Chemistry

The Science of Matter

Qualities vs. Quantities

- Chemical properties seem qualitative.
  - Alchemy was almost entirely qualitative.
  - Colour, consistency, taste, odour, hardness, what combines with what.
  - Chemical change is a change of quality.
- Terminology:
  - "Virtues"
  - "Active principles"
- All ancient precepts

Quantities only, please…

- The new science, since Newton, required that all facets of the physical world be describable with measurable quantities.
  - Everything is to be understood as *matter and motion.*

Phlogiston Theory

- Phlogiston theory was the first workable chemical theory that was conceived entirely on mechanist principles.
  - Its origin was from alchemy.

A Biblical interpretation

- J. J. Becher was a German scientist/philosopher of the mid 17th century, the son of a Lutheran minister.
  - He noted that the book of *Genesis* spoke only of organic materials, and concluded that they were the sole basis of creation.
  - Metals, he concluded, were byproducts of organic matter.

Terra Pinguis

- Becher believed that there were three principles of compound bodies:
  - Vitreous
  - Mercury
  - *Terra Pinguis* (fatty earth).
- *Terra pinguis* is what gave bodies their properties of taste, odour, and combustibility.

Phlogiston

- Georg Ernst Stahl (1660-1734), a German physician, took the notion of *terra pinguis* as an essential explanatory principle.
- He changed its name to *phlogiston*, the fire principle.
  - Through phlogiston, Stahl endeavoured to explain all of chemistry.

Phlogiston's properties

- Phlogiston is released when:
  - Wood burns.
  - Metals calcify or rust.
- Escaping phlogiston stirs up particles and thereby produces heat.
- Phlogiston is found in great quantities in organic matter.

Confirming phenomena

- Metal calces are powders, like ash, resulting from heating metals in a fire.
  - Stahl's idea was that phlogiston was driven out of the metal when the calx was produced.
  - If he reheated the calx in an oven filled with charcoal (which he believed was very rich in phlogiston), the calx turned back into the original metal.

Confirming phenomena, 2

- Plants, he believed, absorbed phlogiston from the atmosphere.
- They burned readily because they had much phlogiston to release. (That being the definition of burning.)

Confirming phenomena, 3

- Combustion, he found, was impossible in a vacuum.
  - Explanation: There was no air present to carry off the phlogiston.

Minor hitch in the theory

- Typically, metal calces weighed more than the original metal.
  - How can this be if the calcification process drives off the phlogiston in the metal?
  - Answer: Phlogiston possesses levity; i.e., it is lighter than nothing.

Levity is an ancient idea.

- Levity, or inherent lightness, is an idea found in Aristotle.
  - Air and fire rise because they possess levity, while earth and water fall because they possess heaviness.
  - These are qualitative notions. They do not fit in quantitative, mechanist explanations.

All air is not the same

- Parallel to phlogiston theory, another concept entered chemistry about the same time: the notion that "air" is not just one thing, but that there are different kinds of "airs."

Gases

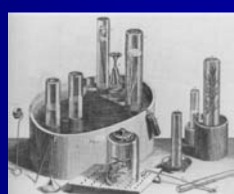
- Johann Baptista van Helmont (1577-1644) introduced the term "gas" to refer to different kinds of airs.
  - "Gas" comes from the Greek word χαοσ, from which we get "chaos" in English.

Air versus Gases

- The ancient concept was that air was just air, sometimes permeated with solid bits floating in it (e.g., smoke), but not composed of different gaseous substances.
- Hence gases ("airs") were ignored by alchemists.

Collecting gases

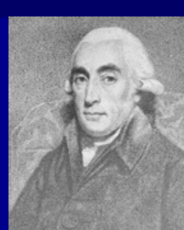
- The problem with studying gases is that they escaped.
- An ingenious device was invented by Stephen Hales in 1727 to collect gases from chemical reactions.



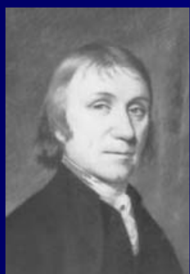
The pneumatic trough for collecting gases.

New gases

- Joseph Black (1728-1799), in Scotland, identified several new gases, giving them names consistent with phlogiston theory.
  - E.g., "fixed air," what we call carbon dioxide.
- Other researchers identified other new "airs."
  - E.g., "inflammable air" (hydrogen).



Joseph Priestley



- Another British chemical researcher was Joseph Priestley (1733-1804), a Unitarian cleric and teacher of modern languages in Birmingham, England.
- Priestley was an enthusiastic amateur chemist.

Dephlogisticated air

- Priestley produced different gases by fomenting chemical reactions and collecting the gases produced with a pneumatic trough.
- One of the gases he produced by heating mercuric calx by concentrating the sun's rays on it.

Dephlogisticated air, 2

- According to phlogiston theory, he was re-impregnating the mercury with phlogiston, taken from the surrounding air.
- Hence, the air that remained was deficient in phlogiston. He called it "dephlogisticated air.

Dephlogisticated air, 3

- Experimenting with his new air, Priestley found that:
  - A candle burned brighter in it.
  - A mouse put in a closed flask of the air lived longer than one he put in a flask of ordinary air.
  - He tried breathing it himself, and it made him feel great.

The mechanist view supported

- The fact that dephlogisticated air improved combustion *and* improved respiration suggested a connection between the two.
  - This provided greater support for the mechanist viewpoint and the idea that the body is really a machine.

Priestley fled to the U.S.

- Priestley was an enthusiastic supporter of the American and French revolutions. His outspoken radical views enraged a mob that burned down his house and library. Priestley escaped to the United States where he lived for the remainder of his life.

Antoine Lavoisier

- 1743-1794
- A tax collector for the French monarchy.
- Devoted his time to chemical research.
- Searched for the "elements" of chemistry – the simplest substances.
- Sought to be the Euclid of chemistry.

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Lavoisier's ideas

- Lavoisier viewed heat as one of the elements, "caloric."
- Air he thought was compounded of different substances.
- He thought that Priestley's "dephlogisticated air" was actually an element.

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Lavoisier's classic experiment

- Lavoisier took mercury and a measured volume of air and heated them together.
- This produced a mercuric calx and reduced the volume of the air.

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Lavoisier's classic experiment, 2

- He then reheated the mercuric calx by itself at a lower temperature and saw it go back to mercury.
- In the process it produced a gas, equal in volume to the first amount lost from the first procedure.

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Lavoisier's classic experiment, 3

- Lavoisier concluded that instead of the original heating driving off phlogiston from the mercury, the mercury was combining with some element in the air to form a compound, which was the mercuric calx.
- He called that element "oxygen," meaning "acid maker."

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Oxygen displaces phlogiston

- Phlogiston theory had everything upside down.
- Instead of driving off phlogiston during combustion, burning causes a compound to form with the gas oxygen.
  - In the case of a metal, the compound is the calx produced.
  - In the case of something rich in carbon, e.g., wood, the compound is a gas, carbon dioxide.

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Phlogiston exits

- Phlogiston was an incorrect idea, but it helped to sort out and categorize chemical reactions.
- When the chemical elements were finally identified, phlogiston was seen to be an effect, not a substance.

Lavoisier's untimely end.

- Unlike Priestley who was persecuted for being pro-republican, Lavoisier was too closely associated with the French monarchy. During the French revolution he was arrested by a mob and guillotined, bringing to an end a promising scientific career.

The Elements of Chemistry

- Lavoisier's goal was to identify the fundamental, elementary substances out of which all matter was made.
- He recognized that many ordinary substances (e.g., water) were actually made up of more elementary constituents.
  - E.g., Hydrogen and Oxygen for water.

Lavoisier's List of Elements

TABLE OF SIMPLE SUBSTANCES.

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

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

Oxydable and Acidifiable ſimple Subſtances not Metallic.

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

Oxydable and Acidifiable ſimple Metallic Bodies.

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

Salifiable ſimple Earthy Subſtances.

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

Before Lavoisier's untimely death, he had established a list of the elements that he had identified. Note that the list includes Light and Heat.

John Dalton

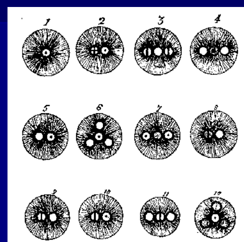
- – 1766-1844
- A 19th century Quaker schoolmaster in Manchester, England.
- Dalton made a painstaking, methodical study of gases in the atmosphere

Atoms and molecules

- Dalton's central idea was that the elements come in discrete bits, or particles, which he called *atoms* – the ancient Greek word for indivisible units.
- Atoms, he believed, formed together in small clusters that he called *molecules.*

Dalton's molecules

- Dalton thought that (sperical) atoms were held together in (spherical) molecules in a suspension of caloric.



Molecules of different substances. Atoms suspended in caloric.

Combining ratios

- In compounds, the constituent elements always combine in a constant ratio by weight.
- Dalton postulated that all atoms of the same element are essentially identical and must have the same mass.

Inferring the relative sizes of atoms

- Dalton's idea of a molecule was a small number of atoms of each constituent element (e.g., one of each) bound together in a fixed way.
- Example: water
  - Made of oxygen and hydrogen.
  - The oxygen weighs seven times as much as the hydrogen.
  - So, assuming one atom of each, one oxygen atom weighs seven times one hydrogen atom.

Multiple Proportions

- Some elements form themselves into more than one compound.
- Example: carbon and oxygen form two different gases.
  - In one gas: the carbon weighs ¾ that of oxygen.
  - In the other gas: carbon weighs 3/8 that of oxygen.

Inferring composition of the compounds

- Taking the first gas as the simplest case, it must contain one atom of carbon and one of oxygen (CO), and therefore a carbon atom has ¾ the weight of an oxygen atom.
- The second gas must contain two atoms of oxygen and one of carbon (CO_2).

A Pythagorean concept

- Note that the function of atoms for Dalton is much the same as that of numbers for Pythagoras.
  - They are space-filling tiny spheres.
  - They are the ultimate smallest units.
  - They combine in simple ratios of whole numbers.

Chemistry and the Mechanist Model

- With Dalton, chemistry was completely expressed in mechanical concepts:
  - Mass and weight
  - Matter and motion
- Phlogiston, with its ancient concept of levity (lightness) had no place in this model, and served no useful purpose as a concept.

Heat: A substance or an effect?

- Heat was a mystery concept. Lavoisier viewed it as an element. Dalton kept this idea but gave it a special role – to hold a molecule together.
- If heat was to fit into the mechanical model, it had to be either matter or motion.

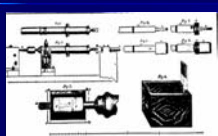
Heat as matter or as motion

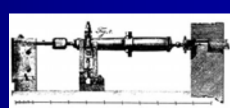
- Matter
  - Lavoisier's concept of caloric. It was to be added and subtracted in chemical reactions, just like matter.
- Motion
  - Heat could be produced by friction, i.e. motion.

Count Rumford

- Benjamin Thompson, an American with monarchist sympathies, fled to Germany and became engaged in the manufacture of artillery.
- He was so popular in Gemany that he was made "Count Rumford" by the Elector of Bavaria.

Count Rumford and the boring of cannon shafts





- Rumford developed a technique for making straight-shooting cannons by boring out the shafts from a solid metal cylinder.
  - To prevent overheating the boring tool, he immersed the entire machine in water to keep the metal cool.

Unlimited heat from boring

- The cannon-making process produced so much heat that the water the machine was immersed in boiled away. No matter how often it was replenished, it continued to boil.
- **The heat was inexhaustible.**

Heat cannot be matter

- If the heat could be produced at will, it could not be a substance, caloric, that was being released by the boring.
  - It was a generally accepted principle of the mechanist view of the world (and other views too) that the total amount of matter in the world is a constant.

Heat must be motion

- But unlimited amounts of heat were being created by the motion of the boring machine.
- In the mechanist world view, there are only two kinds of things, *matter* and *motion.*
- If heat was not a substance, it must be some kind of motion.

What are atoms?

- Are they real particles or a convenient fiction?
- What is known about atoms: They have weight
  - Dalton's rules determined only *relative* weights.
  - His atomism could be interpreted phenomenologically.

Numbers of atoms

- How many atoms are there in a given weight or volume?
  - Amadeo Avogadro studied volumes of gases in compounds.
  - In 1811 he put for the hypothesis that a given volume of gas contains a fixed number of molecules.

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Avogadro ignored

- Avogadro was ignored until about 1860.
- Then, using Dalton's concepts of atoms and molecules, chemists began to compute relative atomic weights.
  - They still had no way to determine the weight of an individual atom of an element.

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Avogadro revived

- Avogadro's hypothesis that a given volume of gas contains a fixed number of molecules (now called Avogadro's number) provided a way to divide the weights of an element in a compound by the number of atoms in a fixed quantity of it, giving the weight of a single atom.

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So, atoms differ by weight

- Using Avogadro's number and Dalton's relative weights, chemists calculated the masses of atoms of all the known elements.
- Was this the *only* property that atoms had that made them differ from each other?

Accounting for *all* the differences

- It seemed impossible that a single quantity, *mass*, was sufficient to account for all the differences from each other that the elements displayed.
- Other phenomena to be accounted for:
  - What other elements it forms compounds with.
  - Melting point, boiling point.
  - Hardness, colour, taste, etc., etc.

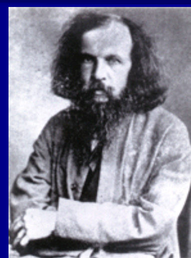
If not just mass, then what?

- Differences in the mechanist model must have to do with size, shape, or configuration, i.e., *quantities*.
- Otherwise, an appeal to *qualities* is made, which violates the mechanist model.
- It seemed totally improbable that all the differences between the elements was due to one quantity alone.

Dmitri Ivanovich Mendeleev

– Russian chemist, 1834-1907

- Mendeleev undertook to make sense of the differences among the elements.
- He set out all the known properties of each element on index cards, and then looked for patterns.

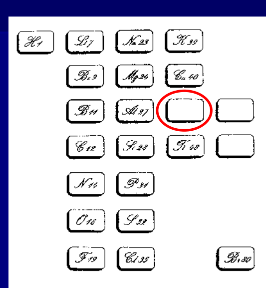


Dmitri Ivanovich Mendeleev

- Mendeleev noted that if elements are arranged according to their atomic weights, them seem to fall in groups or families.
  - All in Group I form compounds with oxygen in a 2:1 ratio.
  - All in Group II form compounds with oxygen in a 1:1 ratio, etc.

Gaps indicate missing elements

- He found gaps in periodic sequence and decided that there must be undiscovered elements that go in those places.
- Mendeleev predicted an element he called eka-Aluminum.
  - Later discovered, named Gallium, in 1874.



The Periodic Table of the Elements

- Mendeleev discovered that the elements fall in periodic groups with similar chemical properties.
- Though the chemical properties seemed to have a regular pattern, no physical structure was known to account for them.