A Brief History of Organic Chemistry

The Phlogiston Theory

Georg Ernest Stahl
(1660-1734)

metal + heat = calx of metal + Ø

e.g., zinc = zinc oxide + Ø

phlogiston (Ø) is lost

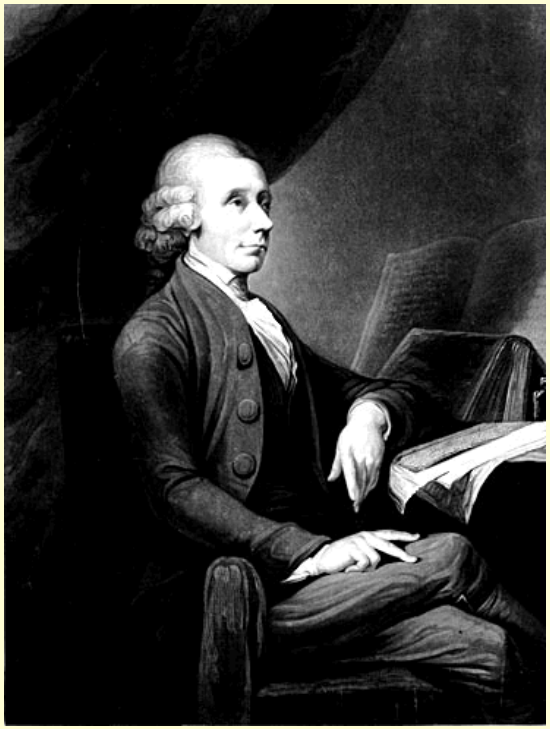
calx + charcoal(Ø) + heat =
metal + (fixed air)

phlogiston (Ø) is gained

Problem:

phlogiston has a negative mass!

The Co-Discoverer of Oxygen



Joseph Priestley
(1733-1804)

Trained in the ministry

Studies on the nature of air - 1775

Mercurius calcinatus + heat =
Mercury + dephlogisticated air

$HgO + heat = Hg + O$

Recognized the role of oxygen in the life cycle

Told Lavoisier of his findings

Held to the phlogiston theory until his death

Lavoisier and Combustion

Antoine-Laurent Lavoisier (1743-1794) and His Wife (Marie-Anne-Pierrette Paulze, 1758-1836), 1788 Jacques-Louis David (French, 1748-1825)

www.metmuseum.org

Quantitative methods

Mass is conserved

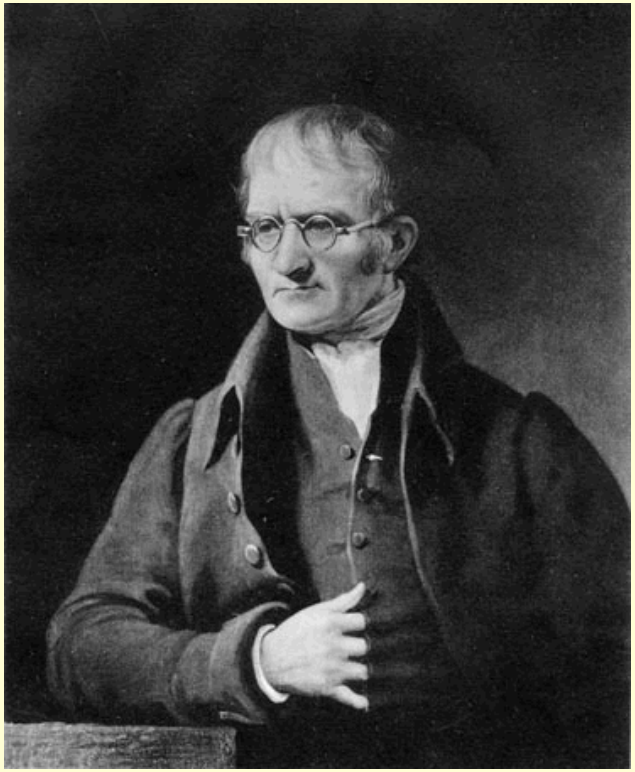
Combustion is not a loss of phlogiston but a gain of oxygen.

Traité de Chimie - 1789

Dual names for salts

Guillotined 1794

Atomic Theory



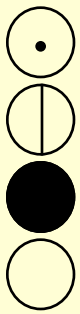
John Dalton

(1766-1844)

1. Elements composed of indivisible atoms

2. Elements have defined and different masses

3. Elements combine in simple numerical ratios - Law of Multiple Proportions



Hydrogen = 1

Azot = 4.2

Carbone = 4.3

Oxygen = 5.5

The Rule of Greatest Simplicity

For Water:

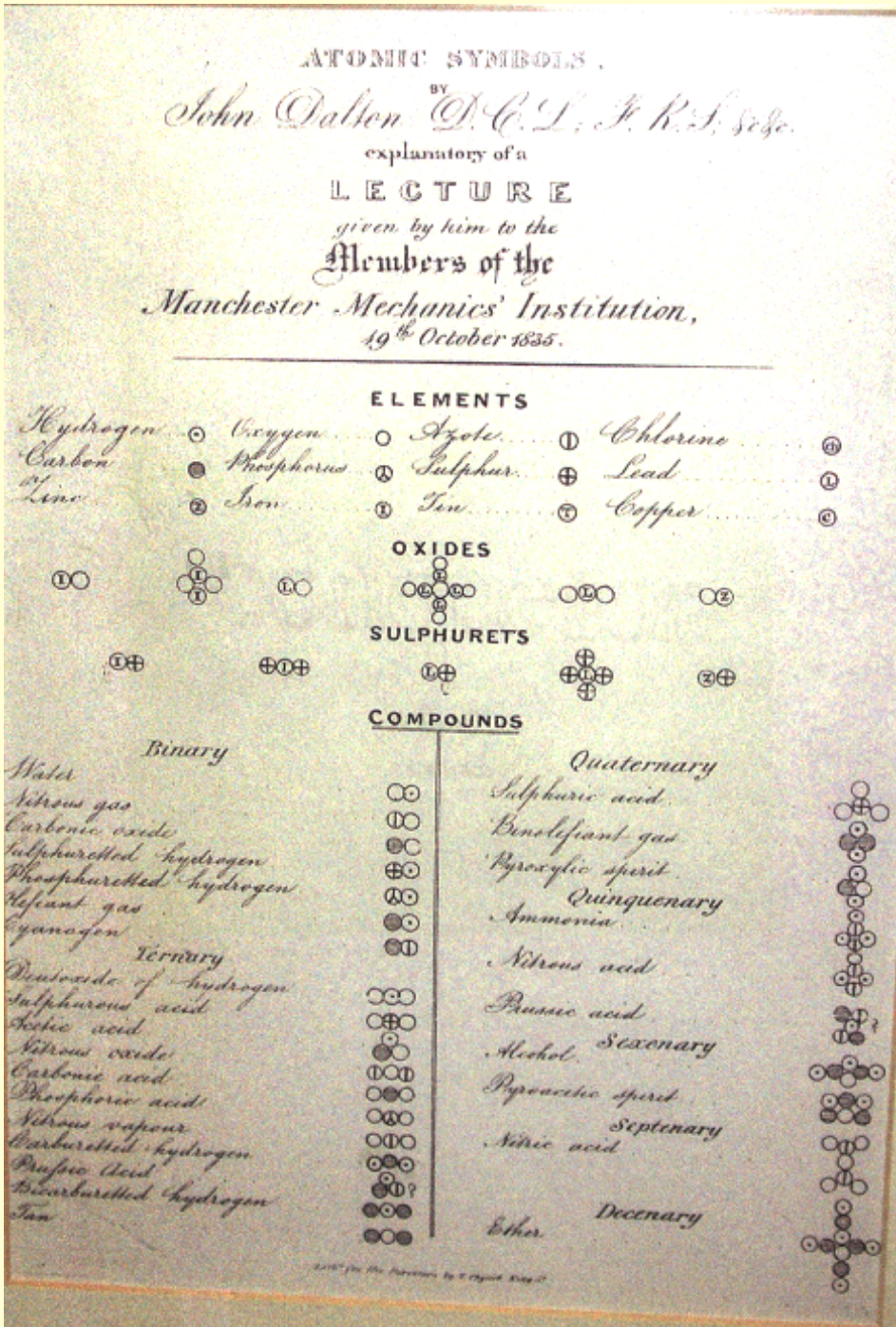
1g of H / 8g of O
Formula = HO

But:

1g of H / 2 x 4g of O
Formula = HO_2

Or:

2 x 1g of H / 16g of O
Formula = H_2O


ATOMIC SYMBOLS.

BY

John Dalton D.C.L. F.R.S. &c.&c.

explanatory of a

LECTURE

given by him to the

Members of the

Manchester Mechanics' Institution,

19th October 1835.

ELEMENTS

Hydrogen Oxygen Azote Chlorine

Carbon Phosphorus Sulphur Lead

Zinc Iron Tin Copper

OXIDES

SULPHURETS

COMPOUNDS

Binary

Water

Nitrous gas

Carbonic oxide

Sulphuretted hydrogen

Phosphuretted hydrogen

Olefiant gas

Cyanogen

Ternary

Bicarbonate of hydrogen

Sulphurous acid

Acetic acid

Nitrous oxide

Carbonic acid

Phosphoric acid

Nitrous vapour

Carburetted hydrogen

Prussic Acid

Bicarburetted hydrogen

Tan

Quaternary

Sulphuric acid

Bicarbonate of hydrogen

Pyroxylic spirit

Quinquenary

Ammonia

Nitrous acid

Prussic acid

Senary

Alcohol

Pyroacetic spirit

Septenary

Nitric acid

Decenary

Ether

"One Christmas was so much like another, in those years around the sea-town corner now and out of all sound except the distant speaking of the voices I sometimes hear a moment before sleep, that I can never remember whether it snowed for six days and six nights when I was twelve or whether it snowed for twelve days and twelve nights when I was six."

"A Child's Christmas in Wales" --- Dylan Thomas

Electrochemical Theory

Jons Jacob Berzelius
(1779-1848)

Chemical analysis

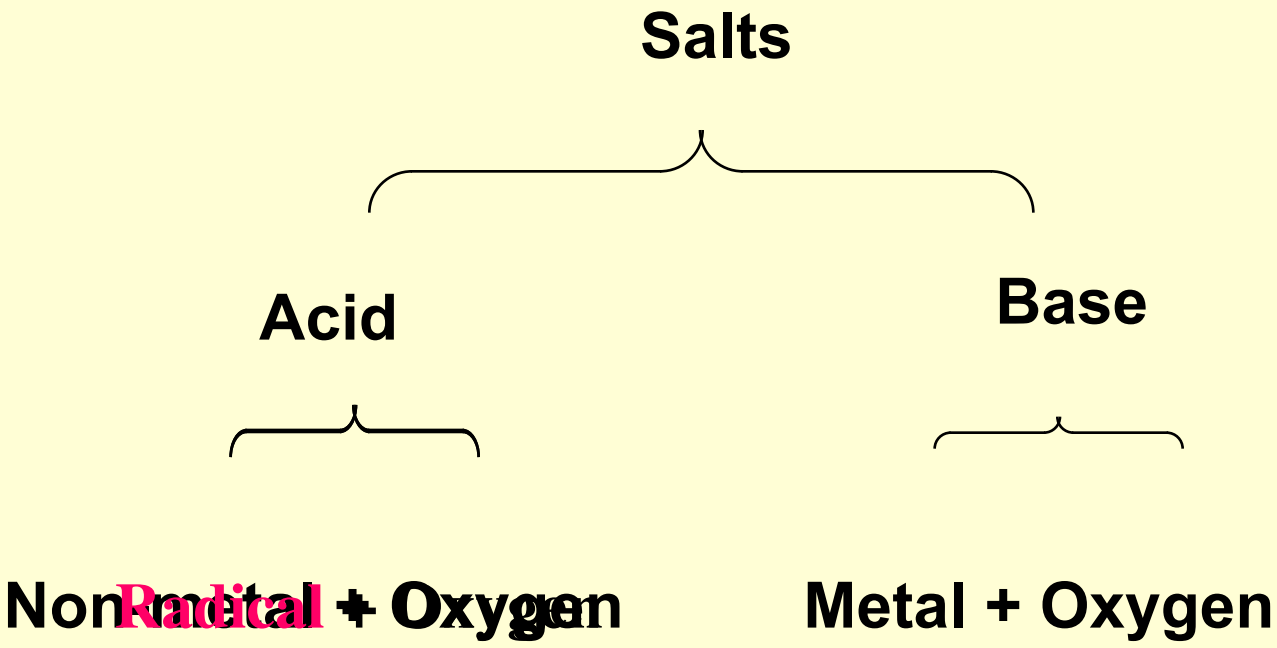
Modern symbols of the elements

Discovers: Ce, Se, Th, Si, Zr, etc.

Defines isomerism

Electrochemical Theory (Dualism)

Electrochemical Theory (Dualism)



Friedrich Wöhler
(1800 - 1882)

The Beginning of the End for Vitalism

1828 - Converts ammonium cyanate

CH_4N_2O (inorganic)

into urea

CH_4N_2O (organic)

An example of isomers

Begins the downfall of Vitalism

On the Preparation of "Artificial" Urea:

I cannot, so to say, hold my chemical water and I must tell you that I can make urea without needing to have kidneys, or anyhow, an animal, be it human or dog.

1828 - Wöhler to Berzelius

For more from the wry pen of Wöhler.

Justus Liebig
(1803-1873)

Radical Theory

Refined chemical analysis

Developed laboratory instruction

Trained many of the chemists of the day

Proponent of Radical Theory along with Dumas

The Benzoyl Radical

1832 - Liebig and Wöhler

Benzoyl hydride C_7H_5O - H

(Oil of bitter almond, Benzaldehyde)

Benzoyl hydroxide C_7H_5O - OH

(Benzoic acid)

Benzoyl chloride C_7H_5O - Cl

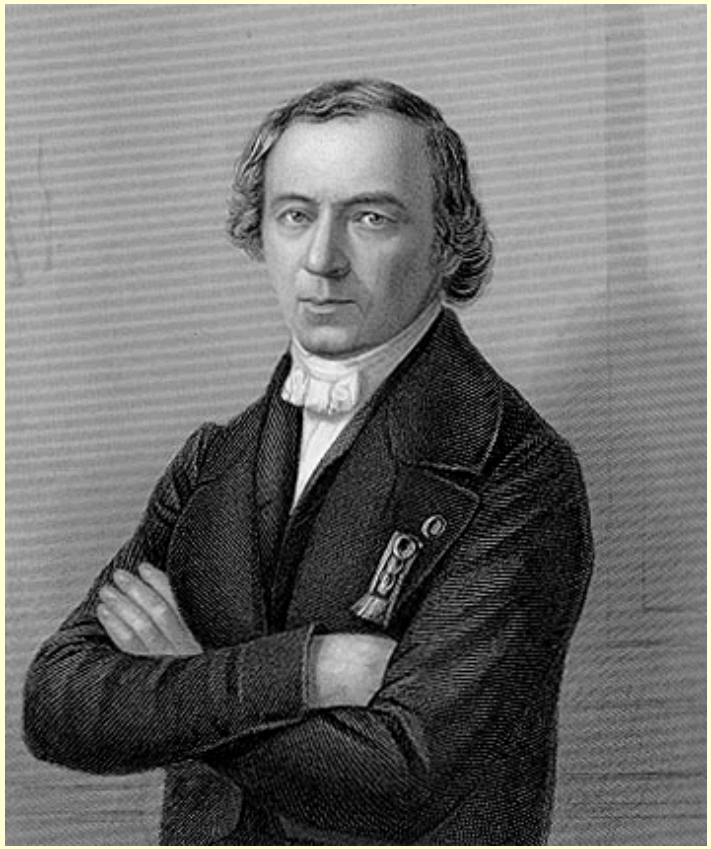
Benzamide C_7H_5O - NH_2

1837 - Dumas and Liebig
Note on the Present State of Organic Chemistry

In mineral chemistry the radicals are simple; in organic Chemistry the radicals are compound; that is all the difference. The laws of combination and of reaction are otherwise the same in these two branches of chemistry.

Leicester and Klickstein, *A Source Book of Chemistry, 1400 - 1900*. Harvard, 1952)

Substitution Theory



J. B. Dumas
(1800 -1884)

1838 - chlorination of acetic acid

$$\underline{C}_4H_4O_2 + Cl_6 = \underline{C}_4HCl_3O_2 + H_3Cl_3$$

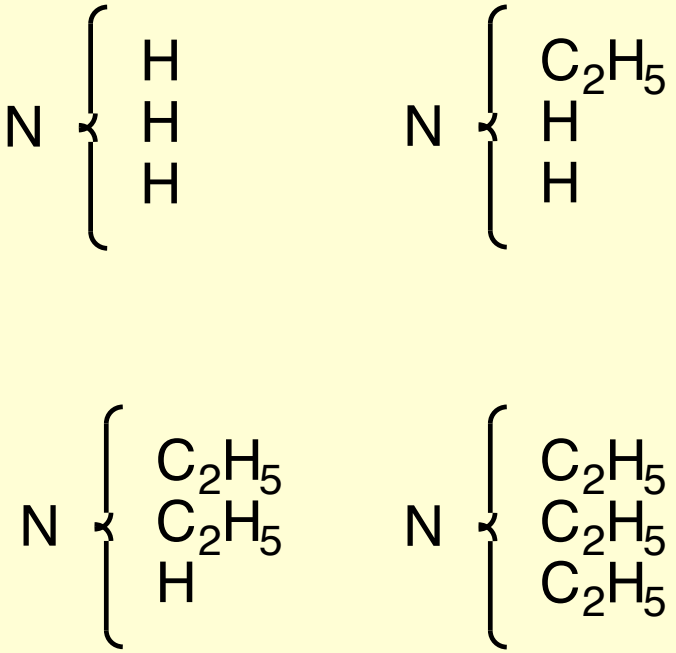
$\underline{C} = 6, O = 16$

$$C_2H_4O_2 + 3Cl_2 = C_2HCl_3O_2 + 3HCl$$

Type Theory

August Wilhelm von Hofmann
(1818-1892)

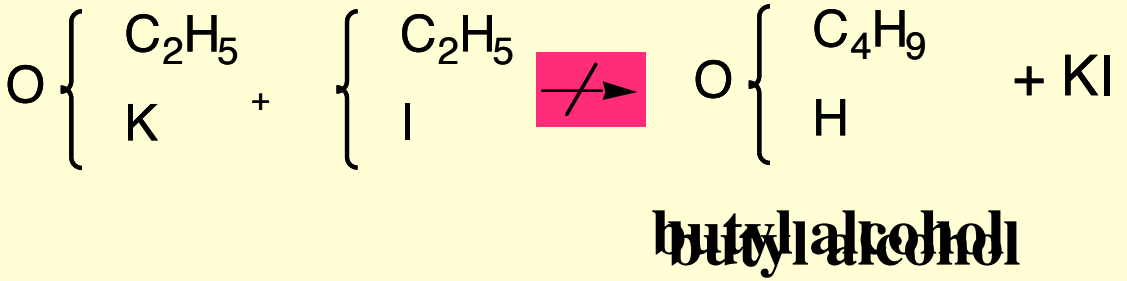
1850 - The ammonia type

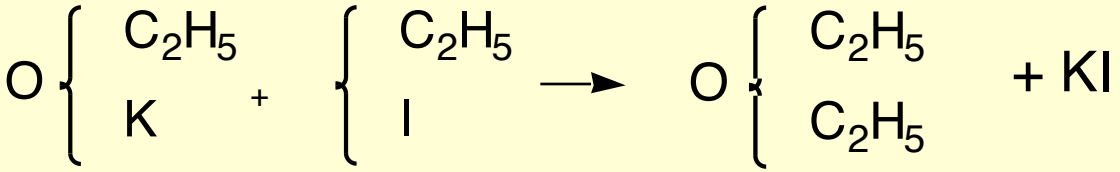


The Water Type

1850 - 1852

Alexander Williamson (1824-1904)





ether

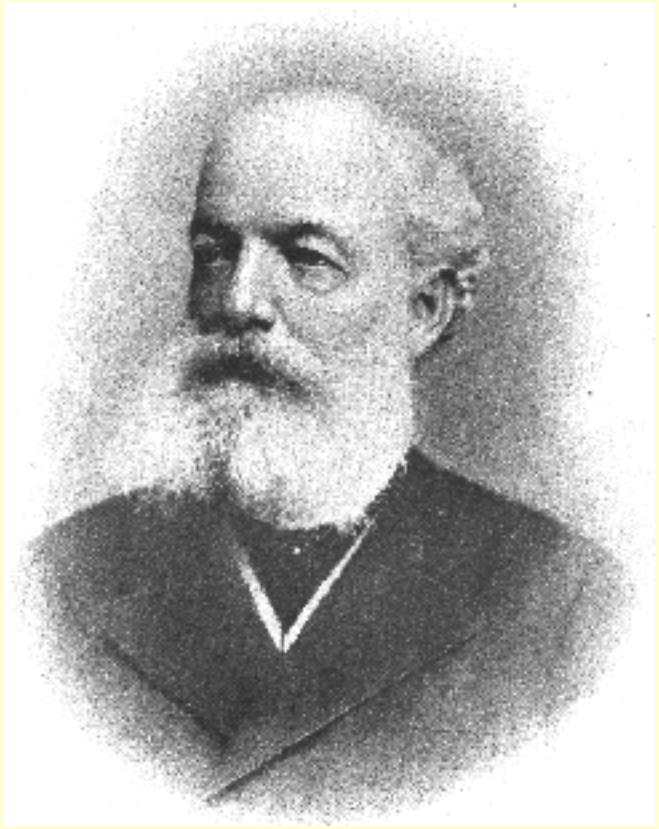
[An expanded version of the ether story]

Valence

Edward Franklin
(1825 - 1899)

1852 - recognizes the ability of N, P, As, and Sb to combine with 3 and 5 other elements.

1857 - Kekule develops the idea of valence with carbon compounds.

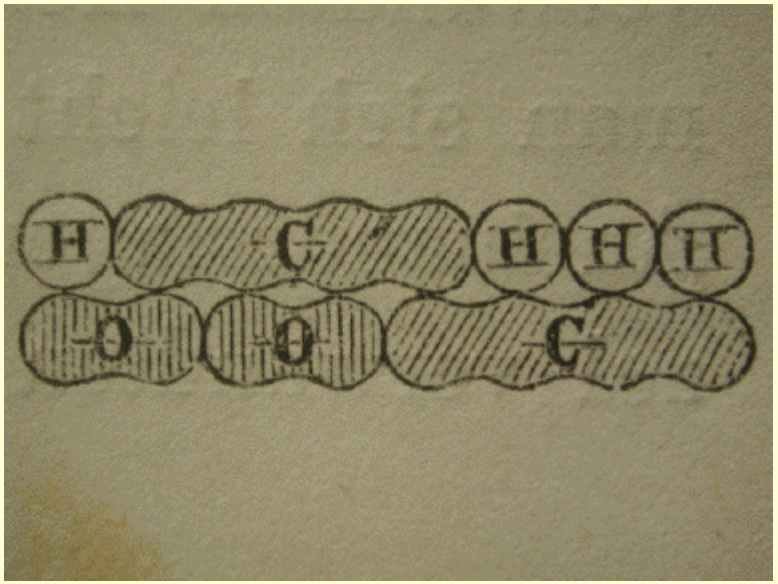


Friedrich August Kekule
(1829-1896)

1858 - Quadravalence of carbon

1865 - Structure of benzene

1861 - Lehrbuch der Organischen Chemie



Acetic Acid

Kekule's

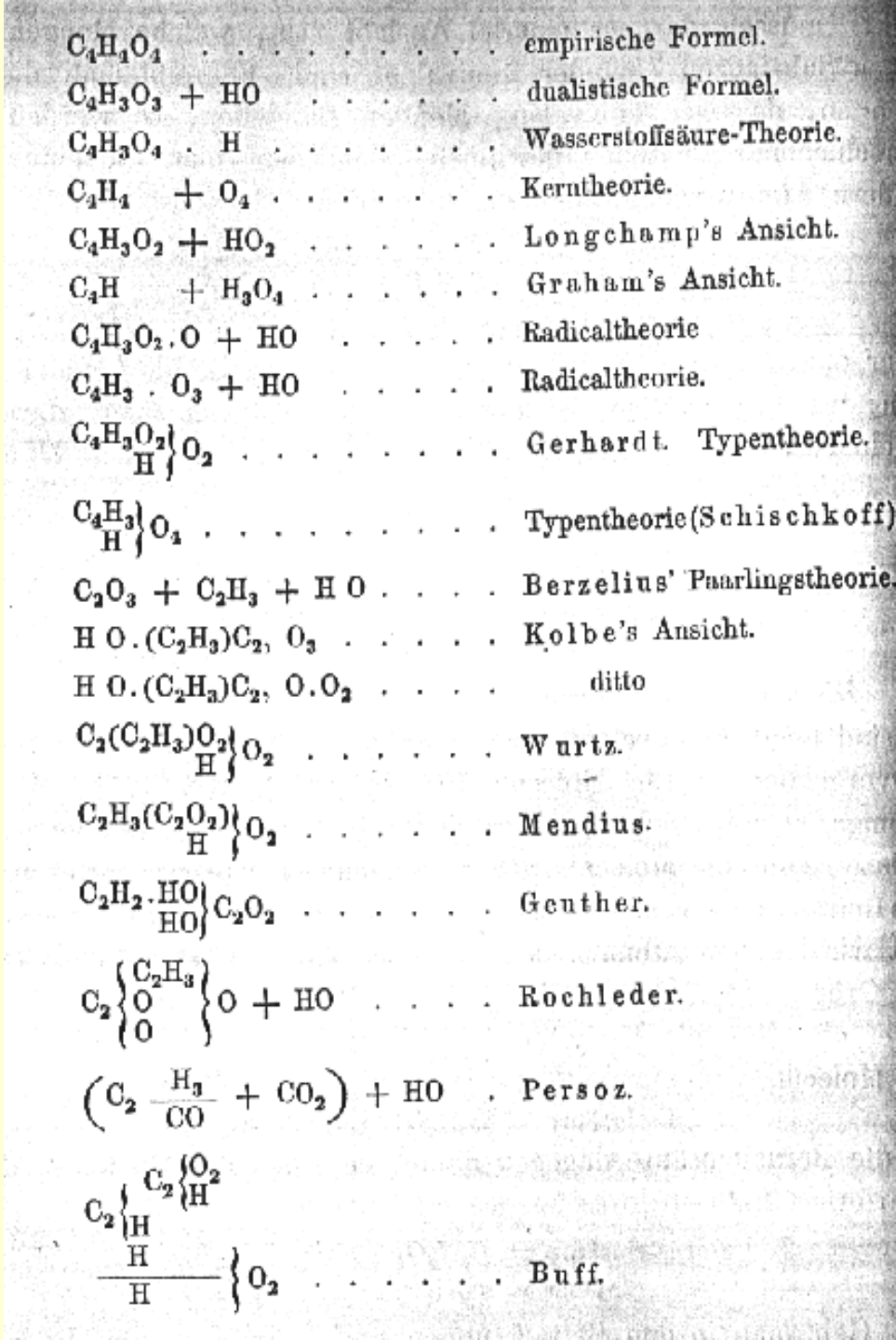
19 formulas

for acetic acid

($C_2H_4O_2$) from his

Lehrbuch der
Organischen Chemie

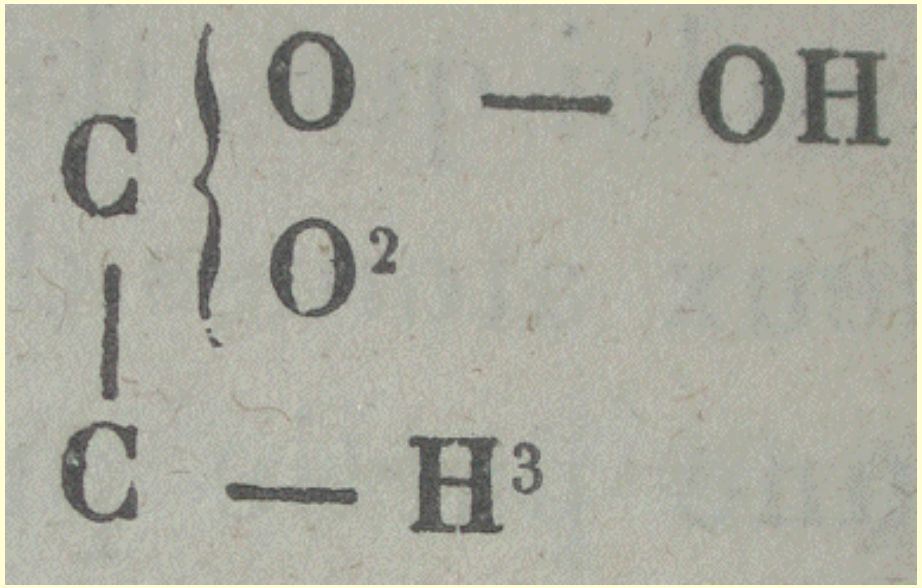
1867 (pg. 164 & 165)



Archibald Scott Couper

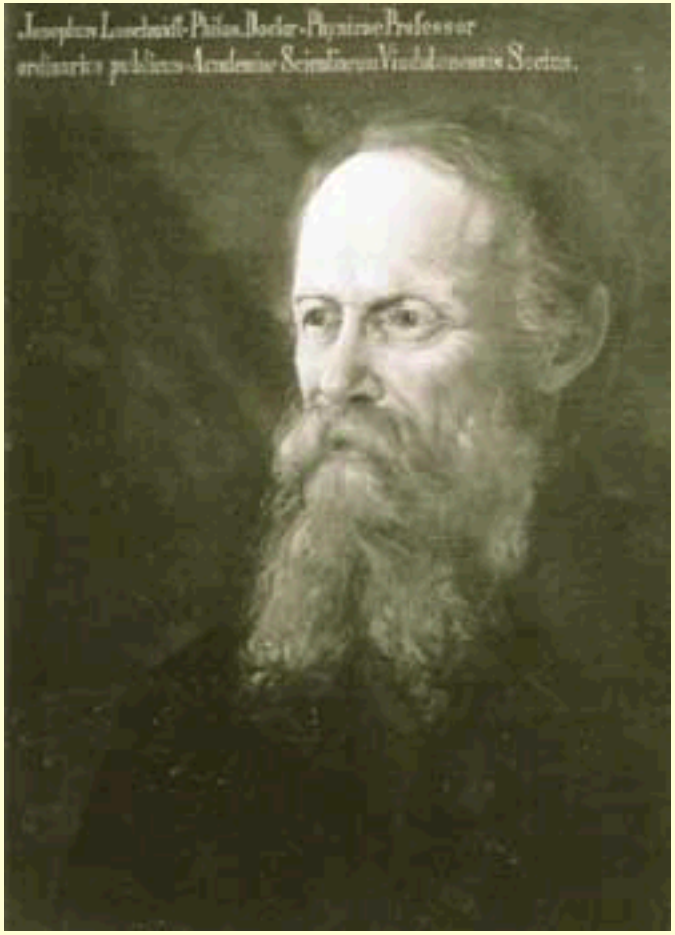
(1831-1892)

1858



Acetic Acid

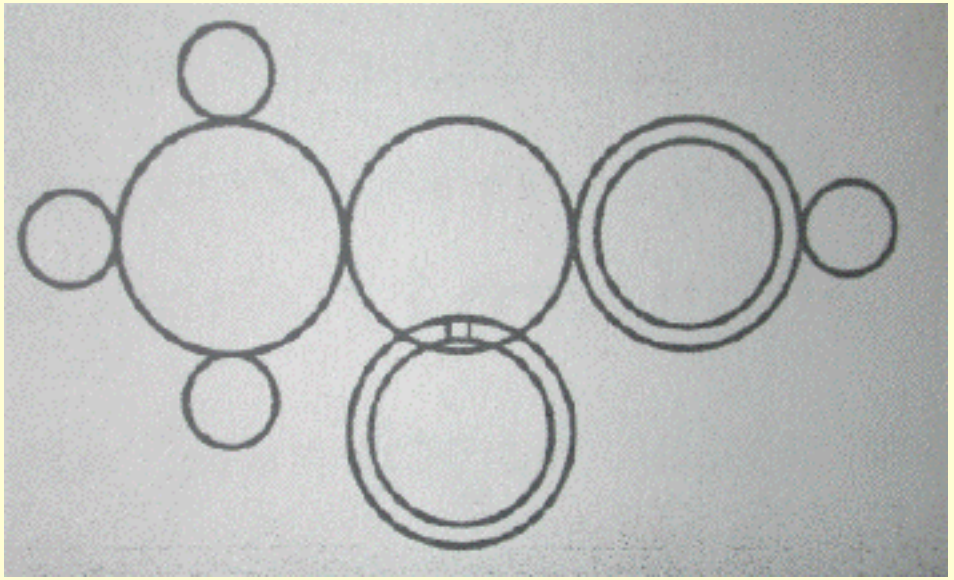
Atoms with lines between them



Joseph Loschmidt
(1821 - 1895)

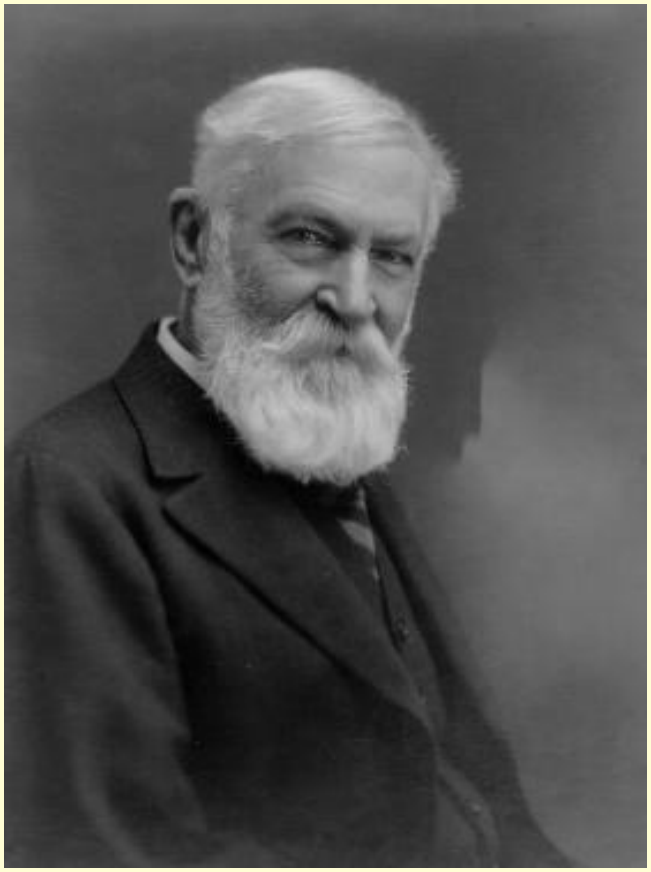
Physicist and Chemist

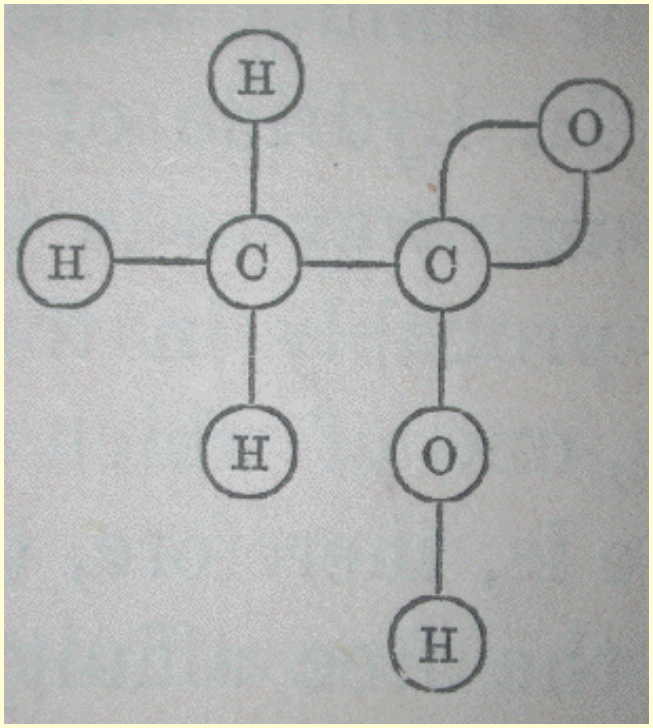
1861 - Diagrammatical Structural Formulae of Organic Chemistry



Acetic Acid

1865





Acetic Acid

Alexander Crum Brown
(1838-1922)

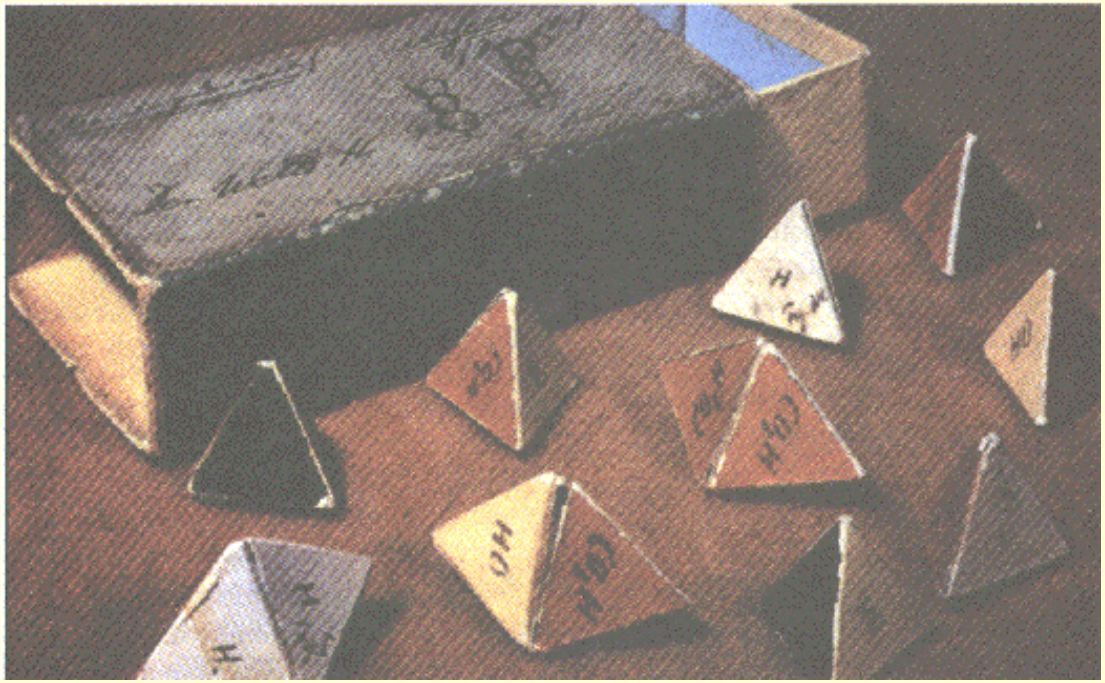
Atom connectivity

Multiple connections

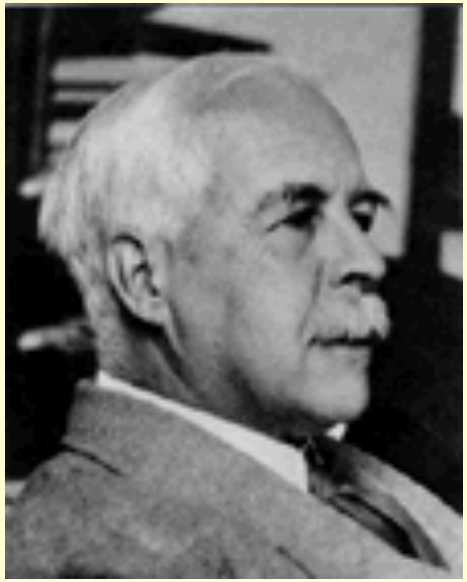
1874 - The Arrangement of Atoms in Space

Jacobus Henricus van't Hoff (1852 - 1911)

Carbon is tetrahedral!



1901 - 1st Nobel Prize in Chemistry



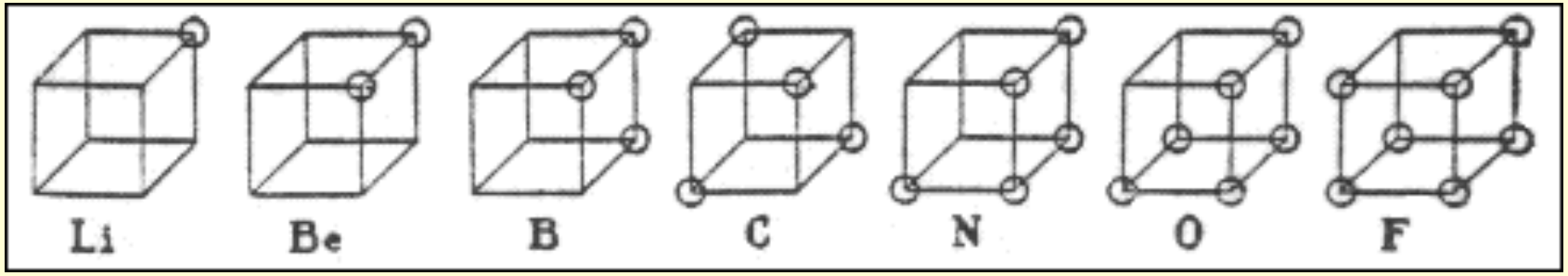
Gilbert N. Lewis
(1875-1946)

1869 - Mendeleev's Periodic Table

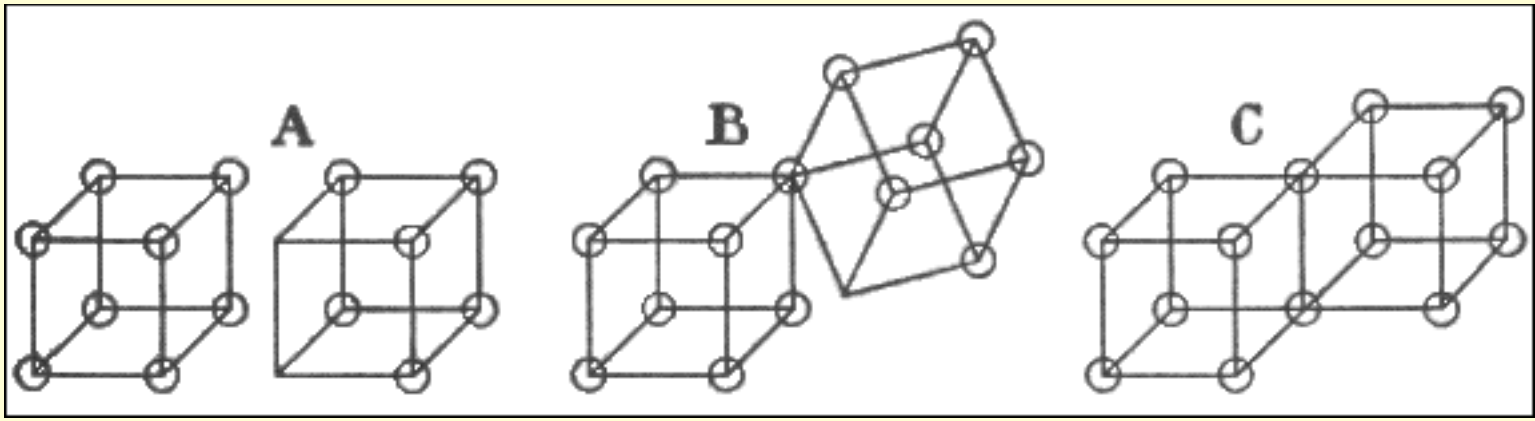
1897 - Thomson Discovers the Electron

1902 - Lewis's Cubic Model of the Atom (Covalence)

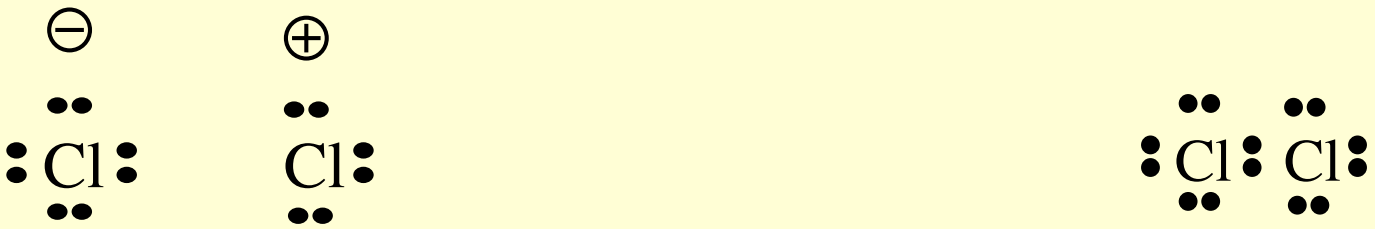
1916 - Lewis Dot Formula



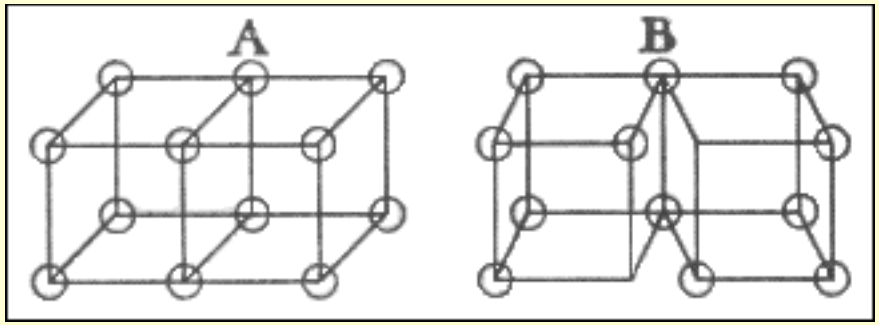
1902



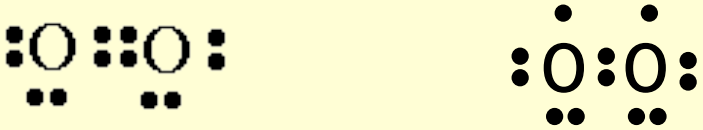
1916



1902



1916



Failure of the Cubic Model

Single bond (Cl_2) → **Edge**

Double bond (O_2) → **Face**

Triple bond (N_2) → **Cube within a cube?**

Linus Pauling
(1901 - 1994)

Quantum Mechanics leads to ...

Resonance

Hybridization

Molecular Orbital Theory

The Nature of the Chemical Bond (1939)


The End