A Brief History of Organic Chemistry
The Phlogiston Theory

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!

Georg Ernest Stahl
(1660-1734)
The Co-Discoverer of Oxygen

Trained in the ministry
Studies on the nature of air - 1775
Mercurius calcinatus + heat = Mercury + dephlogisticated air
\[ \text{HgO + heat} = \text{Hg + O} \]
Recognized the role of oxygen in the life cycle

Joseph Priestley (1733-1804)
Told Lavoisier of his findings
Held to the phlogiston theory until his death
Lavoisier and Combustion

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

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

John Dalton
(1766-1844)
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 = HO₂

Or:

2 x 1g of H / 16g of O  
Formula = H₂O
"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
Jons Jacob Berzelius
(1779-1848)

Electrochemical Theory

Chemical analysis

Modern symbols of the elements

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

Defines isomerism

Electrochemical Theory (Dualism)
Electrochemical Theory (Dualism)

Salts

Acid

Non-metal + Oxygen

Metal + Oxygen

Base

Radical + Oxygen
1828 - Converts ammonium cyanate

\[ \text{CH}_4\text{N}_2\text{O} \text{ (inorganic)} \]

into urea

\[ \text{CH}_4\text{N}_2\text{O} \text{ (organic)} \]

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 $\text{C}_7\text{H}_5\text{O} - \text{H}$

(Oil of bitter almond, Benzaldehyde)

Benzoyl hydroxide $\text{C}_7\text{H}_5\text{O} - \text{OH}$

(Benzoic acid)

Benzoyl chloride $\text{C}_7\text{H}_5\text{O} - \text{Cl}$

Benzamide $\text{C}_7\text{H}_5\text{O} - \text{NH}_2$
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.

Substitution Theory

1838 - chlorination of acetic acid

\[ \text{C}_4\text{H}_4\text{O}_2 + \text{Cl}_6 = \text{C}_4\text{HCl}_3\text{O}_2 + \text{H}_3\text{Cl}_3 \]

\[ \text{C} = 6, \text{O} = 16 \]

\[ \text{C}_2\text{H}_4\text{O}_2 + 3\text{Cl}_2 = \text{C}_2\text{HCl}_3\text{O}_2 + 3\text{HCl} \]

J. B. Dumas
(1800 - 1884)
August Wilhelm von Hofmann
(1818-1892)

Type Theory

1850 - The ammonia type

$\begin{align*}
&N \quad \{ \quad \begin{array}{c}
H \\
H \\
H \\
\end{array} \\
&N \quad \{ \quad \begin{array}{c}
C_2H_5 \\
H \\
H \\
\end{array} \\
\end{align*}$

$\begin{align*}
&N \quad \{ \quad \begin{array}{c}
C_2H_5 \\
C_2H_5 \\
H \\
\end{array} \\
&N \quad \{ \quad \begin{array}{c}
C_2H_5 \\
C_2H_5 \\
C_2H_5 \\
\end{array} \\
\end{align*}$
The Water Type

1850 - 1852

\[
\begin{align*}
\text{O} \left\{ \begin{array}{l}
C_2H_5 \\
K
\end{array} \right\} + \left\{ \begin{array}{l}
C_2H_5 \\
I
\end{array} \right\} \rightarrow \left\{ \begin{array}{l}
C_4H_9 \\
H
\end{array} \right\} + \text{KI}
\end{align*}
\]

\[\text{butyl alcohol}\]

\[
\begin{align*}
\text{O} \left\{ \begin{array}{l}
C_2H_5 \\
K
\end{array} \right\} + \left\{ \begin{array}{l}
C_2H_5 \\
I
\end{array} \right\} \rightarrow \left\{ \begin{array}{l}
C_2H_5 \\
C_2H_5
\end{array} \right\} + \text{KI}
\end{align*}
\]

\[\text{ether}\]

An expanded version of the ether story

Alexander Williamson (1824-1904)
Valence

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.

Edward Franklin
(1825 - 1899)
1858 - Quadrivalence of carbon
1865 - Structure of benzene
1861 - Lehrbuch der Organischen Chemie

Friedrich August Kekule (1829-1896)

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

Atoms with lines between them

Acetic Acid

\[ \text{CO} \quad \text{O} \quad \text{OH} \]

\[ \text{C} \quad \text{O}_2 \quad \text{H}_3 \]
Joseph Loschmidt
(1821 - 1895)

Physicist and Chemist

1861 - Diagrammatical Structural Formulae of Organic Chemistry

Acetic Acid
Alexander Crum Brown (1838-1922)

1865

Acetic Acid

Atom connectivity
Multiple connections
1874 - The Arrangement of Atoms in Space

Carbon is tetrahedral!

Jacobus Henricus van’ t Hoff
(1852 - 1911)

1901 - 1st Nobel Prize in Chemistry
1869 - Mendeleev’s Periodic Table

1897 - Thomson Discovers the Electron

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

1916 - Lewis Dot Formula
Failure of the Cubic Model

Single bond
(Cl\textsubscript{2})

Double bond
(O\textsubscript{2})

Triple bond
(N\textsubscript{2})

Edge

Face

Cube within a cube?
Quantum Mechanics leads to ...

Resonance

Hybridization

Molecular Orbital Theory

Linus Pauling (1901 - 1994)

The Nature of the Chemical Bond (1939)
The End