Wat maakt het element koolstof zo bijzonder voor het leven?

Prof. dr. Jan H. van Maarseveen

Van 't Hoff Instituut voor Moleculaire Chemie
Universiteit van Amsterdam

Woudschoten chemie conferentie 2019
Vrijdag 1 november

United Nations Educational, Scientific and Cultural Organization

International Year of the Periodic Table of Chemical Elements

A Common Language for Science

The Periodic Table of Chemical Elements is one of the most significant achievements in science, capturing the essence not only of chemistry, but also of physics, medicine, earth sciences and biology.

1869 is considered as the year of discovery of the Periodic System, and Dmitri Mendeleev was a major discoverer. 2019 will be the 150th anniversary of the Periodic Table of Chemical Elements and has therefore been proclaimed the "International Year of the Periodic Table of Chemical Elements (IYPT2019)" by the United Nations General Assembly and UNESCO.

https://www.iypt2019.org

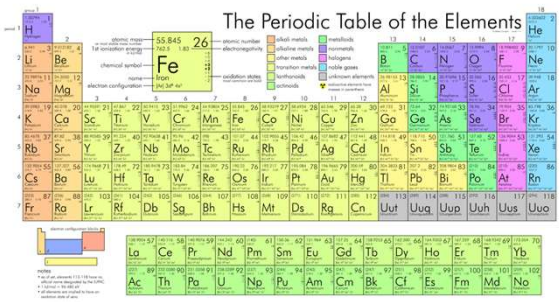
Still, it is the periodic table of the elements that has had the widest and most enduring influence. After evolving for over 200 years through the work of many people, the periodic table remains at the heart of the study of chemistry. It ranks as one of the most fruitful ideas in modern science, comparable perhaps to Charles Darwin's theory of evolution. Unlike theories such as Newtonian mechanics, it has not been falsified or revolutionized by modern physics but has adapted and matured while remaining essentially unscathed. SA

E. R. Scerry, *Scientific American,* **sep 1998**, 78

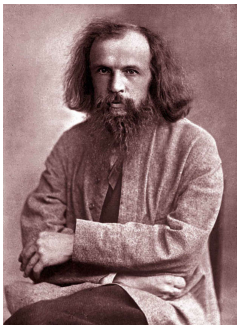
Element song

Tom Lehrer (1928 -)

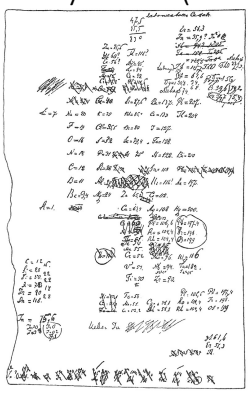
Het Periodiek Systeem



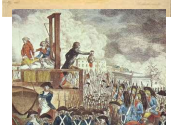
Mendelejev's Periodiek Systeem (1869)



Dmitri Mendelejev (1834-1907)



Lavoisier's lijst met 33 'elementen'

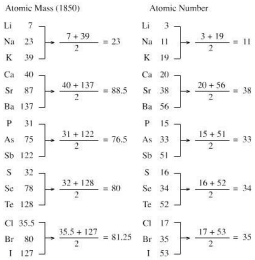


Antoine Lavoisier (1743-1794)

Noms nouveaux.	Noms anciens correspondans.
Lumière	Lumière.
Calorique	Chaleur. Principe de la chaleur. Fluide igné. Feu.
Oxygène	Matière du feu & de la chaleur. Air déphlogistiqué. Air respirable. Air vital. Base de l'air vital.
Azote	Gaz phlogistiqué. Mofette. Base de la mofette.
Hydrogène	Gaz inflammable. Base du gaz inflammable.
Soufre	Soufre.
Phosphore	Phosphore.
Carbone	Charbon pur.
Radical muriatique	Inconnu.
Radical fluorique	Inconnu.
Radical boracique	Inconnu.
Antimoine	Antimoine.
Argent	Argent.
Arsenic	Arsenic.
Bismuth	Bismuth.
Cobalt	Cobalt.
Cuivre	Cuivre.
Etain	Etain.
Fer	Fer.
Manganèse	Manganèse.
Mercure	Mercure.
Molybdène	Molybdène.
Nickel	Nickel.
Or	Or.
Platine	Platine.
Plomb	Plomb.
Tungstène	Tungstène.
Zinc	Zinc.
Chaux	Terre calcaire, chaux.
Magnésie	Magnésie, base du sel d'epsom.
Baryte	Baryte, terre pesante.
Alumine	Argile, terre de l'alun, base de l'alun.
Silice	Terre siliceuse, terre vitrifiable.

Johann Döbereiner: ontdekking familie's van elementen

Johann Döbereiner (1780-1849)



Atomic Mass (1850)

Li	7	$\frac{7+39}{2}$	= 23
Na	23		
K	39		
Ca	40	$\frac{40+137}{2}$	= 88,5
Sr	87		
Ba	137		
P	31	$\frac{31+122}{2}$	= 76,5
As	75		
Sb	122		
S	32	$\frac{32+128}{2}$	= 80
Se	78		
Te	128		
Cl	35.5	$\frac{35,5+127}{2}$	= 81.25
Br	80		
I	127		

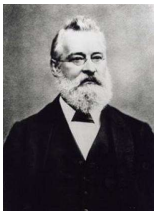
Atomic Number

Li	3	$\frac{3+19}{2}$	= 11
Na	11		
K	19		
Ca	20	$\frac{20+56}{2}$	= 38
Sr	38		
Ba	56		
P	15	$\frac{15+51}{2}$	= 33
As	33		
Sb	51		
S	16	$\frac{16+52}{2}$	= 34
Se	34		
Te	52		
Cl	17	$\frac{17+53}{2}$	= 35
Br	35		
I	53		

H								He
Li	Be	B	C	N	O	F		Ne
Na	Mg	Al	Si	P	S	Cl		Ar
K	Ca	Ga	Ge	As	Se	Br		Kr
Rb	Sr	In	Sn	Sb	Te	I		Xe
Cs	Ba	Tl	Pb	Bi	Po	At		Rn

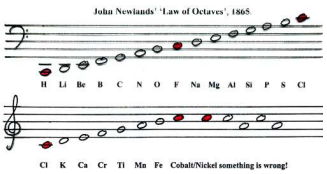
Pas lang hierna ontstaat het inzicht dat indelen op atoommassa onjuist is ...

John Newlands 'law of octaves'



John Newlands (1837-1898)

No.		No.		No.		No.		No.		No.		No.		No.
H	1	F	8	Cl	15	Co & Ni	22	Br	29	Pd	36	I	42	Pt & Ir 50
Li	2	Na	9	K	16	Cu	23	Rb	30	Ag	37	Cs	44	Os 51
G	3	Mg	10	Ca	17	Zn	24	Sr	31	Cd	38	Ba & V	45	Hg 52
Bo	4	Al	11	Cr	19	Y	25	Ce & La	33	U	40	Ta	46	Tl 53
C	5	Si	12	Ti	18	In	26	Zr	32	Sn	39	W	47	Pb 54
N	6	P	13	Mn	20	As	27	Di & Mo	34	Sb	40	Nb	48	Bi 55
O	7	S	14	Fe	21	Se	28	Ro & Ru	35	Te	43	Au	49	Th 56

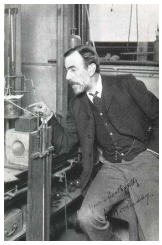


Mendelejev's Periodiek Systeem (1869)

Reihen	Gruppo I. — R^2O	Gruppo II. — RO	Gruppo III. — R^2O^3	Gruppo IV. RH^4 RO^2	Gruppo V. RH^3 R^2O^5	Gruppo VI. RH^2 RO^3	Gruppo VII. RH R^2O^7	Gruppo VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

Welke zeer belangrijke elementen missen we nog?

William Ramsay ontdekte de edelgassen



William Ramsay (1852-1916)

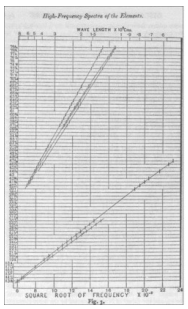
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Ca											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Ru	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac															

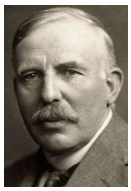
58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Nobelprijs scheikunde 1904

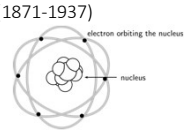
Henry Moseley en Ernest Rutherford: atoomnummer bepaalt element

Henry Moseley (1887-1915)

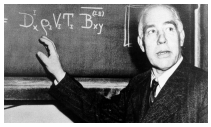




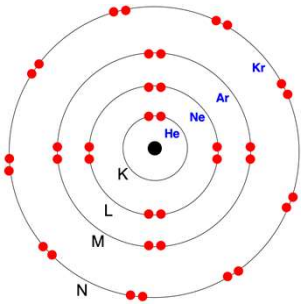
Ernest Rutherford (1871-1937)



Het huidige atoommodel is van Niels Bohr



Niels Bohr
(1885-1962)



Van empirie naar theorie: verfijning atoommodel van Rutherford

Opbouw periodiek systeem met de kwantumgetallen

Hoofdkwantumgetal: n

n=1: K-schil
n=2: L-schil
n=3: M-schil
n=4: N-schil
n=5: O-schil
n=6: P-schil
n=7: Q-schil

Nevenkwantumgetal: l (l=0, 1, 2, …, n-1)

Magnetisch kwantumgetal: -l tot +l

Het kwantummechanische periodiek systeem

Het nevenkwantumgetal l (l=0, 1, 2, …, n-1) zegt iets over de verschillende soorten ruimtes, genoemd orbitalen, waarin elektronen zich kunnen bevinden:
l=0: s-orbitaal
l=1: p-orbitalen
l=2: d-orbitalen
l=3: f-orbitalen

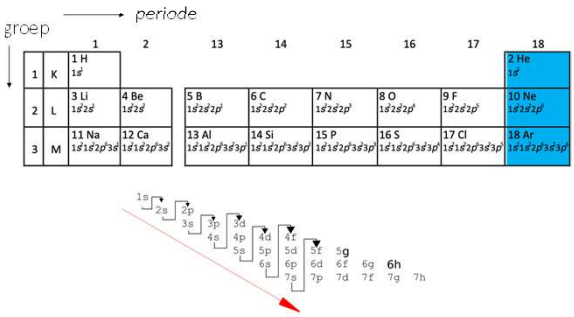
Het magnetisch kwantumgetal zegt hoeveel er van elk soort orbitalen er zijn:
l=0: 0 (dus 1 s-orbitaal)
l=1: -1, 0, 1 (dus 3 p-orbitalen)
l=2: -2, -1, 0, 1, 2 (dus 5 d-orbitalen)
l=3: -3. -2, -1, 0, 1, 2, 3 (dus 7 f-orbitalen)

Het magnetisch spinkwantumgetal zegt dat er zich maximaal twee elektronen in een orbitaal kunnen bevinden (spin ↑ of ↓)

Het kwantummechanische periodiek systeem

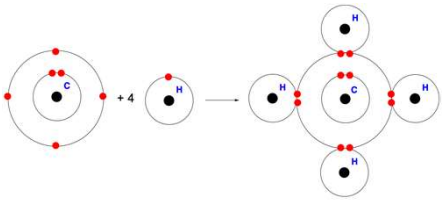
n	l (-l, .., 0, .., l)	schil	orbitalen (aantal)	aantal elektronen	Totaal in schil	Edelgas
1	0 (0)	K	1s (1)	2	2	He
2	0 (0)	L	2s (1)	2	8	
	1 (-1, 0, 1)		2p (3)	6		Ne
3	0 (0)	M	3s (1)	2	18	
	1 (-1, 0, 1)		3p (3)	6		Ar
	2 (-2, -1, 0, 1, 2)		3d (5)	10		
4	0 (0)	N	4s (1)	2	32	Kr
	1 (-1, 0, 1)		4p (3)	6		
	2 (-2, -1, 0, 1, 2)		4d (5)	10		
	3 (-3, -2, -1, 0, 1, 2, 3)		4f (7)	14		

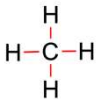
Het kwantummechanische periodiek systeem met elektronenconfiguraties



Heeft deze eindelijk eeuwigheidswaarde?

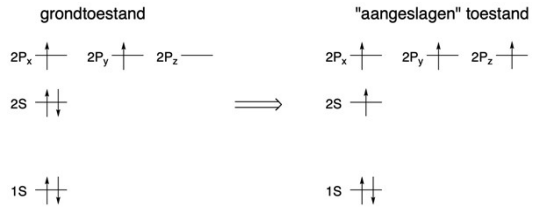
Moleculen met koolstof





Verklaring ruimtelijke vorm vanuit orbitaalbegrip

Elektronen zitten in orbitalen



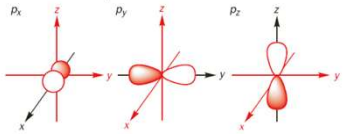
Echter, CH_4 heeft 4 bindingen!

Klopt dit ruimtelijk?

Wat is de vorm van s- en p-orbitalen?

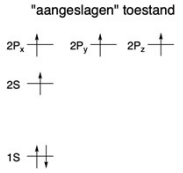
s-orbitaal:

p-orbitaal:



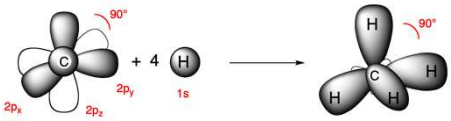
the three degenerate p orbitals are aligned along perpendicular axes

CH_4:



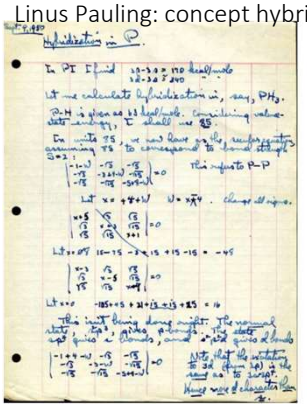
- 3 H's met 2p
- 1H met 2S

Dus ziet methaan er ruimtelijk zo uit:



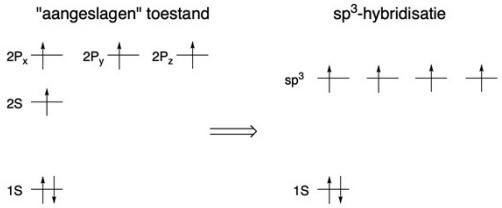
Strookt dit met de werkelijkheid?

Linus Pauling: concept hybridisatie (9-9-1950)



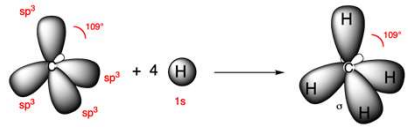
Linus Pauling
(1901-1994)

Hybridisatie

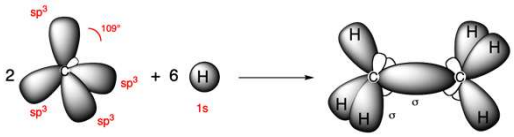


- "Mengen" van de drie 2p-orbitalen en het 2s-orbtiaal levert vier identieke sp^3-orbitalen
- Tetraëdrische omringing
- Bindingshoeken 109°
- 3-Dimensionaal molecuul
- Elektronegativiteit = 2,3
  (= elektropositief = stuwend)

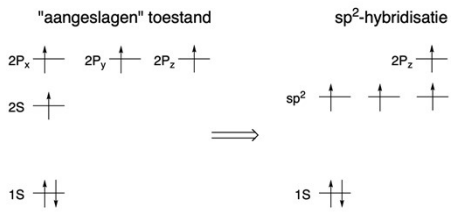
sp^3 orbitalen weergave van methaan



ethaan

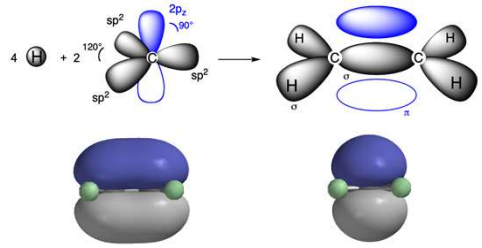


sp^2 hybridisatie

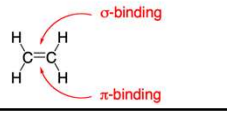


- Drie identieke sp^2-orbitalen
- Trigonale omringing
- Bindingshoeken 120˚
- Vlak molecuul (2-dimensionaal)
- Elektronegativiteit = 3,0
  (= elektronegatief = zuigend)

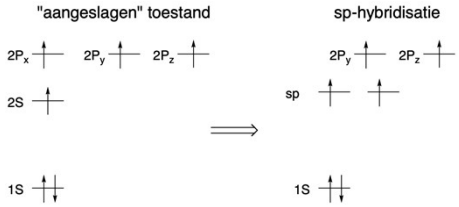
Etheen



GEEN vrije draaibaarheid dubbele (π) C=C binding (star dus)

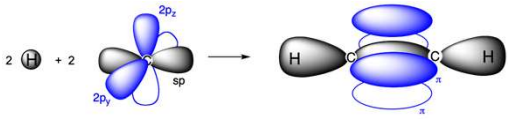


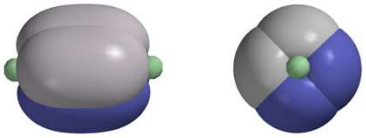
sp hybridisatie



- Twee identieke sp-orbitalen
- Digonale omringing
- Bindingshoeken 180˚
- Lineair molecuul (1-dimensionaal)
- Elektronegativiteit = 3,3
  (= elektronegatief = zuigend)

Ethyn (acetyleen)

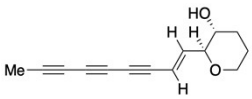




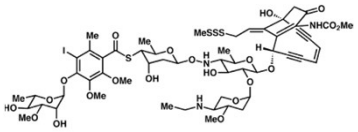
Twee dubbele (π) bindingen en een enkele (σ) (geheel lineair)

Natuurstoffen met sp^3-, sp^2- en sp-gehybridiseerd koolstof

Voorbeeld 1: Ichthyothereol (pijlgif)

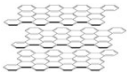


Voorbeeld 2: Calicheamycine (cytostaticum)



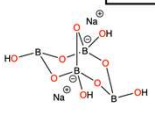
Calicheamicin γ_1

De buren van koolstof

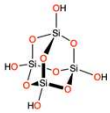


0.001%	0.03%	spoor
B	**C**	**N**
0%	19%	3.3%

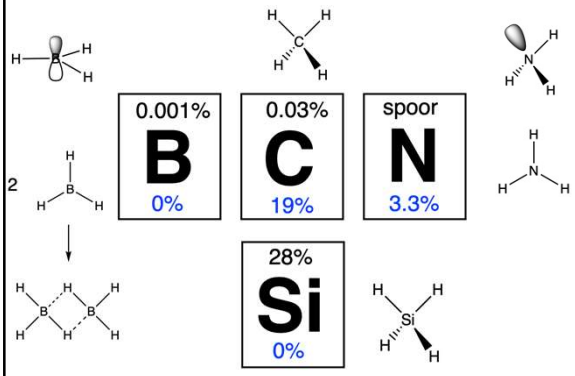
N≡N



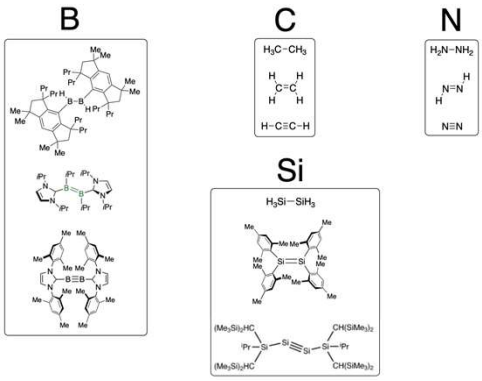
28%
Si
0%



De simpelste moleculen

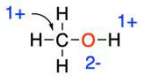


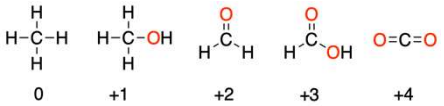
sp³-, sp²- en sp-gehybridiseerd B, C, N en Si



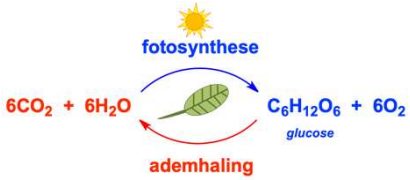
De unieke stabiele oxidatietoestanden van C

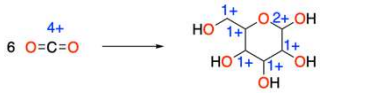
Elektronegativiteiten:
C = 2.5
H = 2.2
N = 3.0
O = 3.4





CO_2 en glucose zijn dé moleculen van het leven!





$H_2O = 2H^+ + O^{2-} \Longrightarrow 2\,O^{2-} \longrightarrow O_2 + 4$ elektronen

Fotosynthese =

CO_2 reductie

+

H_2O oxidatie

Conclusies

- Mendelejev's periodiek systeem is al 150 jaar het hart van de scheikunde en zal dat ALTIJD blijven.
- Koolstof lijkt in bijna niets op haar buren!!!
- Met koolstof zijn stabiele enkele, dubbele en drievoudige bindingen naar zichzelf en andere elementen mogelijk.
- Koolstof kent vele oxidatietoestanden met daartussen betrekkelijk geringe potentialen.
- Fotosynthese is de reactievergelijking van het leven.
- Fotosynthese bewerkstelligt de reductie van CO_2 door de oxidatie van H_2O.