depth but mostly from the fact that it will be used by Lavoisier as a straw-man to be toppled and as means to usher his own ideas on chemical matter.

• Recall that Combustion was the most important analytical tool, which decomposes a body to its constituents. There were bodies that were inflammable (e.g., charcoal) & wherein the 'firey principle' was "fixed" as "heat".

• Indeed, despite the rise of atomistic thought, the ruling theory is still the 4-elements/5-principles. The fiery 'principle' was called the 'sulfur principle'. However, the word 'sulfur' is ambiguous; it is both a real material (brimstone) as well as the 'fiery' element fixed in inflammable materials.

• This ambiguity is disturbing, and hence the 'sulfur principle' will be split into (i) the free element of fire that causes chemical changes, and (ii) the "fixed fire" so called phlogiston- which is the element of inflammability that is fixed into inflammable material.

Let us learn about the evolution of the term Phlogiston

27 The 1st Phlogistonist: Johann Joachim Becher (1635-1682); a mine chemist in Germany and England



• With this experience he tended to emphasize "earthy" elements. In his 1669 book, "Physical Subterranea", he proposed the elements, AIR, WATER, & EARTH, and concluded that EARTH existed in 3 modifications : terra vitrescible, terra fluida & terra pinguis.

 According to Becher: Inflammable bodies were supposed to be rich in *terra pinquis* that gets lost during combustion, or during calcination of metals (conversion of metal to oxide).

• Thus, Becher replaces the 'sulfur principle' by terra pinguis. Nothing terribly new other than renaming of the Paracelian principle.

His Famous Citation: "...Chemists are strange class of mortals, impelled by an almost insane impulse to seek their pleasure among smoke and vapor, soot and flame, poisons and poverty, yet among all these evils I seem to live so sweetly, that [I' d die before I' d] change places with a Persian King"

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Our Next Hero is the father of Phlogiston: Georg Ernst Stahl (1660-1734)

 An Austrian physician, **Professor in Halle** & then the personal physician of Friedrich Wilhelm I, the great Prussian Elector.



• Inspired by Becher, he explains in his book the reason for renaming of the 'inflammable principle': "I have felt... fitting to name it from its general action which it customary shows in all its compounds. And therefore I have chosen the Greek name phlogiston, in German, Brennlich".



Phlogiston Theory

• Using this new term, Phlogiston, Stahl explains combustion as escape of Phlogiston from the inflammable material. For example:

wood[phlogiston] → calx(ash) + phlogiston↑
 metal[phlogiston] → calx + phlogiston ↑

The reverse process is a phlogiston transfer: • calx + charcoal[phlogiston] → metal[phlogiston]



• Using this concept he explains that breathing involves phlogiston too.

• In modern oxidation-reduction terms, phlogiston is equivalent to minus[O] (or an e-)...

• Stahl was pompous and obnoxious, very critical, not answering letters, aggressive towards criticism. These qualities however seemed to have only intensified his reputation, importantly among the French chemists

29

28a

The Phlogiston Theory - An Appraisal

• The phlogiston was not a new concept, it was simply a new name for the same thing (the inflammable element fixed in inflammable bodies).

• In fact, Stahl and the French Stahlists use this term exchangeably with the equivalent terms, e.g., the 'sulfur principle'.

• Our next story will be: How did the Phlogiston theory then become so important that Lavoisier had to target it en route to his constitutional revolution?

Rehearsal Elective Affinity - 1st theory & Nomenclature in chemistry; **its originator**, **and his followers**





We also discussed the explosion of information and the need to formulate a compositional nomenclature, which is achieved by Guyton, who also defines 'simple body'

Phlogiston - A theory that becomes important in France



wood[phlogiston] → calx(ash) + phlogiston↑
 metal[phlogiston] → calx + phlogiston↑
 The reverse process is a phlogiston transfer:
 calx + charcoal[phlogiston] →
 metal[phlogiston]
 breathing involves phlogiston

AIR

• In the 18C, AIR returns to chemistry as a material, and this paves the way to the constitutional revolution. Our story today will focus on AIR

• This is also the story of the "magic of chemistry", since the notion of "fixed air", that exists in solids like lime stone $(CaCO_3)$ started to puzzle chemists. Even more puzzling was the notion of the "free air" that became a celestial influence that trickles into air from the heavens.

• We mentioned Boyle and his important work on air, and we pointed out his that Bolye was unable to view the air as a material entity.

• We saw that Boyle, Hooke and Mayow understood that air and Saltpeter (KNO₃) contained something that helps combustion, but they were still unable to grasp that this was oxygen.

• The Dutchman Drebble even suggested to use Saltpeter in submarines, because when it is heated it helps breathing. But it is doubtful he thought about oxygen.





But all this is going to change soon...