10.
K strukturnoj kemiji

Novija teorija tipova – Kolbe

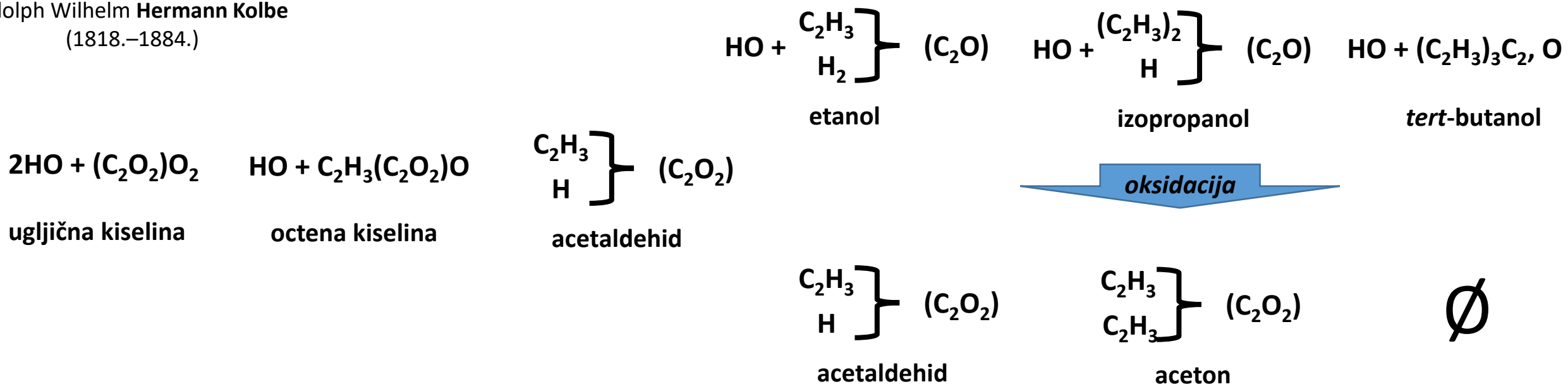
Adolph Wilhelm **Hermann Kolbe**
(1818.–1884.)

1855. Organske kiseline derivati ugljične (C_2O_4):

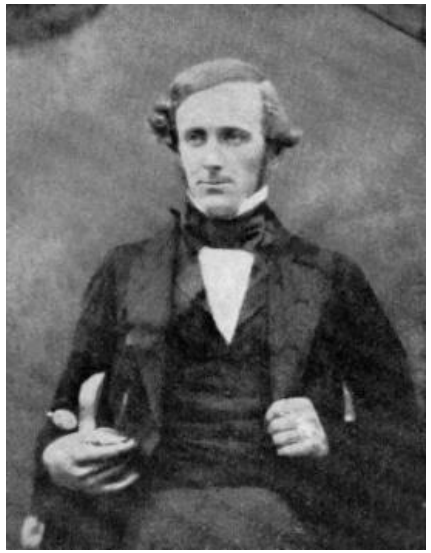
octena kiselina – ugljična u kojoj je ‘jedan ekvivalent’ kisika zamijenjen metilnim radikalom ($C_2O_3C_2H_3$+OH) [C=6; O=8]

→ organski spojevi nastaju supstitucijom iz anorganskih

Složeni radikali sastoje se od jednostavnijih (acetil = karbonil + metil)



Valencija – Frankland



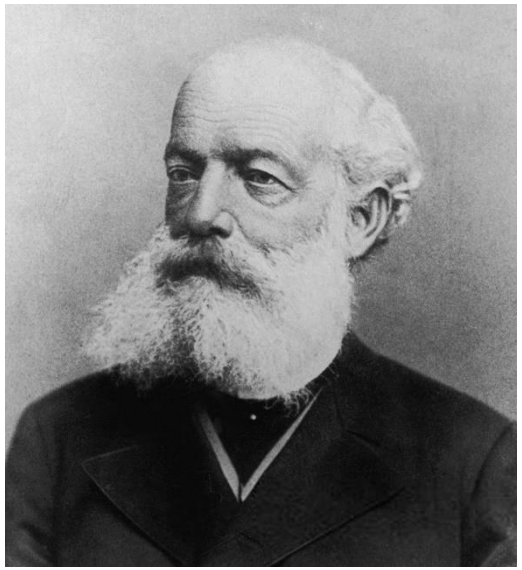
Sir Edward Frankland, (1825.–1899.)

„When the formulae of inorganic chemical compounds are considered, even a superficial observer is impressed with the general symmetry of their construction. The compounds of nitrogen, phosphorus, antimony and arsenic especially exhibit the tendency of these elements to form compounds containing 3 to 5 equivs. of other elements, and it is in these proportions that their affinities are best satisfied; thus in the ternal group we have NO_3, NH_3, NI_3, NS_3, PO_3, PH_3, PCl_3, SbO_3, SbH_3, $SbCl_3$, AsO_3, AsH_3, $AsCl_3$, *&c.; and in the five-atom group,* NO_5, NH_4O, NH_4I, PO_5, PH_4I, *&c. Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, no matter what the character of the uniting atoms may be,* ***the combining-power*** *of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms."*

E. Frankland, On a New Series of Organic Bodies Containing Metals, *Phil. Trans. Roy. Soc.* **142**, (1852) 417-444.

combining-power → *quantivalence* → **valencija**

Razvoj pojma valencije – Kekulé



Friedrich August Kekulé, (**Kekule von Stradonitz;** 1829.–1896.)

'izvorno Liebigov đak, postao sam učenik Dumasa, Gerhardta i Williamsona: sada više ne pripadam nijednoj školi...'

Frankladnova valencija kao osnova organske kemije

1853. Reakcije octene kiseline s fosforovim sulfidom i kloridom:

$$5\ \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}\ O + P_2S_5 \rightarrow 5\ \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}\ S + P_2O_5$$

octena kiselina — **tiooctena kiselina**

ali

$$5\ \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}\ O + 2\ PCl_5 \rightarrow 5\ C_2H_3OCl + 5\ HCl + P_2O_5$$

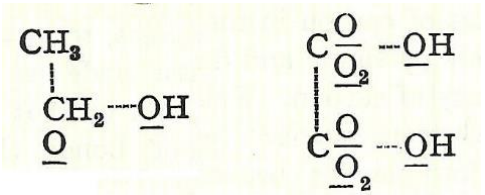
octena kiselina — **acetil-klorid**

→ Klor je jednovalentan a sumpor kao i kisik dvovalentan (*zweibäsig*)

1857. Tip metana – ugljik je **četverovalentan** (*vierbasisch oder vieratomig*)

1858.:'*količina ugljika koju su kemičari prepoznali kao atom uvijek se spaja s četiri atoma uvijek se sjedinjuje s po četiri atoma monoatomnih ili dva atoma dvoatomnih elemenata; općenito, suma kemijskih jedinica koja se sjedinjuje s jednim atomom ugljika je 4*'

1858. Archibald Scott Couper (neovisno):

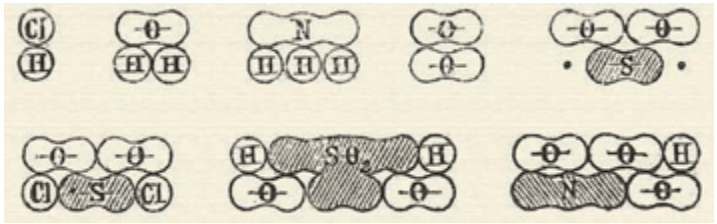


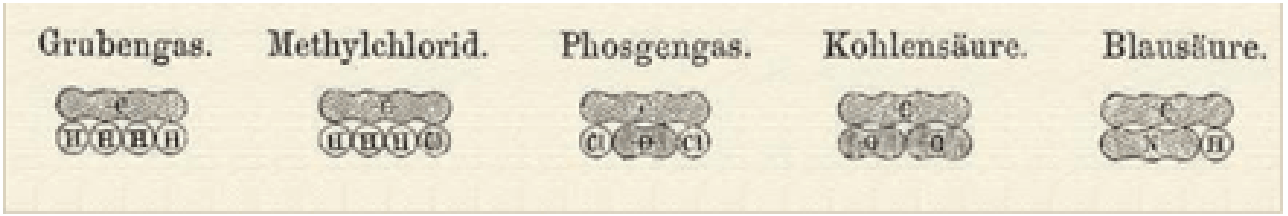
[O = ½O]

Strukturne formule

1861. Butlerov '*O **kemijskoj strukturi** tvari*' – kemijske reakcije odaju stvarne položaje atoma i skupina atoma u molekuli (usp. Gerhardt)

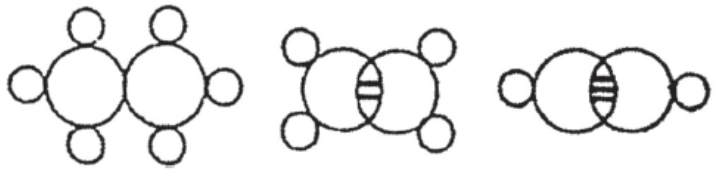
1859. Kekule



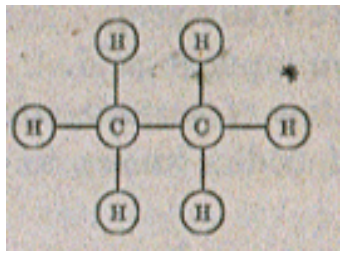


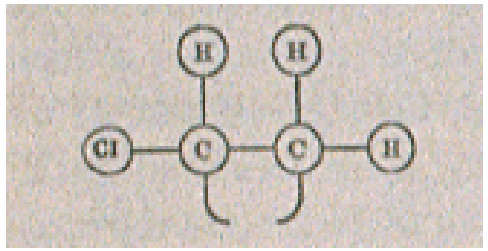
Aleksandar Mihajlovič Butlerov
(Алекса́ндр Миха́йлович Бу́тлеров; 1828.–1886.)

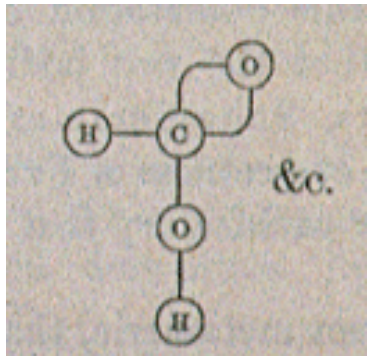
1861. Johann Joseph Loschmidt '*Chemische Studien*'

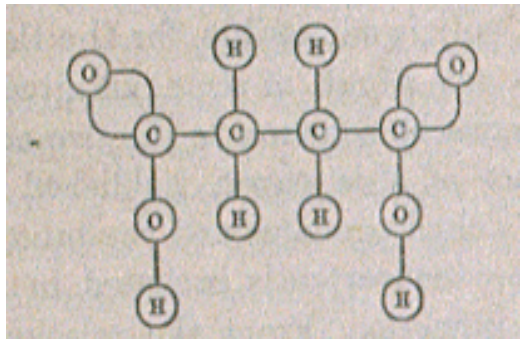


1861. Alexander Crum Brown '*O teoriji kemijskog spajanja*':

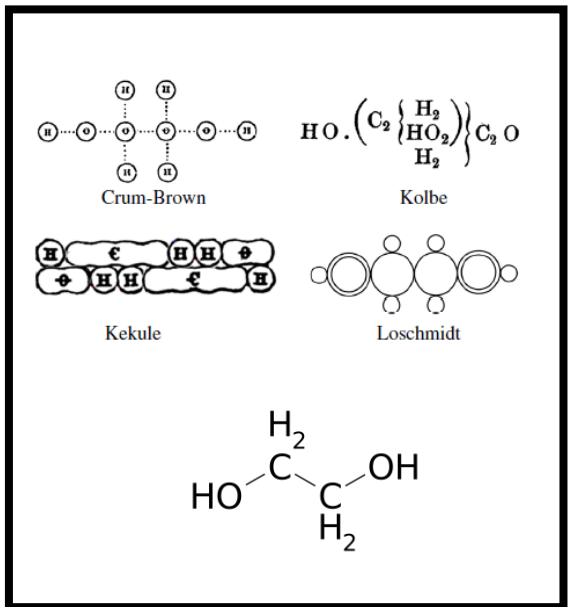








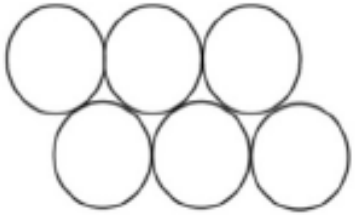
(1866. Frankland – Brownove formule bez *kružića*)



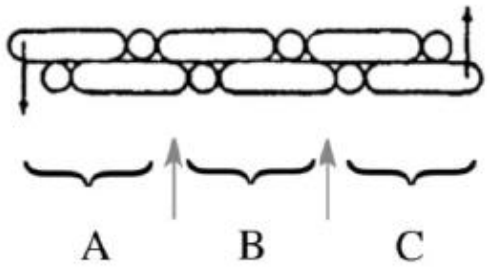
Formula benzena

XVI. st. – *benzoe* (*benzoin*, *benjamin*) balzamična smola iz drveća roda *Stirax*
1556. (Nostradamus!) – suhom destilacijom *benzoe* nastaje *flos benzoae* (benzojeva kiselina)
1825. (Faraday) –benzen izoliran iz rasvjetnog plina (*bicarburet of hydrogen*)
1831.-2. (Liebig i Wöhler) – sastav benzojeve kiseline (srodna s hipurnom)
1833. (Mitscherlich) – benzen suhom destilacijim benzojeve kiseline i vapna (*benzol*)
1836. (Laurent) – radikal '*phène*' (od *φαινω = osvjetljavam)*
1845. (Mansfield) – industrijska proizvodnja iz ugljenog katrana
1855.-60. (Kekulé) – '*aromatski* spojevi' (Hofmann '*alifatski* spojevi')
1858. (Kekulé) – atomi ugljika u benzenu i naftalenu gušće posloženi nego u 'običnim' ugljikovodicima
1861. Loschmit – dvije mogućnosti (L181 i **L182**)
1865. Kekulé – ciklička formula (K1 i K2)
1866. Kekulé – šesterokutna formula formula (K3 i K4)

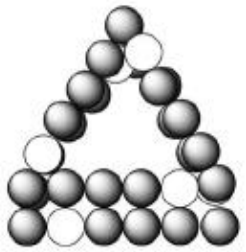
L 181



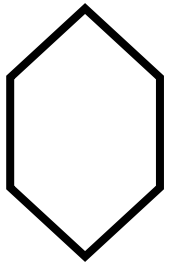
L 182



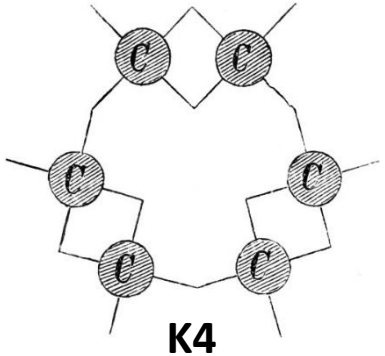
K1



K2



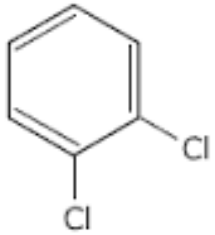
K3

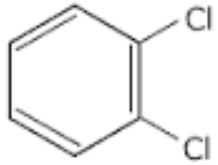


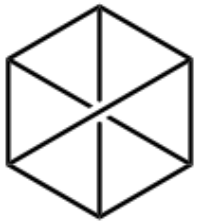
K4

Problem – samo tri izomera disupstituiranih benzena

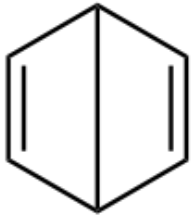
Zašto ne 2 *ortho*-diklorbenzena?







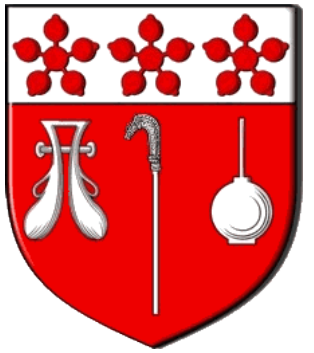
1867. Claus



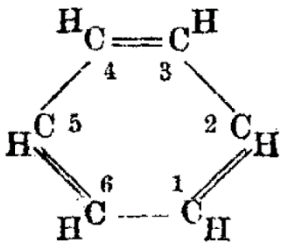
1867. Dewar

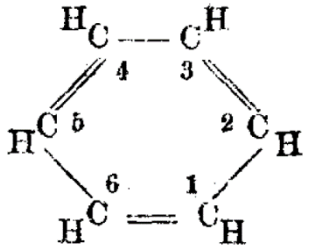
1869. Ladenburg

Sir James Dewar
(1842.–1923.)

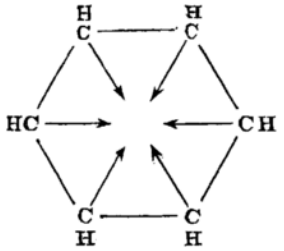


Professor Dewar
Is a better man than you are,
None of you asses
Can condense gases.
E. C. Bentley, 1905.

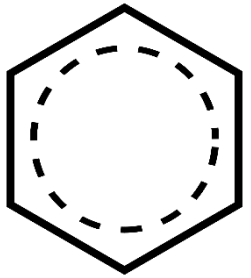




1872. Kekulé



1887. Armstrong



1899. Thiele

Friedrich Karl **Johannes Thiele**
(1865.–1918.)

Stereokemija – Pasteur i vinska kiselina

1812. Jean-Baptiste Biot (1774.-1862.): kvarc zakreće ravninu polarizacije linearno polariziranog svjetla
1815.-35. isto i otopine nekih organskih tvari: terpenzin, ekstrakti limuna i lovora, kamfor, šećer, **vinska kiselina** (1832.)...; organske tvari zadržavaju to svojstvo kao krutine; kvarc ga taljenjem gubi

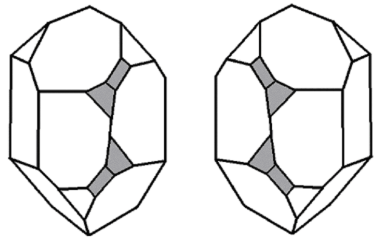
1815. René Just Haüy (1743.–1822.): kristali kvarca imaju hemiedrijske plohe

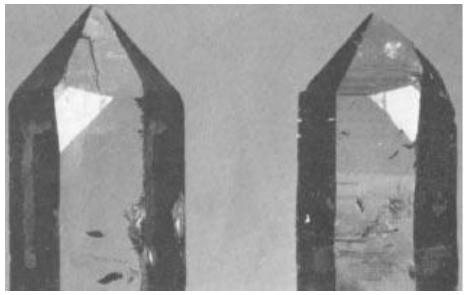
1820. Sir John Frederick William Herschel (1792.–1871.): Hemiedrijske plohe kvarca; lijevi i desni kristali kvarca zakreću ravninu polarizacije u suprotnim smjerovima

1826. Gay Lussac: kuhanjem zasićene otopine vinske kiseline – **racemična kiselina** (izomer vinske)

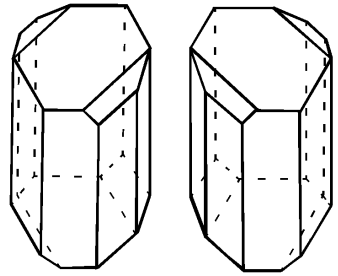
1844. Mitscherlich: vinska kiselina i tartarati su oprički aktivni, racemična kiselina i racemati nisu.

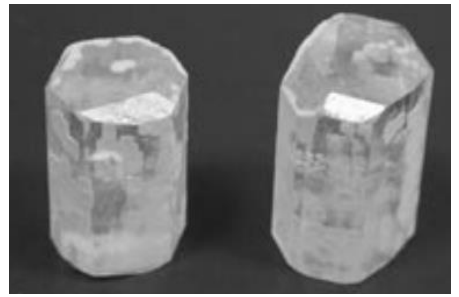
1847. Pasteur: kristali natrijevog amonijevog tartarata imaju hemiedrijske plohe – ali i kristali natrijevog amonijevog racemata!





Lijevi i desni kvarc
(shema i fotografija)





Lijevi i desni natrijev amonijev tartarat
(shema i fotografija)

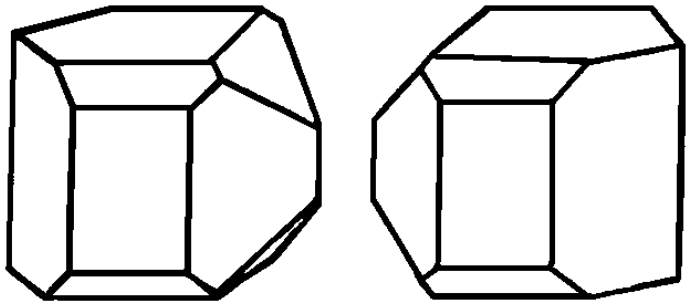
Louis Pasteur (1822 – 1893)

1. Racemična kiselina nije čisti spoj nego smjesa jednakih količina ‘lijeve’ i ‘desne’ vinske kiseline koje se razlikuju samo u smjeru zakretanja ravnine polarizirane svjetosti. Optička rotacije dviju komponenti se tako poništi te je racemična kiselina optički inaktivna

2. Optička aktivnost organskih spojeva, njihovih otopina i talina rezultat je nedostatka simetrije (‘*dissimetrije*’) molekulâ

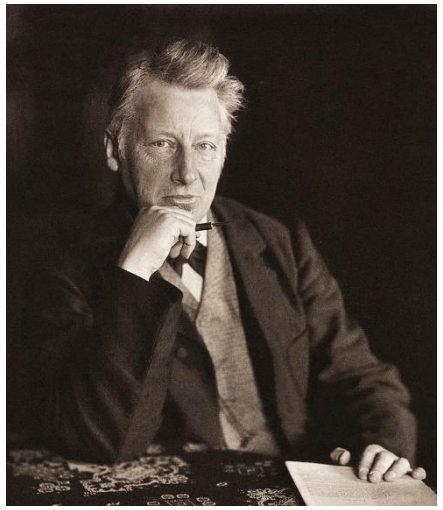
3. Optička aktivnost kristalâ čije otopine (ili taline) nisu optički aktivne (npr, kvarc ili natrijev klorat) je rezultat ‘*dissimetričnog*’ pakiranje ‘*nedissimetričnih’* (t.j. simetričnih) molekula

4. Upravo kao i njihovi kristali, molekule ‘lijeve’ i ‘desne’ vinske kiseline su **zrcalna slika** jedna druge



Kristali ‘lijeve’ vinske kiseline (prirodne) i ‘desne’ (Pasteur, 1847.)

Stereokemija

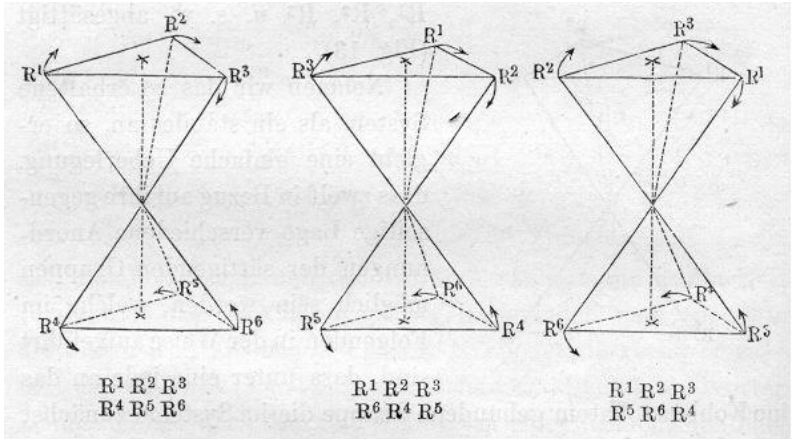


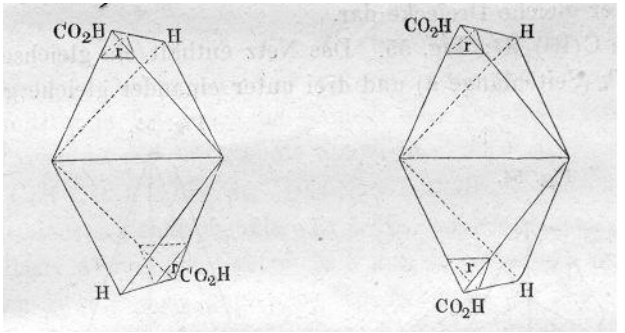
Jacobus Henricus van 't Hoff
(1852–1911)

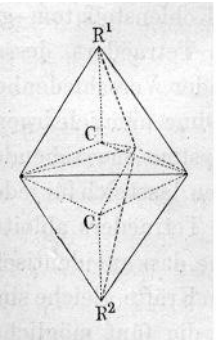
1874. van ’t Hoff ‘*Voorstel tot Uitbreiding der Tegenwoordige in de Scheikunde gebruikte Structuurformules in de Ruimte, benevens een daarmee samenhangende Opmerking omtrent het Verband tusschen Optisch Actief Vermogen en chemische Constitutie van Organische Verbindingen*’

→ kemijske formule u 3D – **ako je ugljik u središtu tetraedra, to može objasniti sve opažene slučajeve konfiguracijske i stereoizomerije**

(1901. – prva Nobelova nagrada za kemiju)



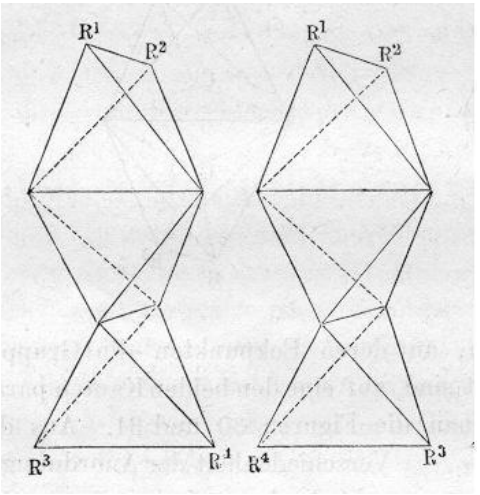




Joseph Achille Le Bel
(1847–1930)

Kasnije 1874. Le Bel – slični zaključci, nerazumljivije napisano i bez slika

(Le Bel-van ’t Hoffovo pravilo:
Broj stereoizomera molekule s *n* asimetrično supstituiranih atoma = 2^n)



Potvrda 3D strukturnih modela i apsolutne konfiguracije – rentgenska difrakcija

1895. **Wilhelm** Conrad **Röntgen** – 'X-zrake'

1896. **Arnold Sommerfeld '***Mathematische Theorie der Diffraction*' – valna duljina 'X-zraka' oko 1 Å

1912. **Max** Theodor Felix **von Laue** (+ Paul Knipping and Walter Friedrich) – kristali kao difrakcijska rešetka za rentgenske zrake

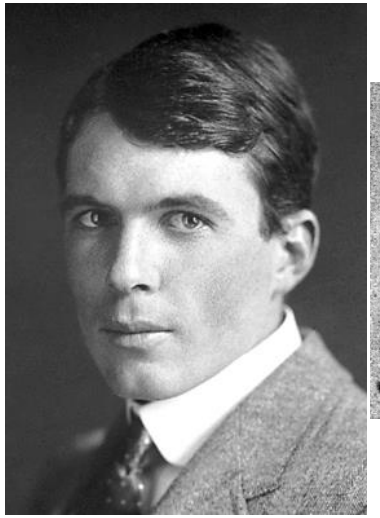
1913. **Bragg** i **Bragg** – iz difrakcije odrediva kristalna struktura (NaCl, dijamant (potvrda tetraedarske strukture!),...)

1913. **Georges Friedel** – Friedelov zakon: difrakcijska slika je uvijek centrosimetrična (intenziteti refleksa 'Friedelovih parova' identični)
...

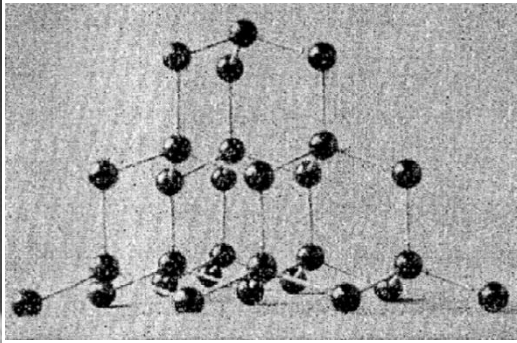
1949. **Johannes Martin Bijvoet** – anomalna disperzija – odstupanje od Friedelovog zakona zbog apsorpcije zračenja

1951. Apsolutna konfiguracija **vinske kiseline** temeljem difrakcije rentgenskih zraka na kristalu natrijeva rubidijeva tatrarata

Sir **William Henry Bragg** (1862.–1942.)

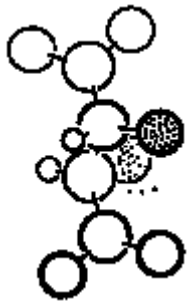


Sir William **Lawrence Bragg** (1890.–1971.)



Prvi model strukture dijamanta (1913.)

Johannes Martin Bijvoet (1892–1980)



Apsolutna konfiguracija L(+)-tartaratnog iona (1951.)

CIP

1966. Cahn, Ingold i Prelog – konvencija o pravilima prioriteta za određivanje apsolutnih konfiguracija (IUPAC od 1974.)

Robert Sidney Cahn (1899–1981)

Sir Christopher Kelk Ingold (1893–1970)

Vladimir Prelog (1906–1998)

Buergenstock Declaration

Whereas we the stereochemists of many lands, being gathered together in Solemn conclave at the Buergenstock in the Half-Canton of Nidwalden belonging to the Helvetian Confederation, do freely recognize, agree, affirm, and proclaim that the RULES of CAHN, INGOLD and PRELOG, as set down in their articles, are just rules and fair, causing harm to no man,

Each of us, being of sound mind, does freely agree

1. to observe the aforesaid RULES in all such cases as they may be applicable, and

2. to refrain from using other rules as may have been or as may be proposed by other powers.

Whereupon we do affirm that any infringement of this Agreement shall be punished, in the first instance by a penalty amounting to 1 (one) glass of liquid refreshment to be supplied at the costs of the infringer to all stereochemists present; and in further instances by the infringer being compelled to read the aforesaid articles by CAHN, INGOLD and PRELOG in their entirety.

Signed, this day, Friday, 13th May, 1966, by

A. Dreiding, model-maker, resident in Erlenbach, Switzerland

K. Mislow, chirosophist, resident in Princeton, New Jersey

and witnessed by

R. S. Cahn
R.S. Cahn

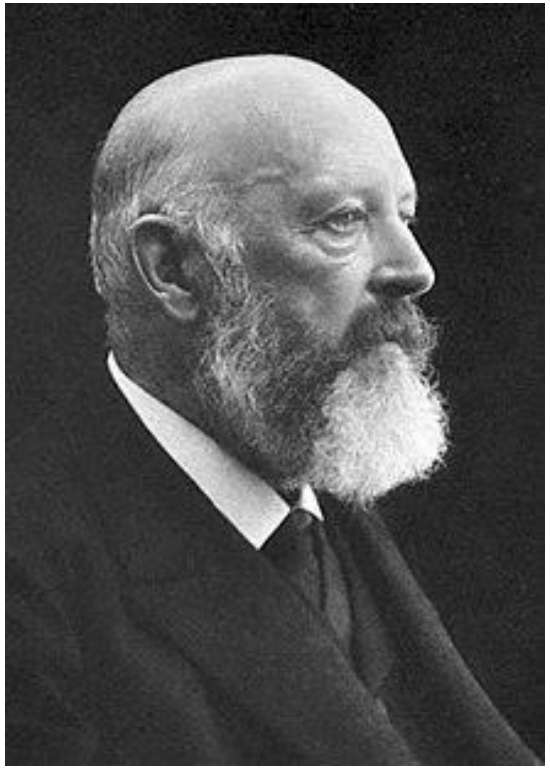
Sir Christopher Ingold
Ch Ingold

V. Prelog
prelog V

K. Mislow
chirosophist

as a model
to critically minded
dissidents
André Dreiding
stereosophist
stereotechnician

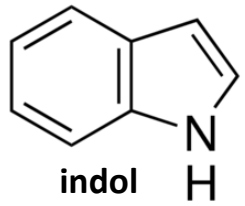
Struktura i sinteza



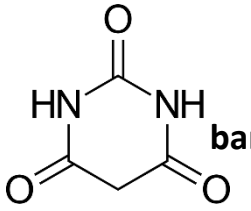
Johann Friedrich Wilhelm
Adolf von Baeyer
(1835 –1917)

Baeyer:

1860.-ih . Derivati mokraćne kiseline (barbiturna)



indol

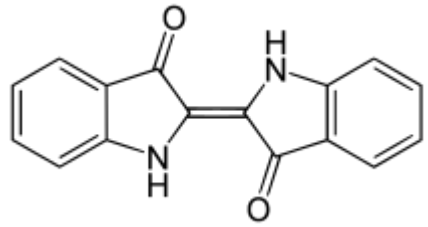


barbiturna k.

Poliacetileni, oksonijeve soli, nitrozo-spojevi

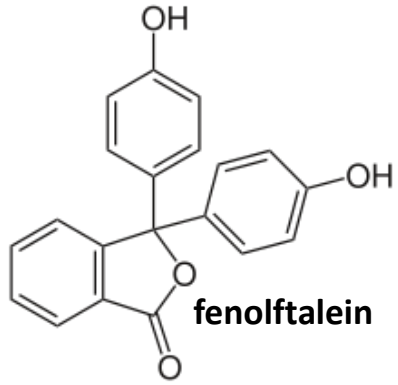
1869. Indol

1870. Indigo (empirijska formula – 1840. Dumas)

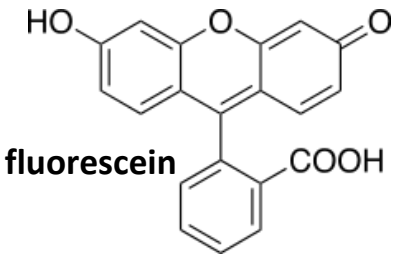


indigo

1871. Ftaleinske boje – fenolftalein



fenolftalein



fluorescein

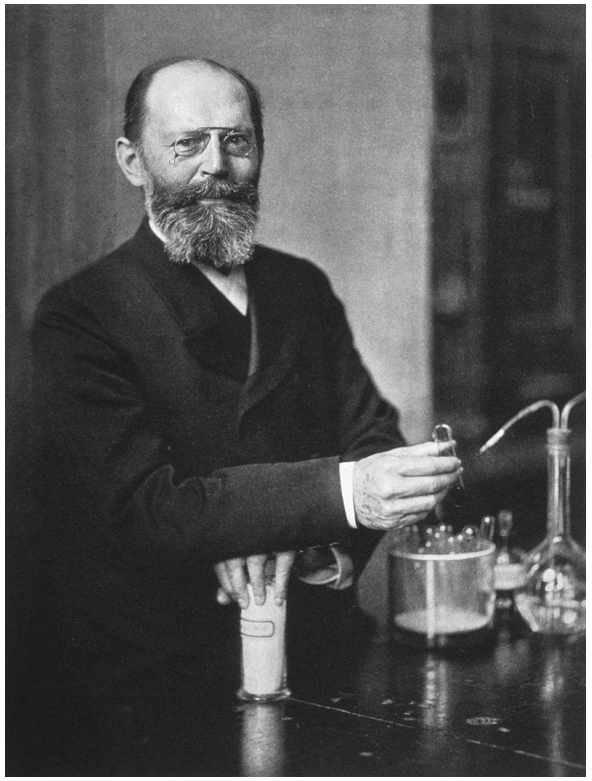
1872. Kondenzacija fenola i formaldehida – preteča ***bakelita***

1884. *Tautomerija* – izatin postoji u dva oblika: **laktam**skom i **laktim**skom

Napetost u prstenastim spojevima (ne postoje cikloalkini, najstabilniji 5- i 6-člani prstenovi)
– ne vrijedi za jako velike prstenove (Ružička, 1926.)

Baeyer-Villigerova oksidacija, Baeyerov reagens...

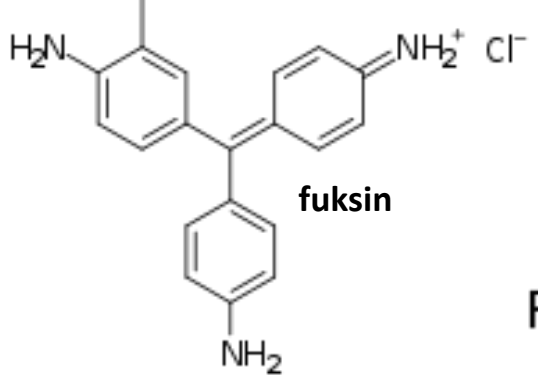
Struktura i sinteza



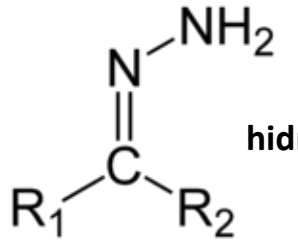
Hermann **Emil** Louis **Fischer**
(1852–1919)

Fischer:

1875. Hidrazin + aldehid/keton → hidrazon



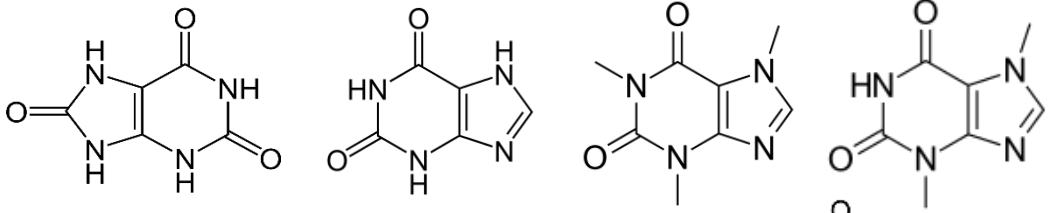
fuksin



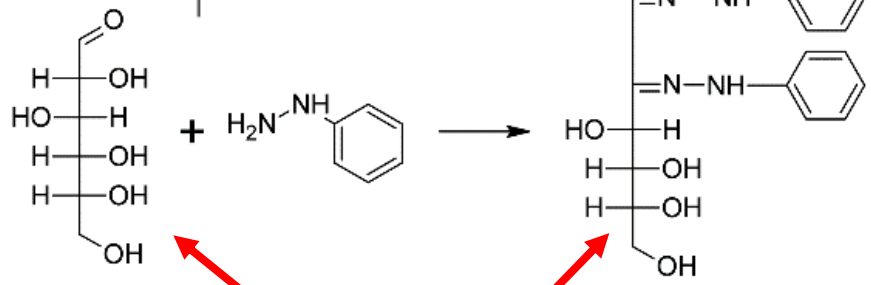
hidrazoni

1878/9. fuksinske boje

1881./2. purini: mokraćna kiselina, ksantin, kafein, teobromin



1884. Fenilhidrazin sa šećerima daje osazone
→ Sinteza glukoze i 15 ($2^4 - 1$) stereoizomera
→ Sinteze ostalih šećera
→ Relativne konfiguracije (D/L-glukoza/gliceraldehid)
→ Projekcijske formule (temeljem van't Hoffovog modela)

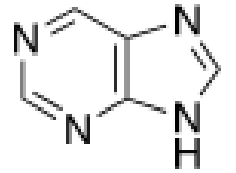


glukoza **glukosazon**

Fischerova projekcija

Do 1900. oko 130 derivata purina
Od 1899. Aminokiseline i oligopeptidi

1904. Barbital (dietilberbiturna kiselina)



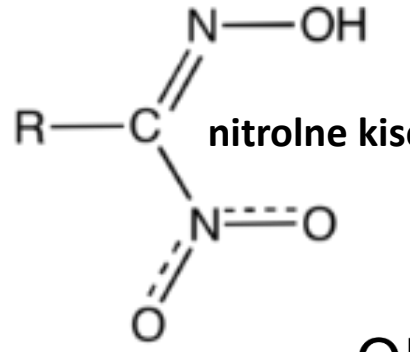
purin

Fischerova sinteza peptida, Fischer-Speierova esterifikacija, Fischerova glikozidacija...

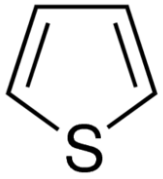
Struktura i sinteza (Viktor) Meyer

Viktor (Victor) Meyer
(1848.–1897.)

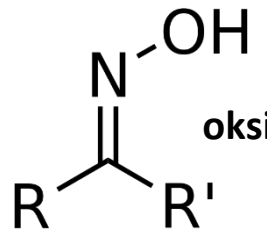
1869. Aromatske karboksilne kiseline iz sulfonskih kiselina i formijata
1872. Nitroalkani iz alkil jodida i srebrova nitrita (test za prim-, *sec*- i *tert*- alkohole)
1874. Nitrolne kiseline
1878. Nova metoda za gustoće plinova (*aparatura Viktora Meyera*) – arsenov oksid As_4O_6, metali monoatomni, halogeni na visokim temperaturama disociraju
1880. Glukoza je aldehid
1882. Oksimi iz aldehida i ketona
1882. Tijekom predavanja: tiofen u benzenu (Baeyerov test na benzen zapravo detektira tiofen) – sumporovi heterocikli
1886. Iperit
1888. Pojmovi ‘stereokemija’ i ‘dipol’
1892. Jodozobenzen
1892. Steričko ometanje (*o*-disupstituirane benzojeve kiseline) ‘Zakon eaterifikacije Viktora Meyera)
1894. Jodonijevi kationi (iz jodbenzena i jodozobenzena)



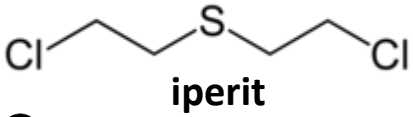
nitrolne kiseline



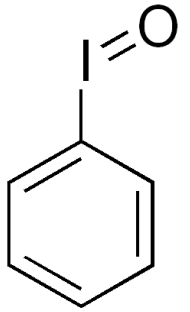
tiofen



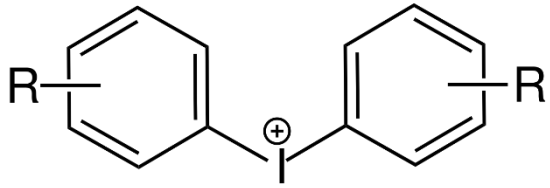
oksimi



iperit

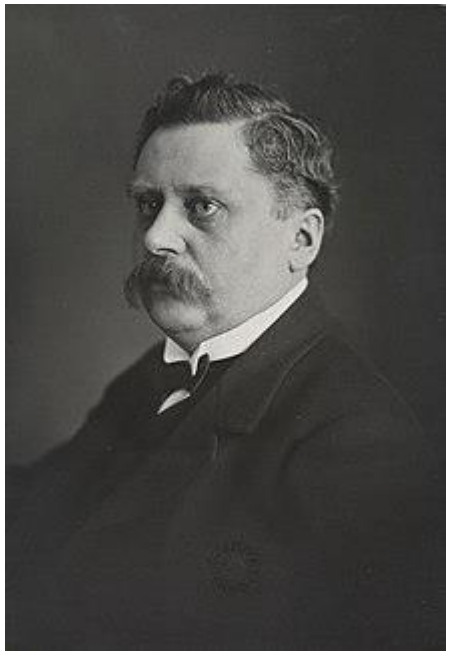


jodozobenzen



Jodonijevi kationi

Anorganska struktura – kompleksni spojevi



Alfred Werner (1866–1919)

1869. Christian Wilhelm Blomstrand (1826.–1897.) i kasnije Sophus Mads Jørgensen (1837.–1914.): sintetizirani mnogi kompleksi, najviše s amonijakom; kompleksi s amonijakom sadrže lance povezanih molekula amonijaka (povezivanje omogućuje peterovalentnost dušika)

1893. Werner.
Hauptvalenz (oksidacijski broj) i *Nebenvalenz* (koordinacijski broj) - $CoCl_3 \cdot 6NH_3$ = $[Co(NH_3)_6]Cl_3$, *Hv*(Co) = 3; *Nv*(Co) = 6 (disocijacija potvrđena mjerenjem vodljivosti).

Ukupni naboj kompleksa = *Hv* – *Nv* * *Z*(ligand)

Dva različita spoja $Co(NH_3)_4Cl_3$ → $[Co(NH_3)_4Cl_2]Cl$; $[Co(NH_3)_4Cl_2]^+$ je oktaedarskog oblika; moguća su dva izomera (*cis*- i *trans*-)

Oktaedri, kvadrati, teraedri.

1914. Kiralnost bez ugljika – *hexol*