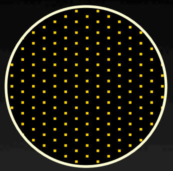
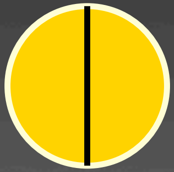
The Evolution of Formulas and Structure in Organic Chemistry During the 19th Century

Dalton's Symbols (1803)



Hydrogen

Carbon



Oxygen

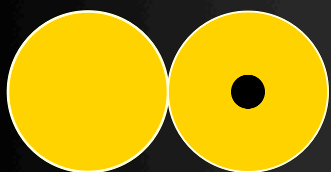
Nitrogen

John Dalton
(1766-1844)

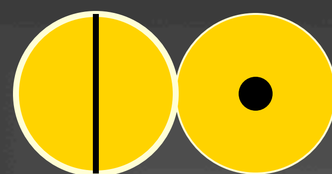
- circles for atoms of elements
- occasional use of letters
  - gold

- must learn the symbol for each element

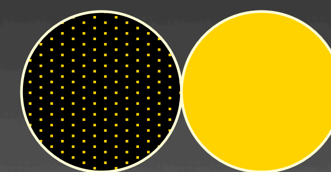
Binary “atoms”



water
OH



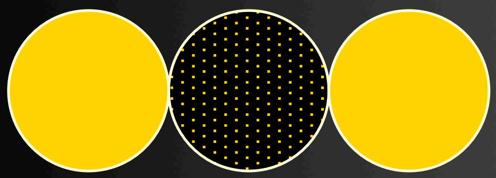
ammonia
NH



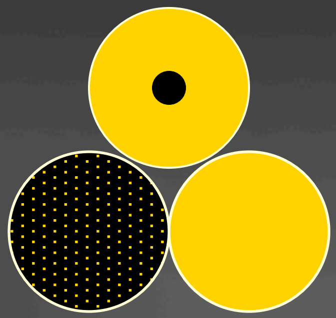
carbon monoxide
CO

Dalton (1803)

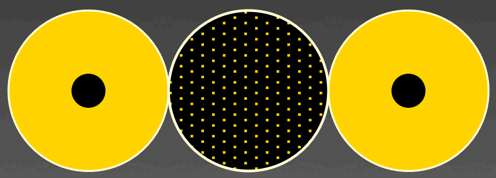
Ternary "atoms"



carbon dioxide
OCO



acetic acid
H
CO



olefiant gas
HCH

Dalton (1803)

J. J. Berzelius
(1779-1848)

- use first letter of Latin name of element

H hydrogen
N nitrogen
O oxygen
S sulfur

- use first two letters when first letter is taken

Si silicon
Se selenium

Latin roots

English	Latin	Symbol
antimony	stibnum	Sb
tin	stannum	Sn
sodium	natrium	Na
potassium	kalium	K

Why Latin?

“Science, like that nature to which it belongs, is neither limited by time nor space, it belongs to the world, and is of no country and of no age”

Sir Humphry Davy

Affinity of the elements

Oxygen *(most electronegative)*

. . .   .

. . .   .

. . .   .

(most electropositive) Potassium

Dualism … the electrochemical theory

By arranging the atoms in the order of their electrical affinities, one forms an electrochemical system, which is more suitable than any other arrangement to give an idea of chemistry.

Berzelius

Dualism exemplified

$$\overset{+}{\mathrm{K}} \qquad \overset{-}{\mathrm{O}} \qquad\qquad \overset{+}{\mathrm{S}} \qquad \overset{-}{3\ \mathrm{O}}$$

$$\overset{+}{\mathrm{KO}} \qquad\qquad \overset{-}{\mathrm{SO^3}}$$

$$\mathrm{KO,SO^3}$$

Berzelius

sulfate of potash

Sulfate of potash KO,SO^3

- composed of a base KO and an acid SO^3
- formula reflects number and kind of each atom
- each atom has a defined mass (weight)

Berzelius

The dilemma in the early 19th century

- equivalent weights vs. atomic weights
- equivalent weights are relative
- atomic weights are absolute

If hydrogen is assigned a mass of 1,

is oxygen 1 atom of mass 16 or 2 atoms of mass 8?

…and is carbon 1 atom of mass 12 or 2 atoms of mass 6?

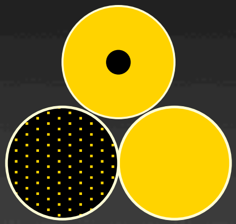
"One Christmas was so much like another, in those years around the sea-town corner now and out of all sound except the distant speaking of the voices I sometimes hear a moment before sleep, that I can never remember …

…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

Constitutional formula - acetic acid exemplified

$C = 6, O = 8$

Dalton  $= C_4H_4O_4$

Berzelius $H^6C^4O^3$ $= \bar{A}$

$C = 12$

$O = 16$

$+ H^2O$ $= H^8C^4O^4$

Gerhardt halved unitary formula $= H^4C^2O^2$

modern formula $= C_2H_4O_2$

Isomerism

Friedrich Wöhler
(1800-1882)

Wöhler (1822)

silver cyanate

AgCNO

Liebig (1823)

silver fulminate

AgCNO

Justus Liebig
(1803 - 1873)

Isomerism

Michael Faraday
(1791-1867)

Faraday (1825)

discovers butylene - same composition as ethylene
(C = 85.7%   H = 14.3%)

but not isomers!

Wöhler (1828)

converts ammonium cyanate into urea   (CH_4N_2O)

On "artificial" urea …

Benjamin Silliman, Sr. (1779-1864)

"*In their properties, they are identical with urea, and their composition is the same*; …Still the artificial urea, although from the mode of its formation it would appear that it contains only cyanic acid and ammonia, yields neither, by chemical agents."

B. Silliman, *Elements of Chemistry*, vol. II, p.601 (1831)

Radical theory

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

Note on the Present State of Organic Chemistry

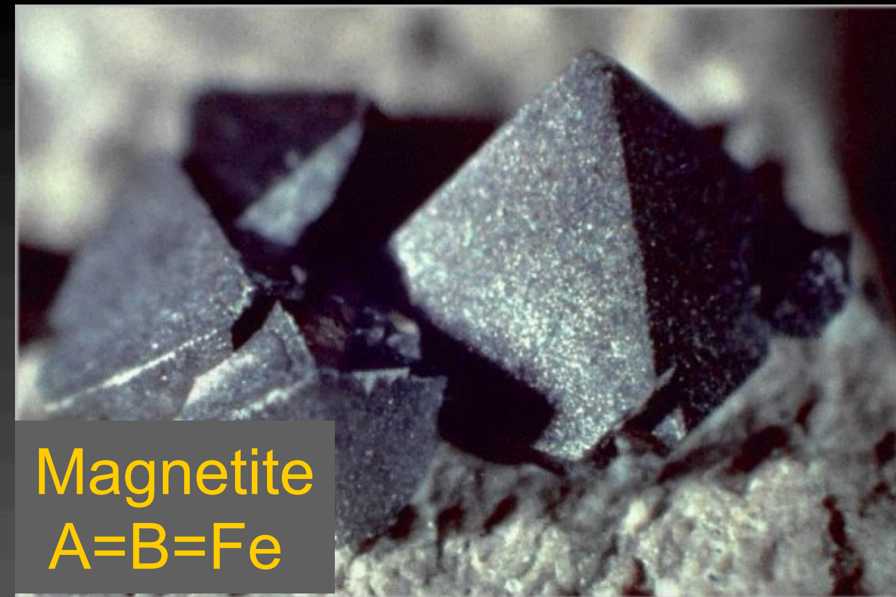
"In mineral chemistry the radicals are simple; in organic chemistry the radicals are compound; that is all the difference. The laws of combination and of reaction are otherwise the same
in these two branches of chemistry."

Dumas and Liebig (1837)

Isomorphism 1819

Eilhard Mitscherlich
(1794-1863)

Octahedral spinels
AB_2O_4



Magnetite
A=B=Fe

Minerals with similar chemical compositions have the same crystal structure.

Franklinite
A=Zn, Fe, Mn
B=Fe, Mn

Substitution Theory (1834)

Jean Baptiste Dumas
(1800-1884)

Metalepsy or exchange

"Chlorine possesses the remarkable power of seizing hold of the hydrogen in certain substances, and replacing it atom for atom."

Chlorination of acetic acid

Early Type Theory

$$C_2H_4O_2 + 3Cl_2 \longrightarrow C_2HCl_3O_2 + 3HCl$$

Substitution (Nucleus) Theory (1835)

Auguste Laurent
(1807-1853)

- Substitution of chlorine for hydrogen in naphthalene ($C_{10}H_8$) does not fundamentally alter its properties.

- Naphthalene - radicaux fondmentaux

- Chloronaphthalenes - radicaux dérivés

- Location of atoms determines properties

Berzelius's Opposition to Substitution Theory (1838)

"An element so eminently electronegative as chlorine can never enter into an organic radical: this idea is contrary to the first principles of chemistry; its electronegative nature and its powerful affinities would prevent it from entering except as an element in a combination peculiar to itself."

Copulae *(Paarlinge)*

acetic acid ($C_2H_4O_2$)

$C_2H_3 + C_2O_3 + HO$

(C=6, O=8)

trichloroacetic acid

$C_2Cl_3 + C_2O_3 + HO$

The Genesis of the New Type Theory

Auguste Laurent
(1807-1853)

- the metal oxide R^2O corresponds to water H^2O (1846)

SUBSTANCES.	FORMULES.
Eau	$H^2\ O$
Hydrates...............	HMO
Oxydes................	$M^2\ O$
Acide sulfhydrique.....	H^2S
Sulfures acides	HMS
Sulfures neutres........	M^2S

Preparation of Alkylamines (1849)

Charles Wurtz
(1817-1884)

- alkylamines prepared from alkylisocyanates
  $RNCO \longrightarrow RNH_2$

- Methylamine and ethylamine have properties similar to ammonia

- They are of the same “type”

The Ammonia Type (1850)

August Wilhelm von Hofmann
(1818-1892)

$$N \left\{ \begin{array}{l} H \\ H \\ H \end{array} \right.$$

ammonia

$$N \left\{ \begin{array}{l} C_2H_5 \\ H \\ H \end{array} \right.$$

ethylamine

$$N \left\{ \begin{array}{l} C_2H_5 \\ C_2H_5 \\ H \end{array} \right.$$

diethylamine

$$N \left\{ \begin{array}{l} C_2H_5 \\ C_2H_5 \\ C_2H_5 \end{array} \right.$$

triethylamine

The Water Type (1850-1852)

Alexander Williamson
(1824-1904)

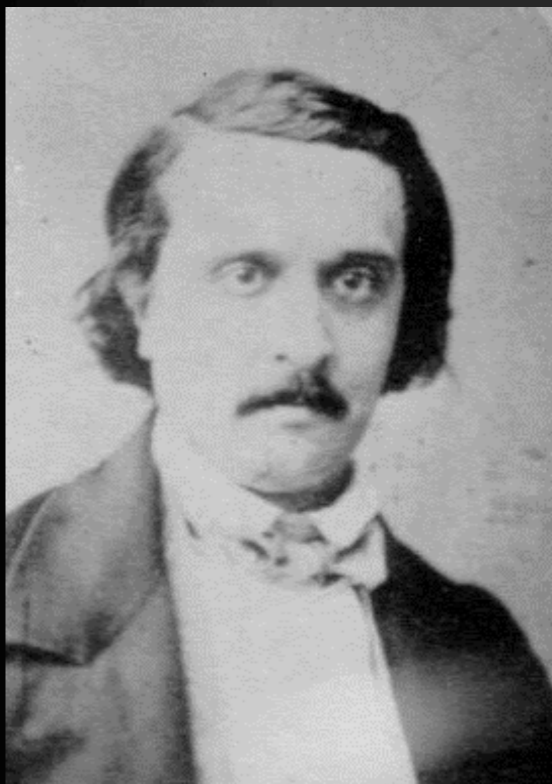
$$O\left\{\begin{matrix}C_2H_5\\K\end{matrix}\right. + \left\{\begin{matrix}C_2H_5\\I\end{matrix}\right. \not\longrightarrow O\left\{\begin{matrix}C_4H_9\\H\end{matrix}\right. + KI$$

butyl alcohol

$$O\left\{\begin{matrix}C_2H_5\\K\end{matrix}\right. + \left\{\begin{matrix}C_2H_5\\I\end{matrix}\right. \longrightarrow O\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right. + KI$$

ether

The Four Types (1853)



Charles Gerhardt
(1816-1856)

L'eau	H^2O,
L'hydrogène	H^2,
L'acide chlorhydrique	HCl,
L'ammoniaque	H^3N.

- Système unitaire - fusion of Dumas type theory and older radical theory

- Types do not show the arrangement of atoms but only the analogies of their metamorphoses, i.e., type formulas are not structural.

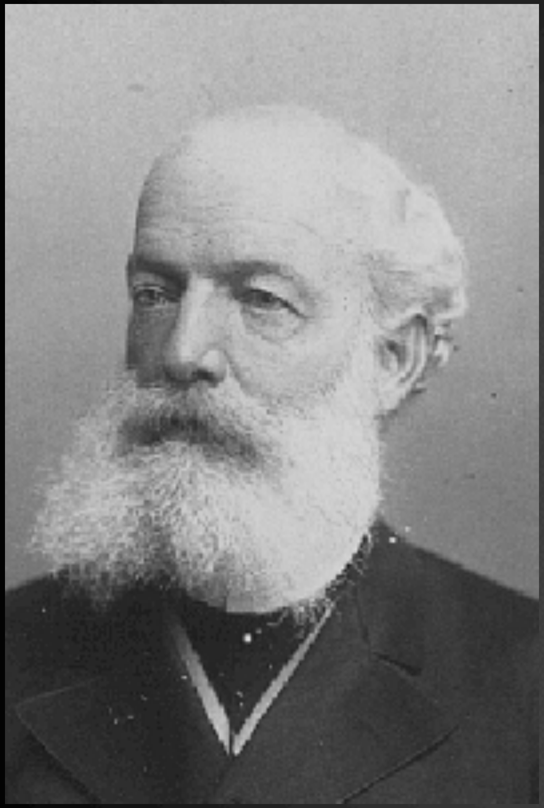
The Concept of Valence (1850-1852)

Edward Frankland
(1825-1899)

"…the compounds of nitrogen, phosphorus, antimony and arsenic especially exhibit the tendency of these elements to form compounds containing 3 or 5 equiv. of other elements, and it is in these proportions that their affinities are best satisfied…"

$SbCl_3$ SbO_3

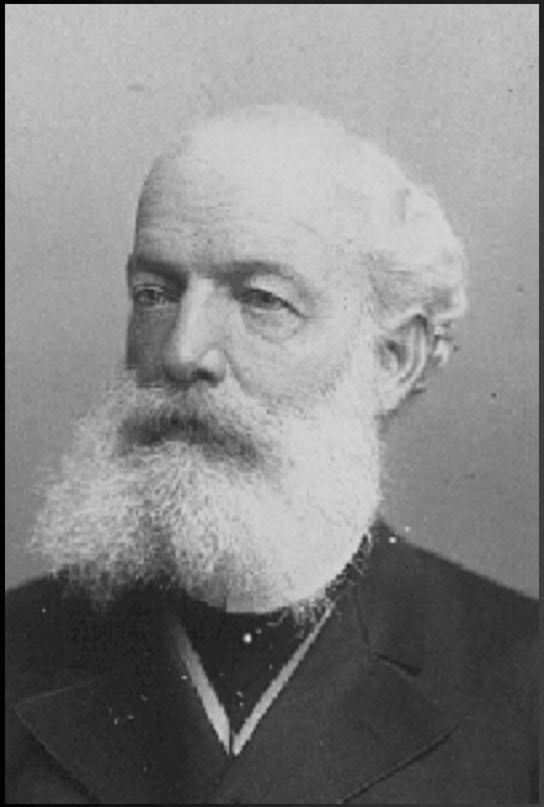
The Tetravalence of Carbon (1858)



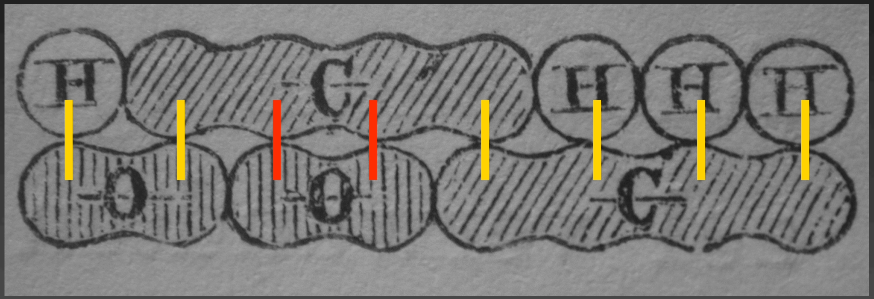
August Kekulé
(1829-1896)

"If we look at the simplest compounds of this element, CH_4, CH_3Cl, CCl_4, $CHCl_3$, $COCl_2$, CO_2, CS_2, and CHN, we are struck by the fact that the quantity of carbon, which is considered by chemists as the smallest amount capable of existence - the atom - always binds four atoms of a monoatomic or two of a diatomic element, so that the sum of the chemical units of the elements combined with one atom of carbon is always equal to four. We are thus led to the opinion that carbon is tetratomic."

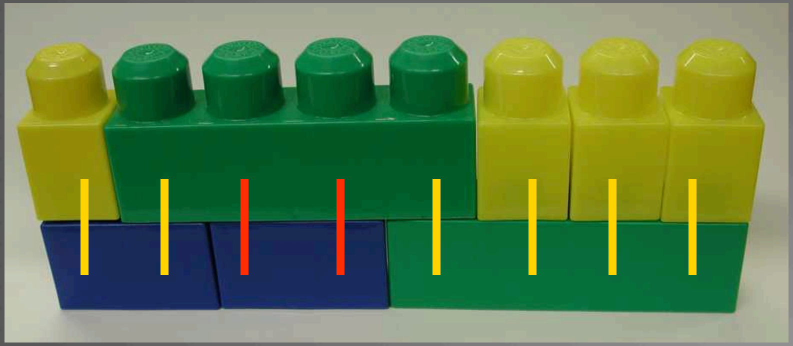
“Sausage” Formulae (1859)



August Kekulé
(1829-1896)



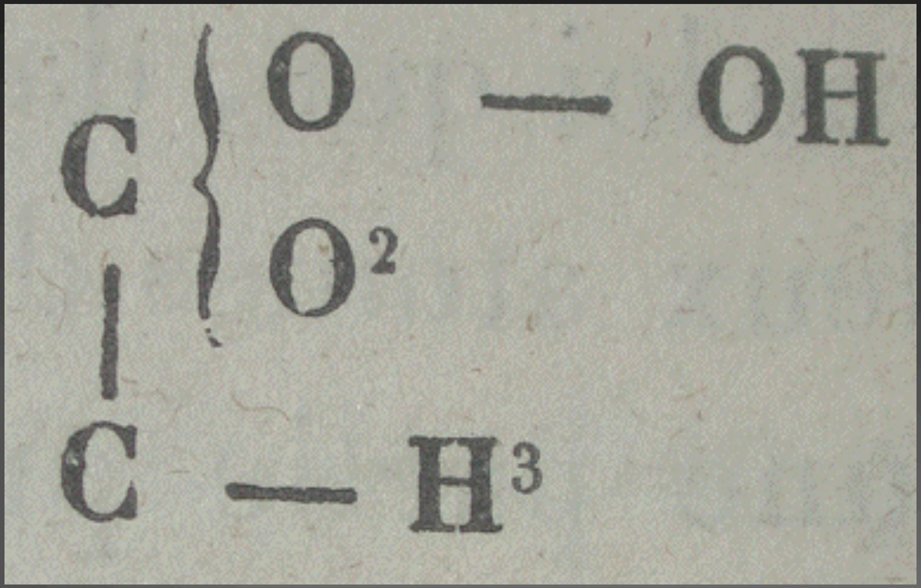
Acetic Acid



Lego Acetic Acid

“Bonds” Appear in Structures (1858)

Alexander Scott Couper
(1831-1892)

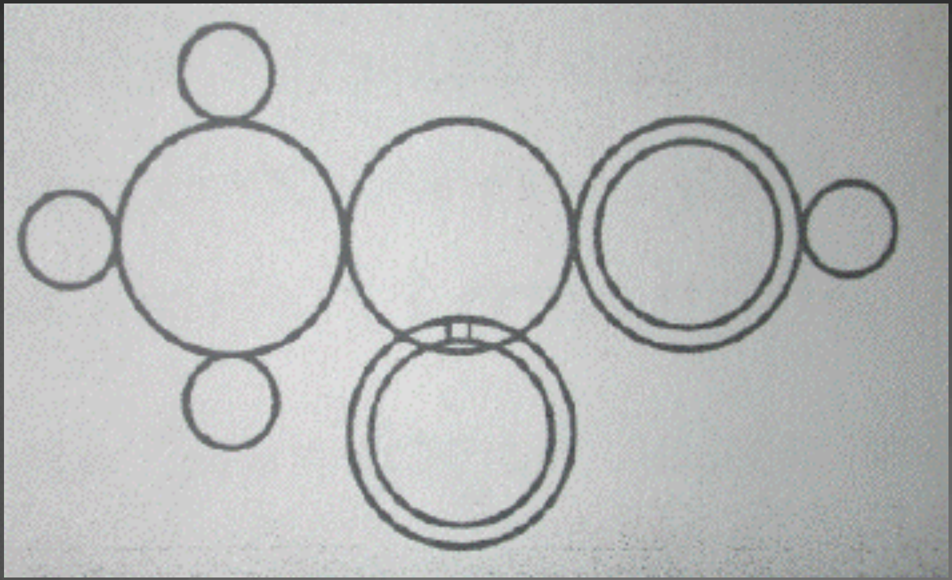


Acetic Acid

Self-linking of carbon atoms
Graphic formula
June 1858

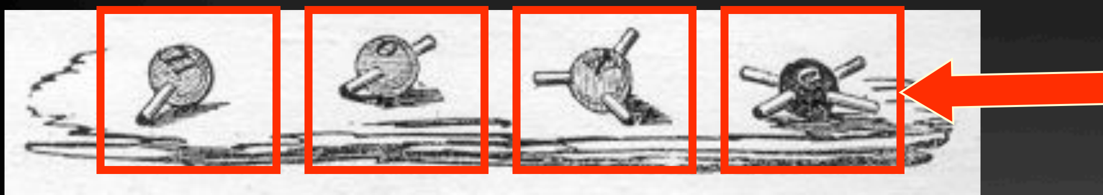
Diagrammatical Structural Formulae (1861)

Joseph Loschmidt
(1821 - 1895)



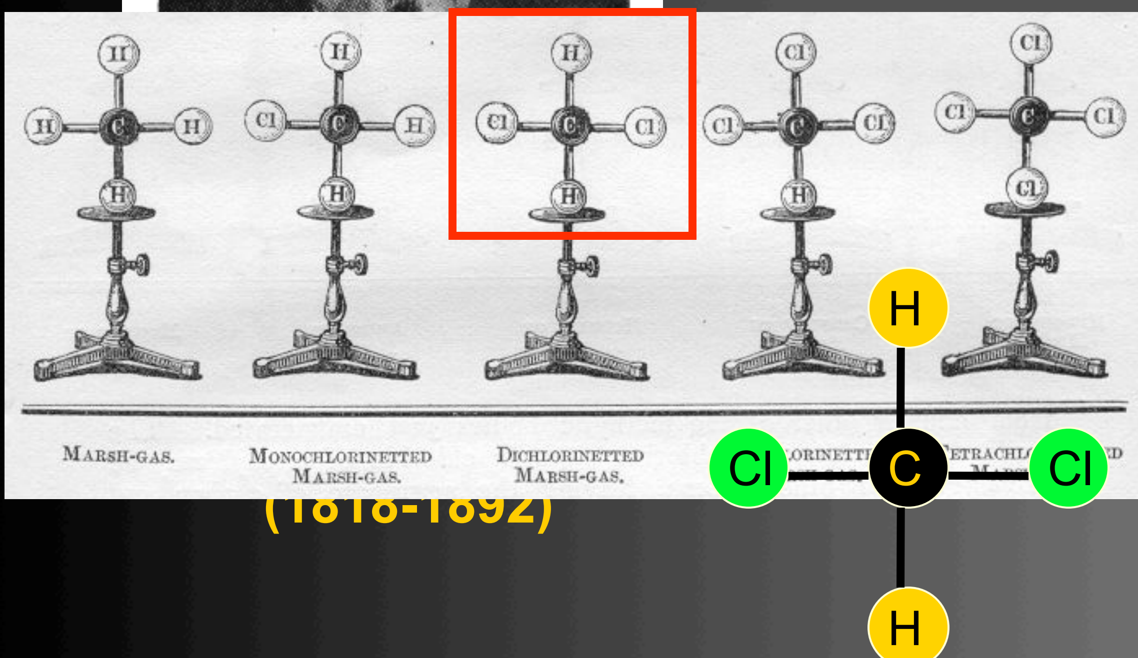
Acetic Acid

A. W. Hofmann's Physical Models (1865)



Note planar arrangement of bonds about carbon

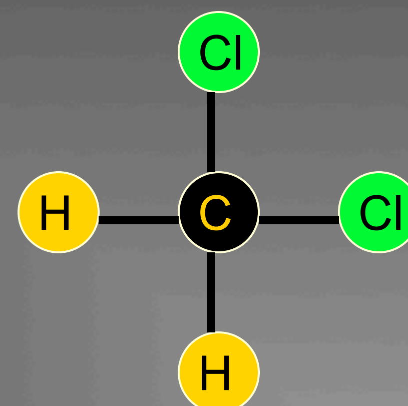
H - monovalent O - divalent N - trivalent C - tetravalent



(1818-1892)

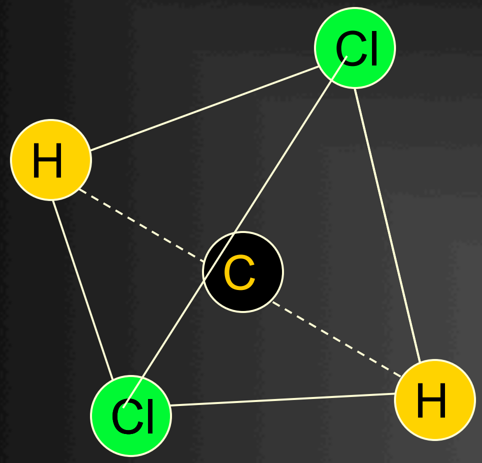
Is

different from



?

Van't Hoff's Tetrahedral Model (1874)

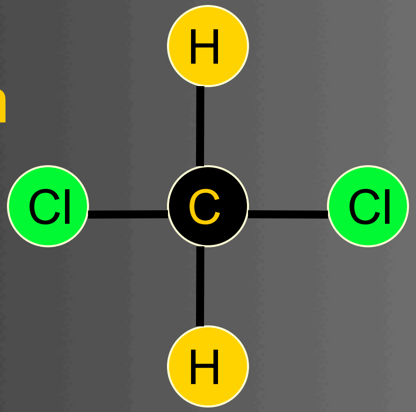


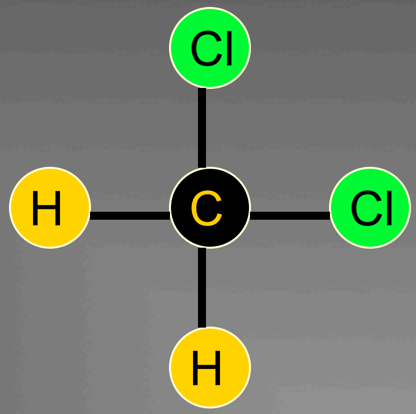
Are there two dichloromethanes?

Only one was known …

or ever found.

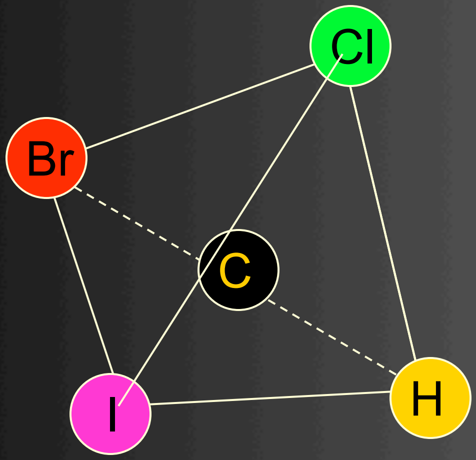
A 3D tetrahedral arrangement of hydrogen and chlorine with carbon in the center predicts only one isomer.

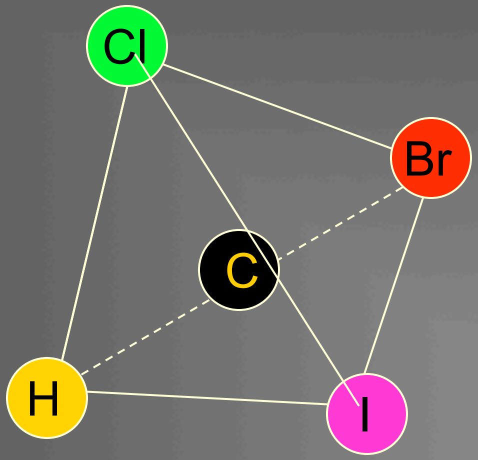




Van't Hoff's Tetrahedral Model (1874)

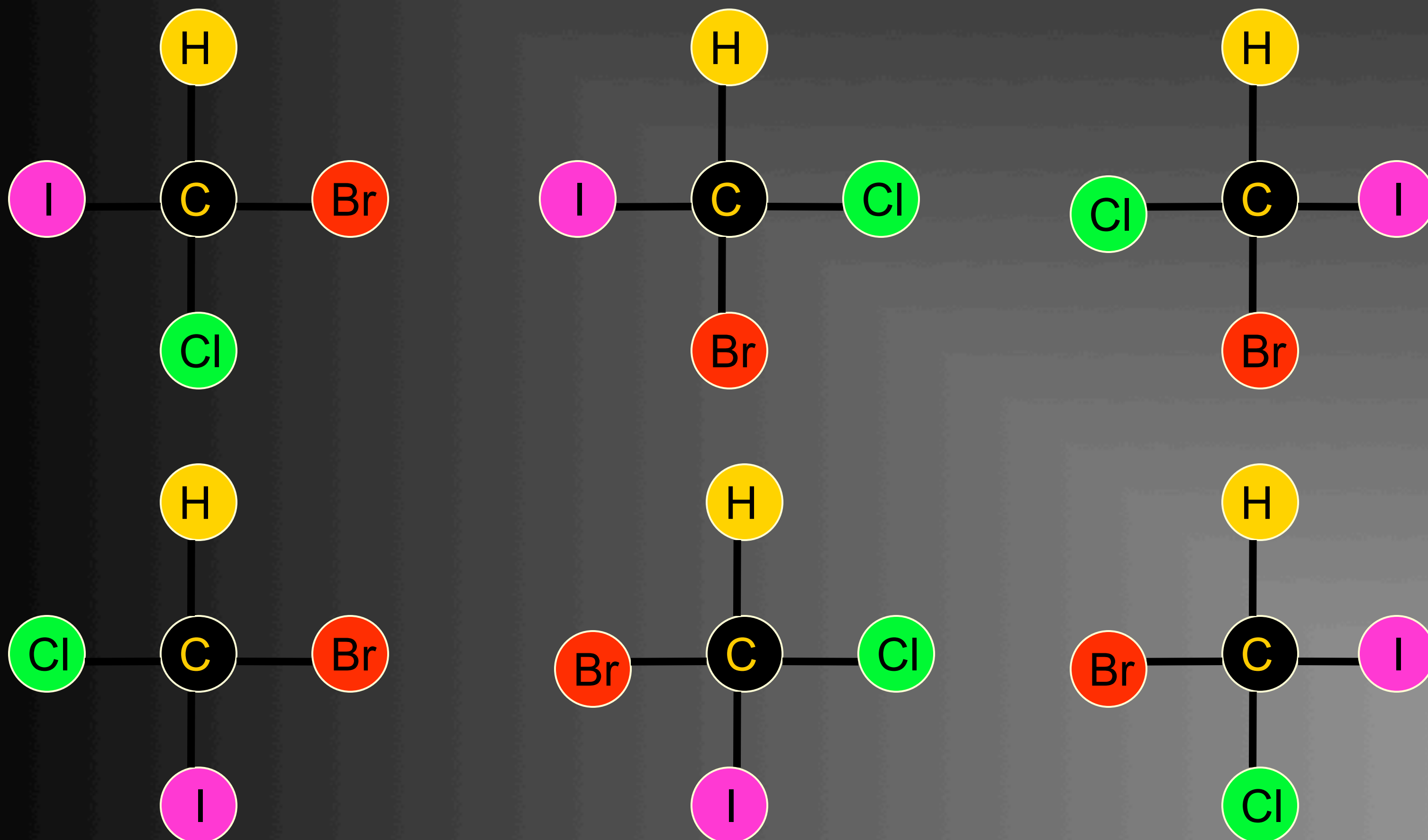
The tetrahedral model explains the existence
of one racemic bromochloroiodomethane as a pair
of enantiomers …non-superimposable mirror images.





Van't Hoff's Tetrahedral Model (1874)

Planar bromochloroiodomethane requires three pairs of enantiomers.



The End

…for a while