Version 3: Online from January 8, 2013

Version 4: Online from January 29, 2013

Version 5: Online from July 12, 2013

Version 8 from September 29, 2017

eISBN 978-973-86211-1-4

http://ph.academicdirect.org

General Chemistry

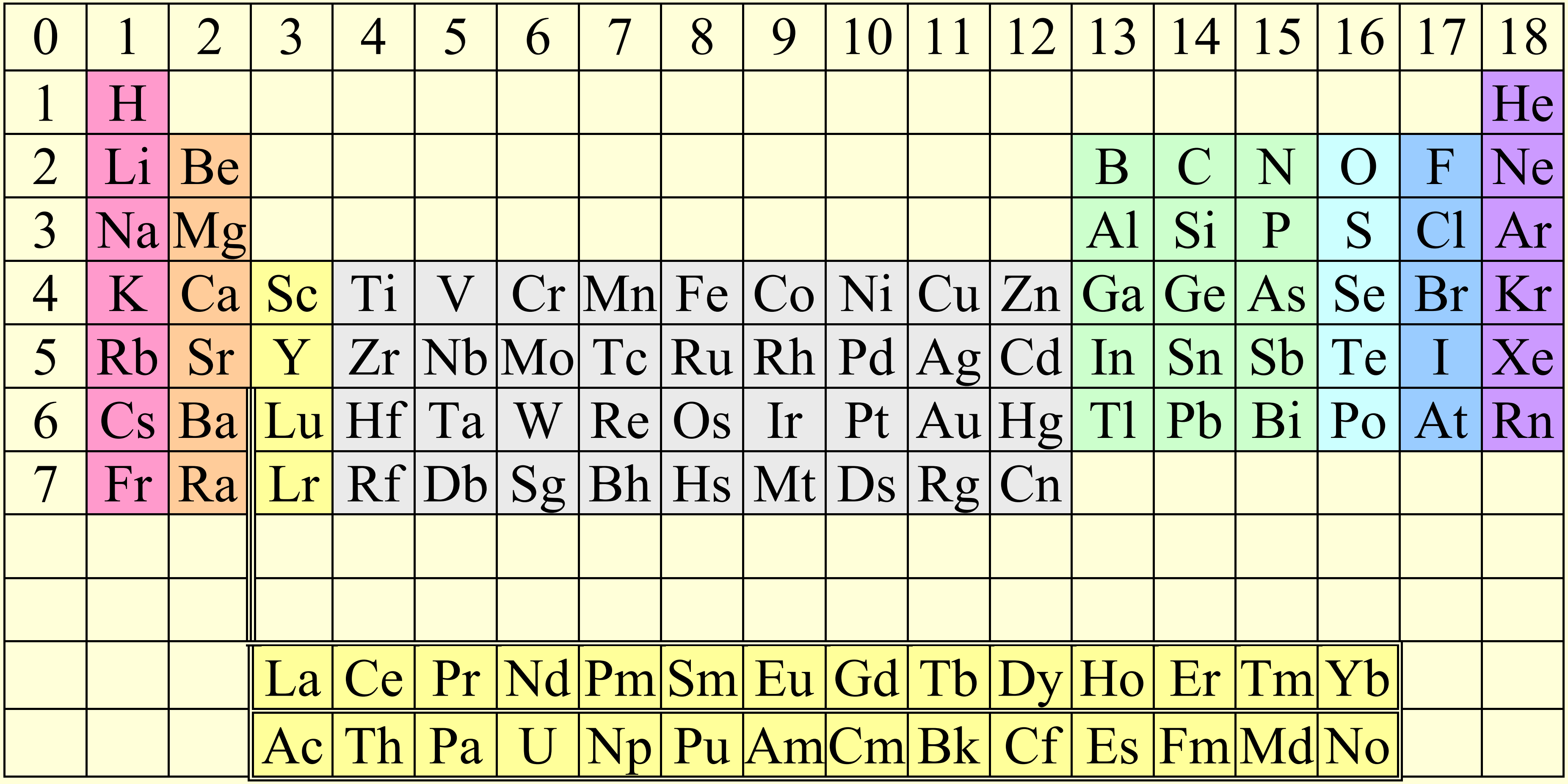
Lorentz JÄNTSCHI

Course 1

Periodic system
Periodical properties
Electronic structure

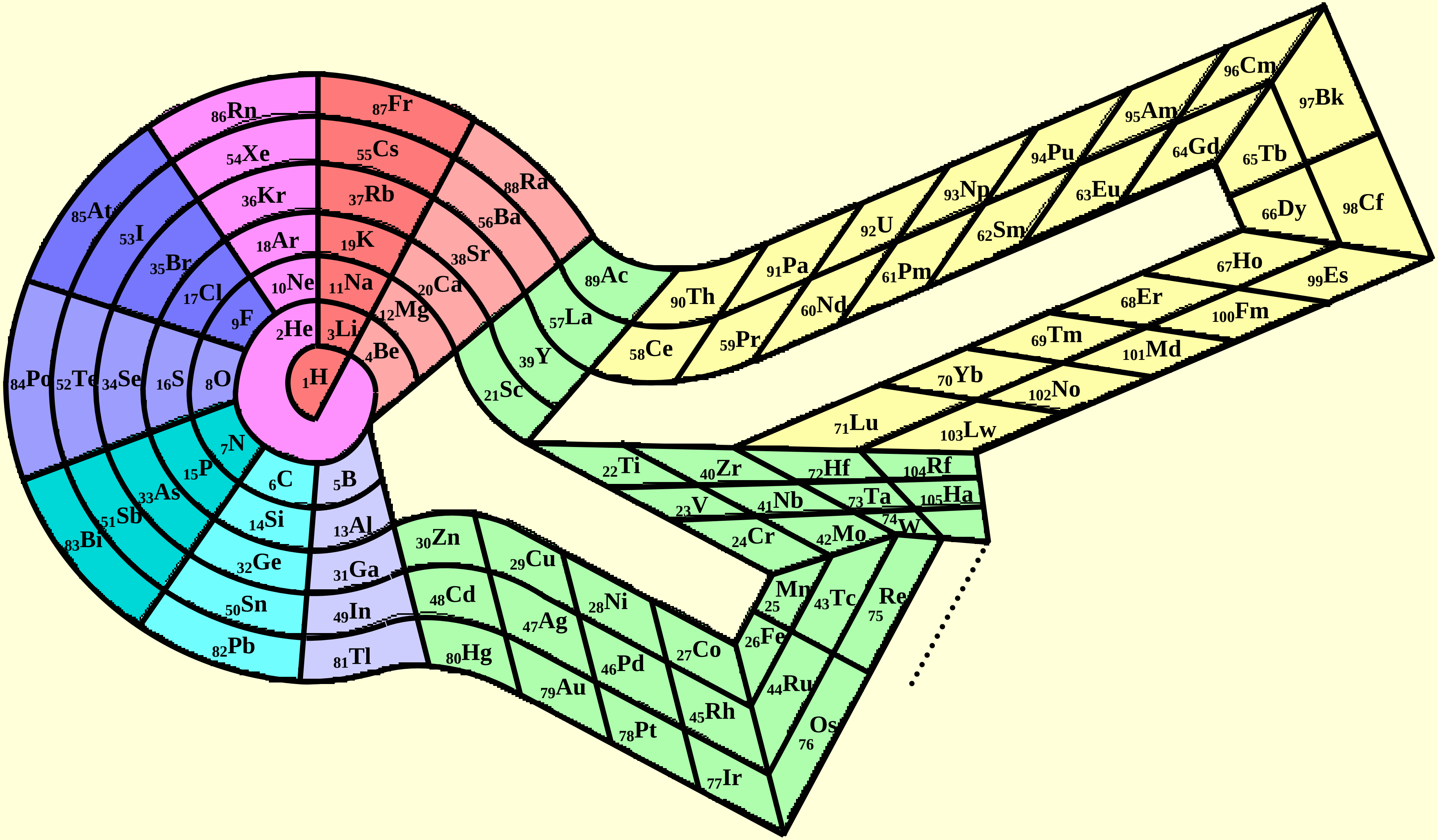
http://vl.academicdirect.org/general_chemistry/periodic_system

Periodic system



0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn						
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

- At the basis of the classification of the elements stays the ***atomic number***, *Z* – representing the total number of electrons in the atom and in same time the number of protons in the nucleus
- Elements in the periodic system are placed on vertical columns – the ***groups***, and in horizontal rows – *the **periods.*** The succession in the periods is with respect to the ***main levels of energy*** and to the electrons layers. The ***period number*** is equal to the ***main quantum number*** (of the layer being filled). The ***number of the group*** represents the ***number of the electrons of this layer being filled****,* and plays the main role in the expression of the chemical properties. Thus, it exists a similarity of the properties inside groups.
- Chemical properties are determined by the atom's tendency to reach as much as possible at stable electron configurations and to use as many as possible the orbital valences.


1 H
2 He
3 Li
4 Be
5 B
6 C
7 N
8 O
9 F
10 Ne
11 Na
12 Mg
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 Rb
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
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
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
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 Lw
104 Rf
105 Ha

- The **periodic "law"** of chemistry recognizes that properties of the chemical elements are periodic functions of their atomic number (that is, the number of protons within the element's atomic nucleus). The **periodic table** is an arrangement of the chemical elements ordered by atomic number in columns (**groups**) and rows (**periods**) presented so as to emphasize their periodic properties.
- There are many different ways, sometimes ingenious, of arranging the chemical elements according to which properties are of particular interest but that shown here is a standard form of the periodic table. The relative merits of various other periodic table organizations is still the subject of debate.

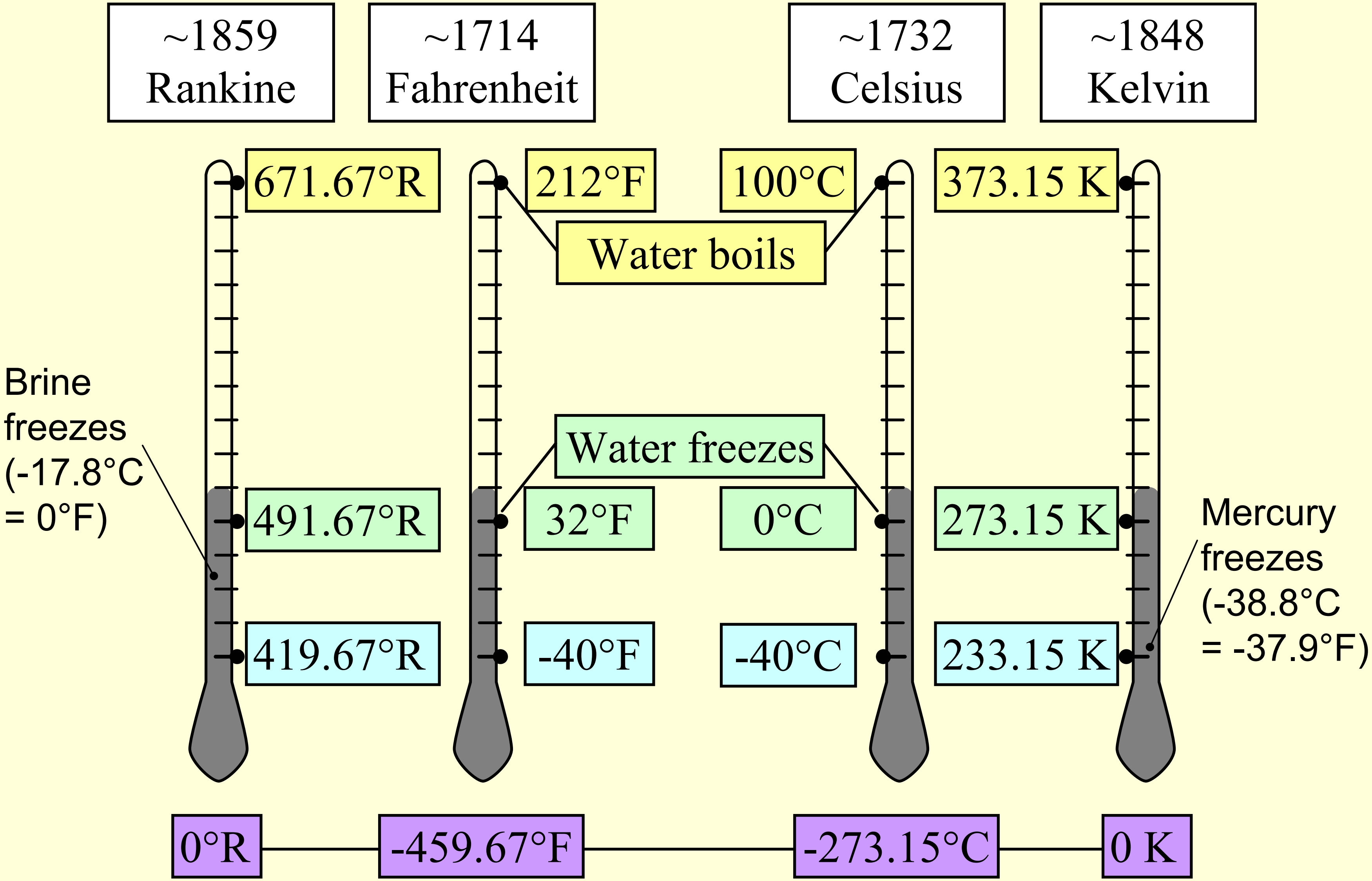
Atomic measures

- Anion: atom or group of atoms containing more electrons than protons – consequence – any negative charged system is referred as anion; Cation: idem opposite
- Atomic radius: measure of the relative dimension of the atoms (see O_2 and H_2O)
- Electron affinity: measure of the ability or tendency of a atom to get electrons – energetic concept – formal definition refers just one electron: $X + 1e^- \rightarrow X^{-1} + E.A.$
- Electronegativity: ability of a bound atom to attract electrons; at the bond level, the electron may be shared or transferred; there are many electronegativity scales.
- Ionization potential: from energetic process leading to the cation: $X + I.P. \rightarrow X^+ + 1e^-$; it exists also superior (or supplementary) ionization potentials (ex. $X^+ + I.P.2 \rightarrow X^{2+} + 1e^-$)

Periodical tendencies

- Refers the change of the atoms properties when moving to another group or period
- In period from left to right: I.P., E.A., electronegativity increases; Dimension (radius) decreases;
- In group from top to bottom: I.P., E.A., electronegativity decreases; Dimension (radius) increases;
- Stability factors – refers the electrons taken or given during the process of bond formation with the purpose of stability increase:
  - Tendency to reach a configuration of a noble gas;
  - Tendency to loose all valence electrons (sometimes only “p” sublevel electrons);
  - Tendency to keep: occupied, half occupied and unoccupied the sets of the orbital

Temperature scale



~1859
Rankine

~1714
Fahrenheit

~1732
Celsius

~1848
Kelvin

671.67°R

212°F

100°C

373.15 K

Water boils

Water freezes

491.67°R

32°F

0°C

273.15 K

419.67°R

-40°F

-40°C

233.15 K

Brine
freezes
(-17.8°C
= 0°F)

Mercury
freezes
(-38.8°C
= -37.9°F)

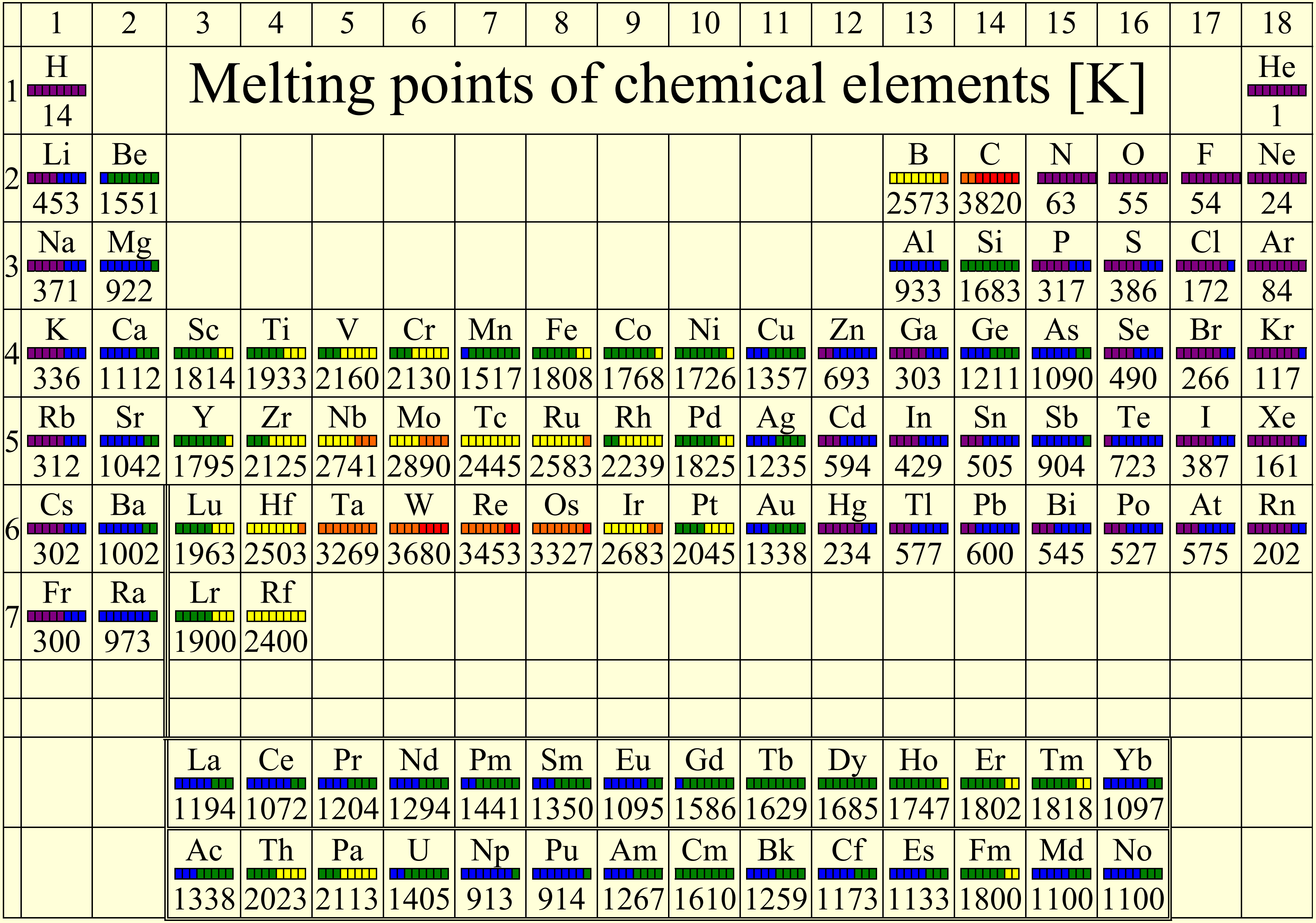
0°R

-459.67°F

-273.15°C

0 K

Melting points of chemical elements [K]

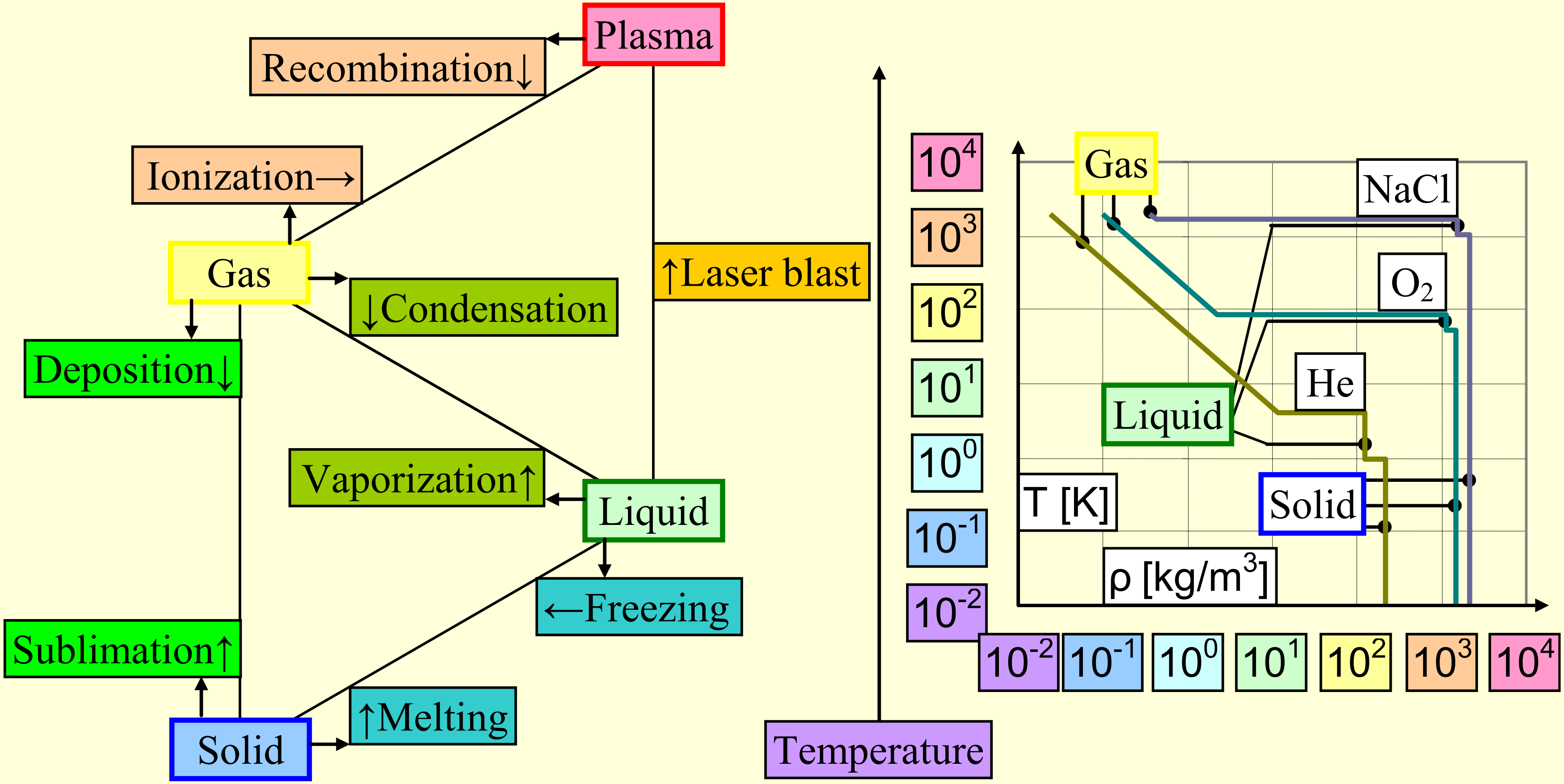


	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 14																	He 1
2	Li 453	Be 1551											B 2573	C 3820	N 63	O 55	F 54	Ne 24
3	Na 371	Mg 922											Al 933	Si 1683	P 317	S 386	Cl 172	Ar 84
4	K 336	Ca 1112	Sc 1814	Ti 1933	V 2160	Cr 2130	Mn 1517	Fe 1808	Co 1768	Ni 1726	Cu 1357	Zn 693	Ga 303	Ge 1211	As 1090	Se 490	Br 266	Kr 117
5	Rb 312	Sr 1042	Y 1795	Zr 2125	Nb 2741	Mo 2890	Tc 2445	Ru 2583	Rh 2239	Pd 1825	Ag 1235	Cd 594	In 429	Sn 505	Sb 904	Te 723	I 387	Xe 161
6	Cs 302	Ba 1002	Lu 1963	Hf 2503	Ta 3269	W 3680	Re 3453	Os 3327	Ir 2683	Pt 2045	Au 1338	Hg 234	Tl 577	Pb 600	Bi 545	Po 527	At 575	Rn 202
7	Fr 300	Ra 973	Lr 1900	Rf 2400														
			La 1194	Ce 1072	Pr 1204	Nd 1294	Pm 1441	Sm 1350	Eu 1095	Gd 1586	Tb 1629	Dy 1685	Ho 1747	Er 1802	Tm 1818	Yb 1097		
			Ac 1338	Th 2023	Pa 2113	U 1405	Np 913	Pu 914	Am 1267	Cm 1610	Bk 1259	Cf 1173	Es 1133	Fm 1800	Md 1100	No 1100		

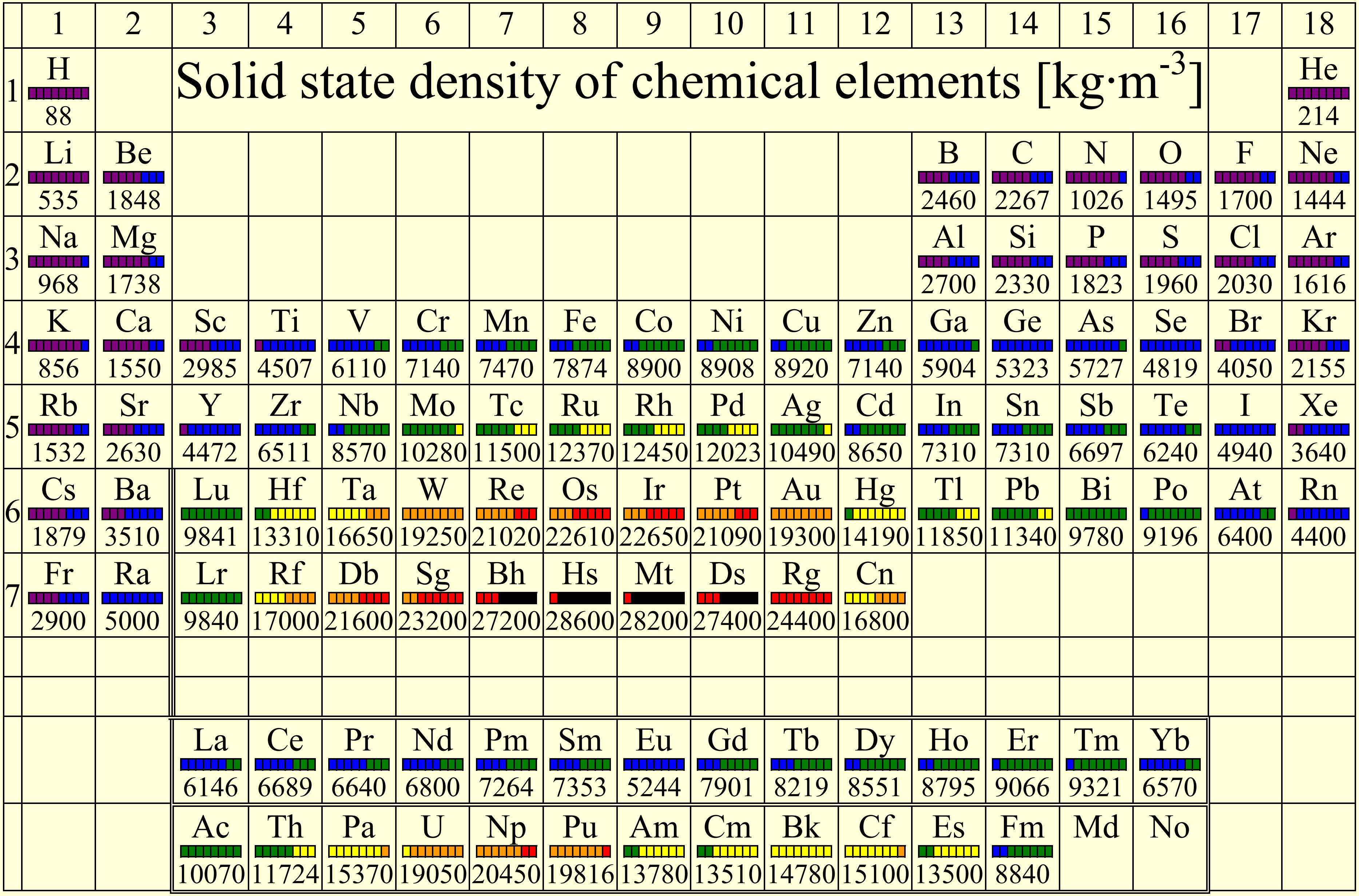
Questions & Responses

By the melting point, the chemical elements can be ordered as follows:		
	0	Cr < Fe < Al < Mg
	0	Rn < Xe < Kr < Ar < Ne < He
	0	W < Re < Os < Ta
	0	C < N < O < F < Ne
	0	C < B < Be < LI < He < H
	1	Mg < Al < Fe < Cr
	1	He < Ne < Ar < Kr < Xe < Rn
	1	Ta < Os < Re < W
	1	Ne < F < O < N < C
	1	H < He < Li < Be < B < C

Solid state and density



Solid state density of chemical elements [kg·m^{-3}]

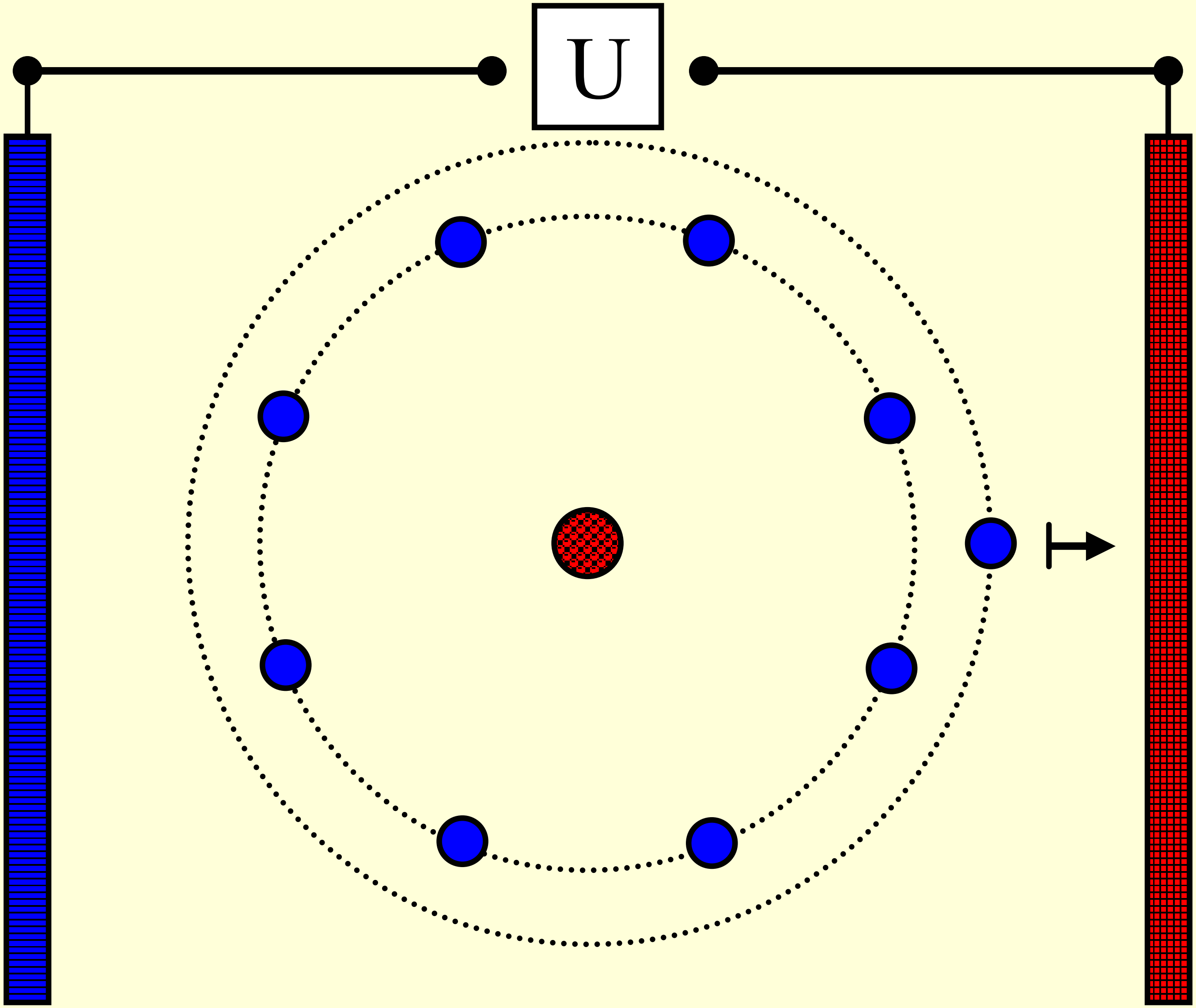


	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 88																	He 214
2	Li 535	Be 1848											B 2460	C 2267	N 1026	O 1495	F 1700	Ne 1444
3	Na 968	Mg 1738											Al 2700	Si 2330	P 1823	S 1960	Cl 2030	Ar 1616
4	K 856	Ca 1550	Sc 2985	Ti 4507	V 6110	Cr 7140	Mn 7470	Fe 7874	Co 8900	Ni 8908	Cu 8920	Zn 7140	Ga 5904	Ge 5323	As 5727	Se 4819	Br 4050	Kr 2155
5	Rb 1532	Sr 2630	Y 4472	Zr 6511	Nb 8570	Mo 10280	Tc 11500	Ru 12370	Rh 12450	Pd 12023	Ag 10490	Cd 8650	In 7310	Sn 7310	Sb 6697	Te 6240	I 4940	Xe 3640
6	Cs 1879	Ba 3510	Lu 9841	Hf 13310	Ta 16650	W 19250	Re 21020	Os 22610	Ir 22650	Pt 21090	Au 19300	Hg 14190	Tl 11850	Pb 11340	Bi 9780	Po 9196	At 6400	Rn 4400
7	Fr 2900	Ra 5000	Lr 9840	Rf 17000	Db 21600	Sg 23200	Bh 27200	Hs 28600	Mt 28200	Ds 27400	Rg 24400	Cn 16800						
			La 6146	Ce 6689	Pr 6640	Nd 6800	Pm 7264	Sm 7353	Eu 5244	Gd 7901	Tb 8219	Dy 8551	Ho 8795	Er 9066	Tm 9321	Yb 6570		
			Ac 10070	Th 11724	Pa 15370	U 19050	Np 20450	Pu 19816	Am 13780	Cm 13510	Bk 14780	Cf 15100	Es 13500	Fm 8840	Md	No		

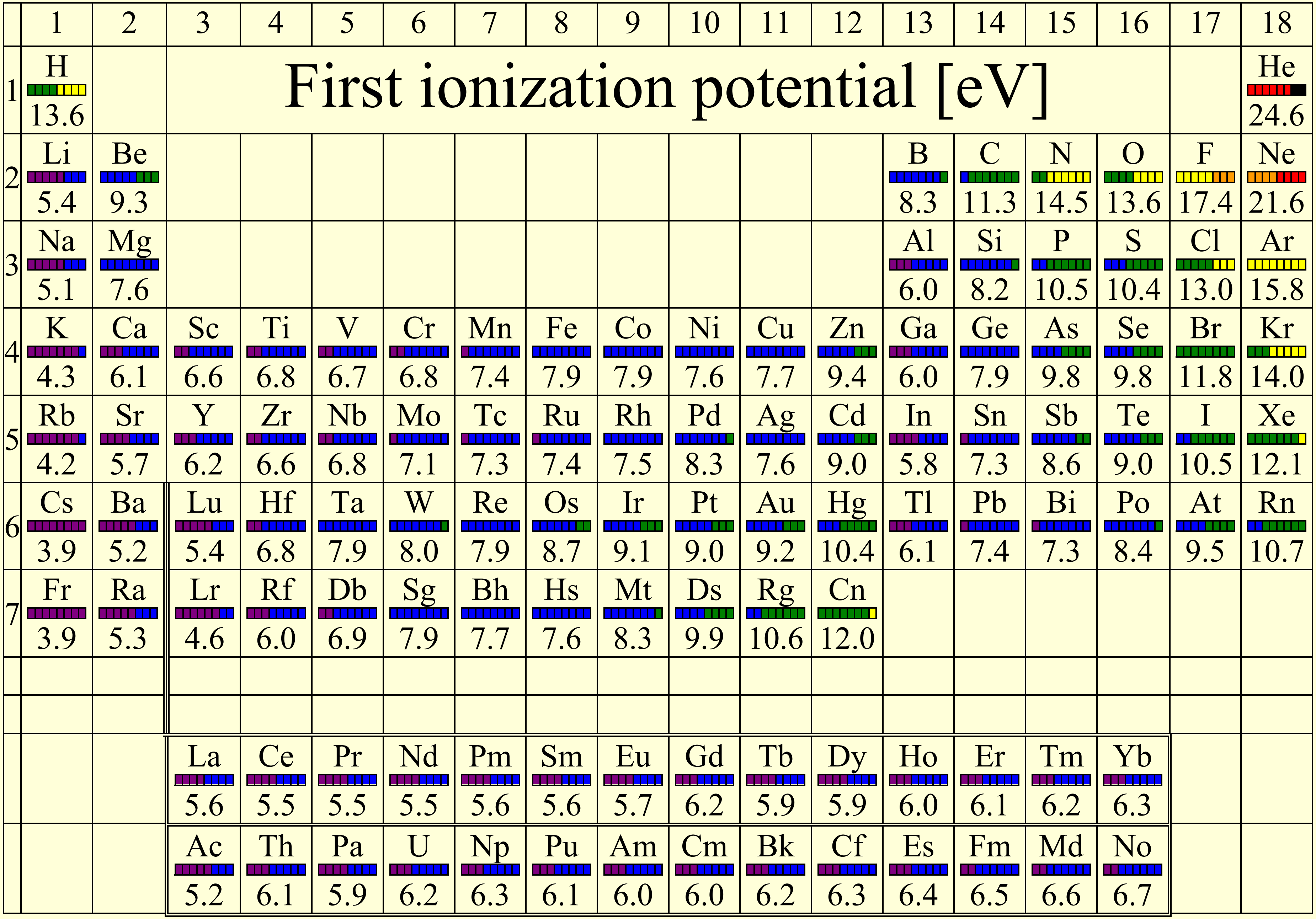
Questions & Responses

By the solid state density, the chemical elements can be ordered as follows:		
	0	Cu < Fe < Al < Mg
	0	Rn < Xe < Kr < Ar < Ne < He
	0	Ir < Os < Pt < Re < Au < W
	0	F < O < N
	0	B < C < N
	0	B < Be < Li < He < H
	1	Mg < Al < Fe < Cu
	1	He < Ne < Ar < Kr < Xe < Rn
	1	W < Au < Re < Pt < Os < Ir
	1	N < O < F
	1	N < C < B
	1	H < He < Li < Be < B

Ionization potential



First ionization potential [eV]

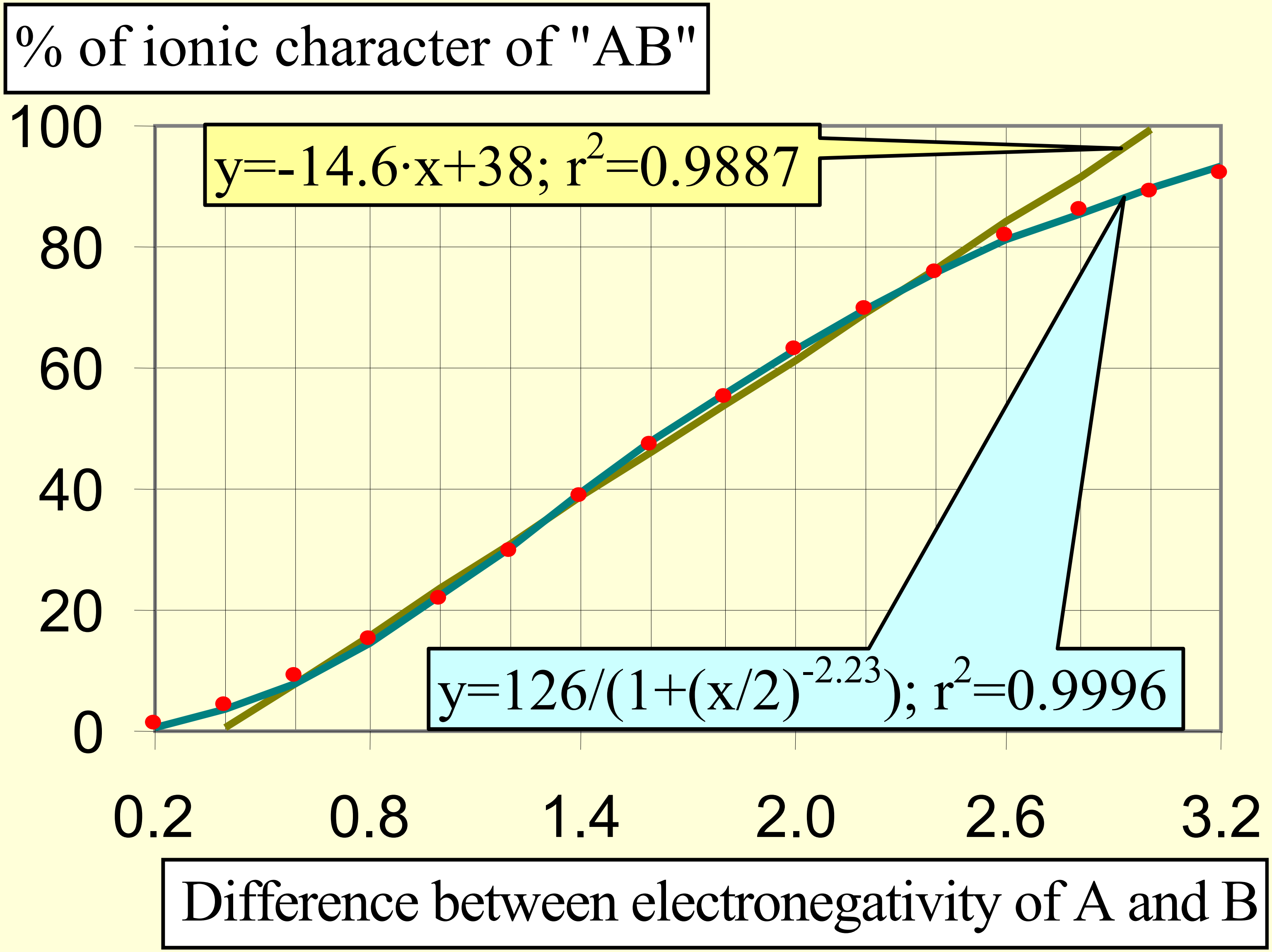


	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 13.6																	He 24.6
2	Li 5.4	Be 9.3											B 8.3	C 11.3	N 14.5	O 13.6	F 17.4	Ne 21.6
3	Na 5.1	Mg 7.6											Al 6.0	Si 8.2	P 10.5	S 10.4	Cl 13.0	Ar 15.8
4	K 4.3	Ca 6.1	Sc 6.6	Ti 6.8	V 6.7	Cr 6.8	Mn 7.4	Fe 7.9	Co 7.9	Ni 7.6	Cu 7.7	Zn 9.4	Ga 6.0	Ge 7.9	As 9.8	Se 9.8	Br 11.8	Kr 14.0
5	Rb 4.2	Sr 5.7	Y 6.2	Zr 6.6	Nb 6.8	Mo 7.1	Tc 7.3	Ru 7.4	Rh 7.5	Pd 8.3	Ag 7.6	Cd 9.0	In 5.8	Sn 7.3	Sb 8.6	Te 9.0	I 10.5	Xe 12.1
6	Cs 3.9	Ba 5.2	Lu 5.4	Hf 6.8	Ta 7.9	W 8.0	Re 7.9	Os 8.7	Ir 9.1	Pt 9.0	Au 9.2	Hg 10.4	Tl 6.1	Pb 7.4	Bi 7.3	Po 8.4	At 9.5	Rn 10.7
7	Fr 3.9	Ra 5.3	Lr 4.6	Rf 6.0	Db 6.9	Sg 7.9	Bh 7.7	Hs 7.6	Mt 8.3	Ds 9.9	Rg 10.6	Cn 12.0						
			La 5.6	Ce 5.5	Pr 5.5	Nd 5.5	Pm 5.6	Sm 5.6	Eu 5.7	Gd 6.2	Tb 5.9	Dy 5.9	Ho 6.0	Er 6.1	Tm 6.2	Yb 6.3		
			Ac 5.2	Th 6.1	Pa 5.9	U 6.2	Np 6.3	Pu 6.1	Am 6.0	Cm 6.0	Bk 6.2	Cf 6.3	Es 6.4	Fm 6.5	Md 6.6	No 6.7		

Questions & Responses

<table>
<tr><td colspan="3">By the first ionization potential, the chemical elements can be ordered as follows:</td></tr>
<tr><td></td><td>0</td><td>N < O</td></tr>
<tr><td></td><td>0</td><td>He < Ne < Ar < Kr < Xe < Rn</td></tr>
<tr><td></td><td>0</td><td>H < Li < Na < K</td></tr>
<tr><td></td><td>0</td><td>F < Cl < Br < I</td></tr>
<tr><td></td><td>0</td><td>He < H</td></tr>
<tr><td></td><td>1</td><td>O < N</td></tr>
<tr><td></td><td>1</td><td>Rn < Xe < Kr < Ar < Ne < He</td></tr>
<tr><td></td><td>1</td><td>K < Na < Li < H</td></tr>
<tr><td></td><td>1</td><td>I < Br < Cl < F</td></tr>
<tr><td></td><td>1</td><td>H < He</td></tr>
</table>

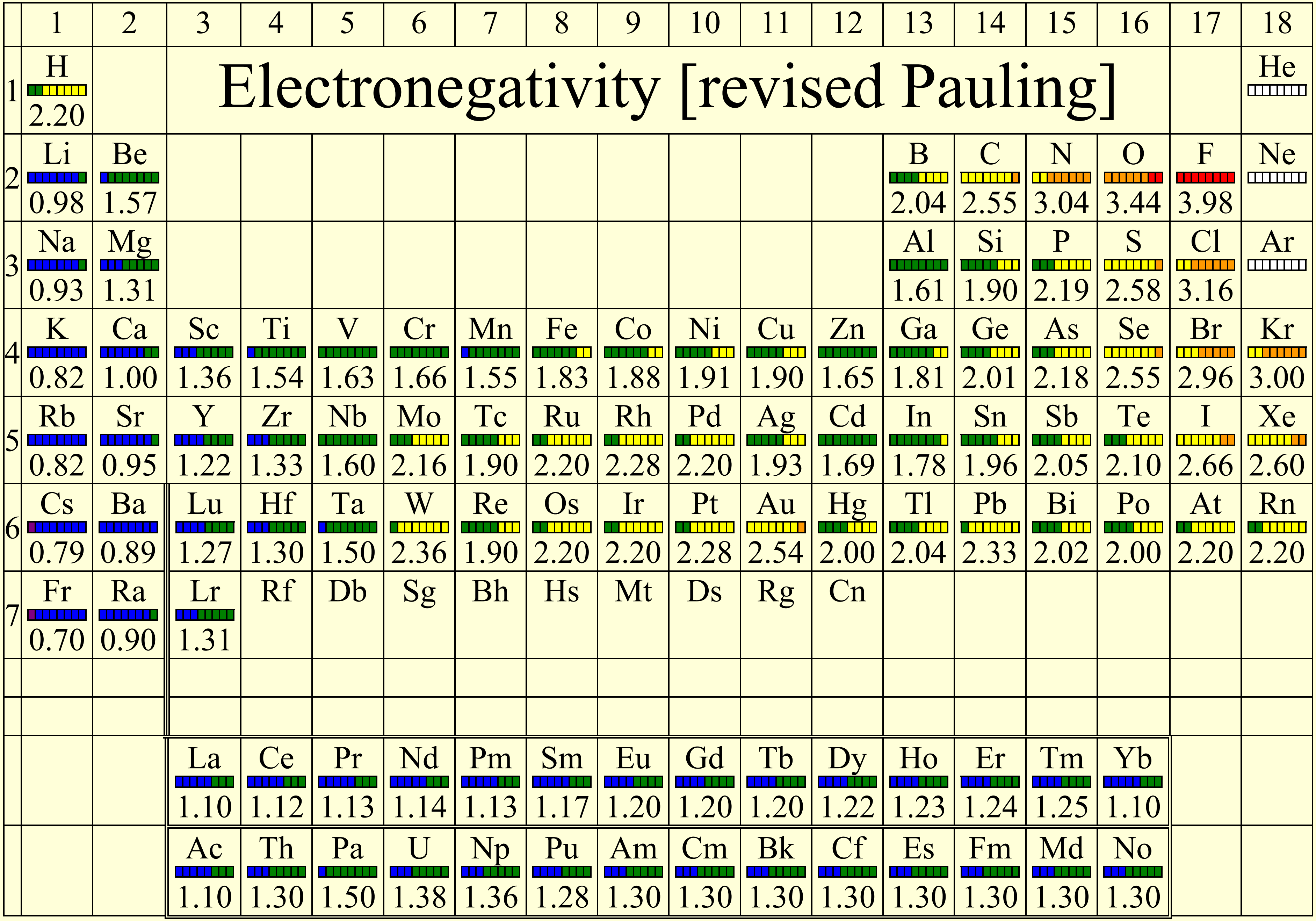
Electronegativity



$y=-14.6\cdot x+38;\ r^2=0.9887$

$y=126/(1+(x/2)^{-2.23});\ r^2=0.9996$

Electronegativity [revised Pauling]



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.60	Mo 2.16	Tc 1.90	Ru 2.20	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.10	I 2.66	Xe 2.60
6	Cs 0.79	Ba 0.89	Lu 1.27	Hf 1.30	Ta 1.50	W 2.36	Re 1.90	Os 2.20	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 2.04	Pb 2.33	Bi 2.02	Po 2.00	At 2.20	Rn 2.20
7	Fr 0.70	Ra 0.90	Lr 1.31	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn						
			La 1.10	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.20	Gd 1.20	Tb 1.20	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.10		
			Ac 1.10	Th 1.30	Pa 1.50	U 1.38	Np 1.36	Pu 1.28	Am 1.30	Cm 1.30	Bk 1.30	Cf 1.30	Es 1.30	Fm 1.30	Md 1.30	No 1.30		

Questions & Responses

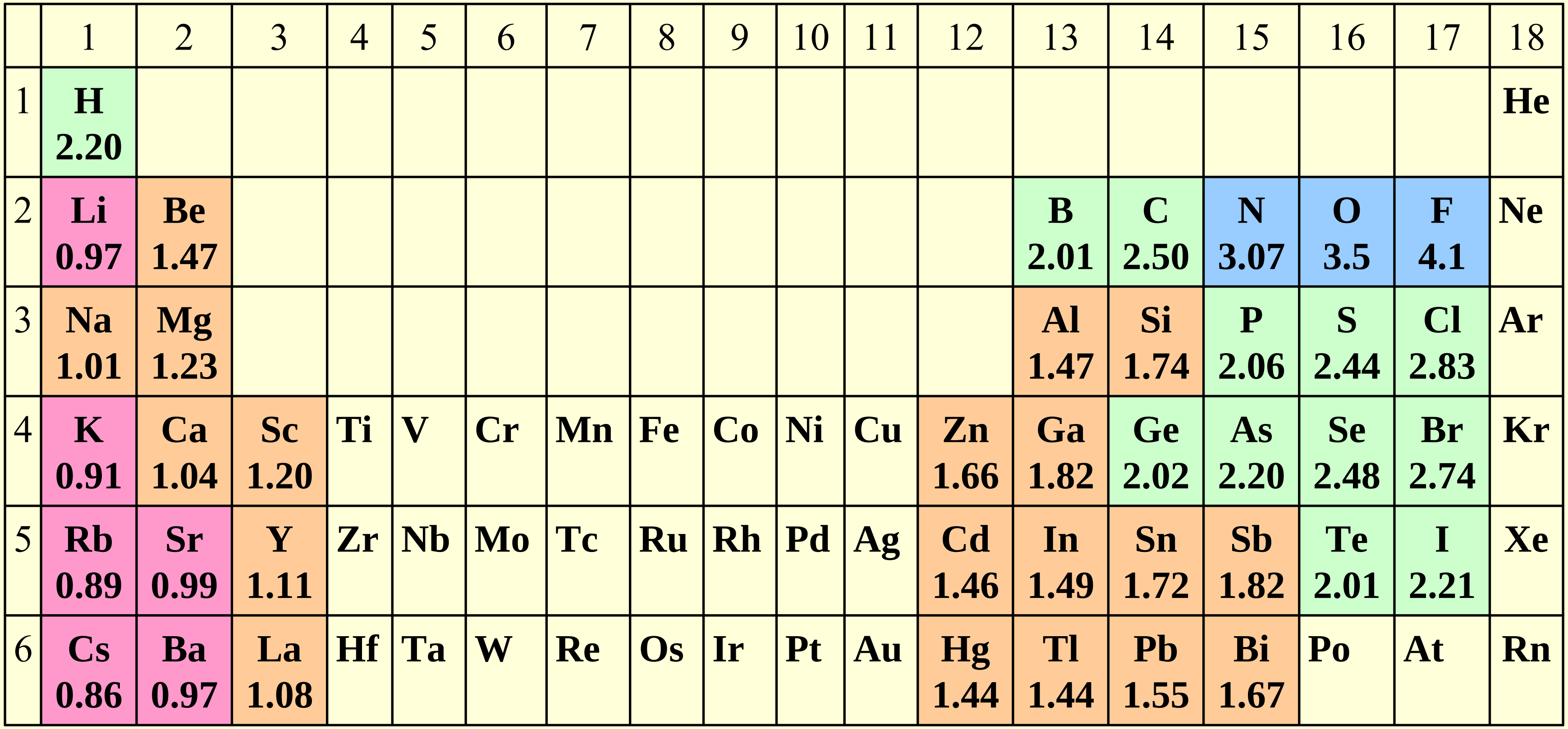
By the electronegativity, the chemical elements can be ordered as follows:		
	0	Ni < Co < Fe < Mn
	0	O < Cl < N < S < C < P < H
	0	H < Li < Na < K < Rb < Cs < Fr
	0	F < Cl < Br < I < At
	0	F < O < N < C < B < Be < Li
	1	Mn < Fe < Co < Ni
	1	H < P < C < S < N < Cl < O
	1	Fr < Cs < Rb < K < Na < Li < H
	1	At < I < Br < Cl < F
	1	Li < Be < B < C < N < O < F

Pauling Electronegativity Scale

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	**H** **2.1**																	**He**
2	**Li** **1.0**	**Be** **1.5**											**B** **2.0**	**C** **2.5**	**N** **3.0**	**O** **3.5**	**F** **4.0**	**Ne**
3	**Na** **0.9**	**Mg** **1.2**											**Al** **1.5**	**Si** **1.8**	**P** **2.1**	**S** **2.5**	**Cl** **3.0**	**Ar**
4	**K** **0.8**	**Ca** **1.0**	**Sc** **1.3**	**Ti** **1.5**	**V** **1.6**	**Cr** **1.6**	**Mn** **1.5**	**Fe** **1.8**	**Co** **1.8**	**Ni** **1.8**	**Cu** **1.9**	**Zn** **1.6**	**Ga** **1.6**	**Ge** **1.8**	**As** **2.0**	**Se** **2.4**	**Br** **2.8**	**Kr**
5	**Rb** **0.8**	**Sr** **1.0**	**Y** **1.2**	**Zr** **1.4**	**Nb** **1.6**	**Mo** **1.8**	**Tc** **1.9**	**Ru** **2.2**	**Rh** **2.2**	**Pd** **2.2**	**Ag** **1.9**	**Cd** **1.7**	**In** **1.7**	**Sn** **1.8**	**Sb** **1.9**	**Te** **2.1**	**I** **2.5**	**Xe**
6	**Cs** **0.7**	**Ba** **0.9**	**La** **1.1**	**Hf** **1.3**	**Ta** **1.5**	**W** **1.7**	**Re** **1.9**	**Os** **2.2**	**Ir** **2.2**	**Pt** **2.2**	**Au** **2.4**	**Hg** **1.9**	**Tl** **1.8**	**Pb** **1.8**	**Bi** **1.9**	**Po** **2.0**	**At** **2.2**	**Rn**

Linus PAULING. 1932. The Nature of the Chemical Bond. IV. The Energy of Single Bonds and the Relative Electronegativity of Atoms. Journal of the American Chemical Society 54(9):3570-3582. doi: 10.1021/ja01348a011

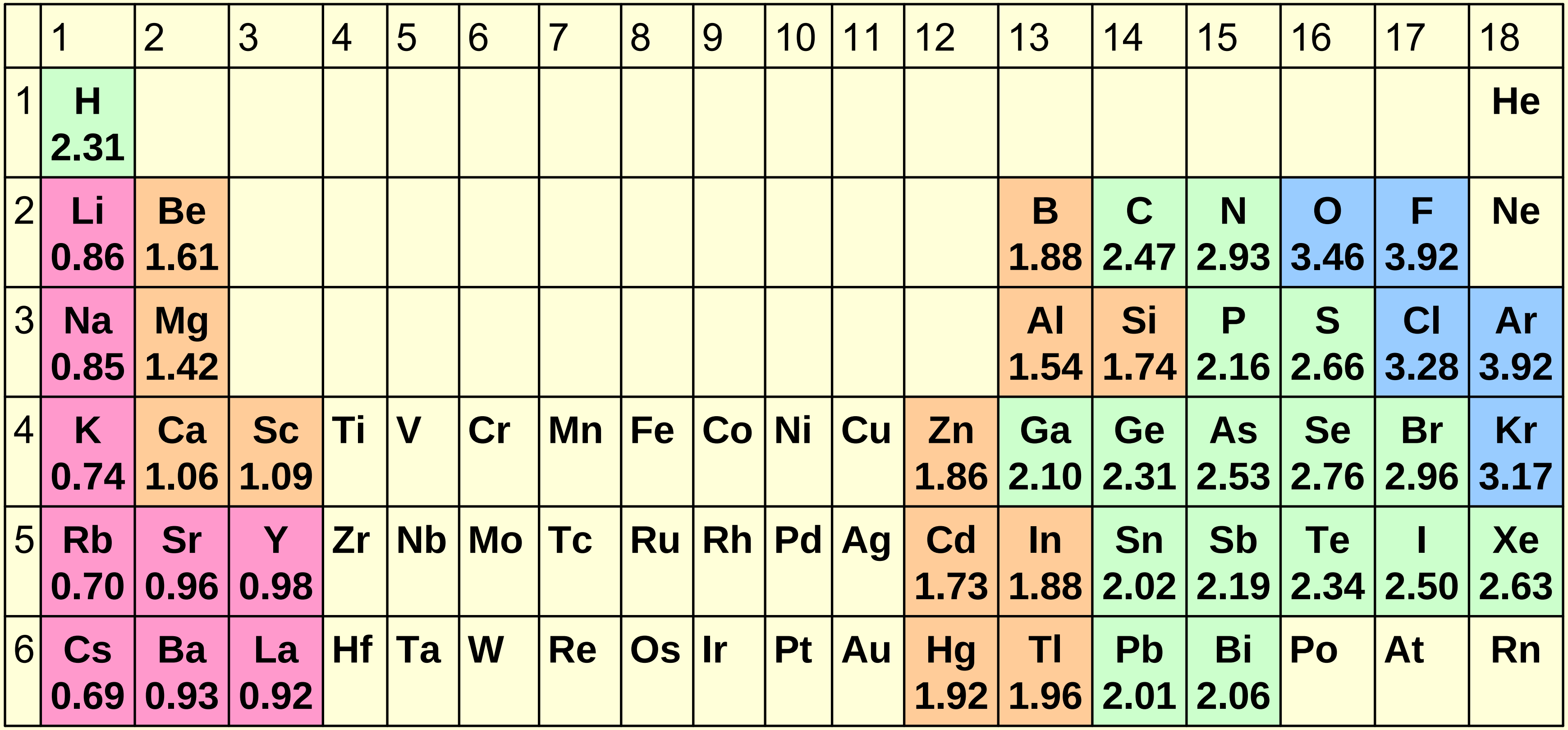
Allred Rochow Electronegativity Scale



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	**H** **2.20**																	**He**
2	**Li** **0.97**	**Be** **1.47**											**B** **2.01**	**C** **2.50**	**N** **3.07**	**O** **3.5**	**F** **4.1**	**Ne**
3	**Na** **1.01**	**Mg** **1.23**											**Al** **1.47**	**Si** **1.74**	**P** **2.06**	**S** **2.44**	**Cl** **2.83**	**Ar**
4	**K** **0.91**	**Ca** **1.04**	**Sc** **1.20**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn** **1.66**	**Ga** **1.82**	**Ge** **2.02**	**As** **2.20**	**Se** **2.48**	**Br** **2.74**	**Kr**
5	**Rb** **0.89**	**Sr** **0.99**	**Y** **1.11**	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd** **1.46**	**In** **1.49**	**Sn** **1.72**	**Sb** **1.82**	**Te** **2.01**	**I** **2.21**	**Xe**
6	**Cs** **0.86**	**Ba** **0.97**	**La** **1.08**	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg** **1.44**	**Tl** **1.44**	**Pb** **1.55**	**Bi** **1.67**	**Po**	**At**	**Rn**

Louis A. ALLRED, Eugene G. ROCHOW, 1958. A scale of electronegativity based on electrostatic force. Journal of Inorganic and Nuclear Chemistry 5(4):264-268. doi: 10.1016/0022-1902(58)80003-2

Sanderson Electronegativity Scale



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	**H** **2.31**																	**He**
2	**Li** **0.86**	**Be** **1.61**											**B** **1.88**	**C** **2.47**	**N** **2.93**	**O** **3.46**	**F** **3.92**	**Ne**
3	**Na** **0.85**	**Mg** **1.42**											**Al** **1.54**	**Si** **1.74**	**P** **2.16**	**S** **2.66**	**Cl** **3.28**	**Ar** **3.92**
4	**K** **0.74**	**Ca** **1.06**	**Sc** **1.09**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn** **1.86**	**Ga** **2.10**	**Ge** **2.31**	**As** **2.53**	**Se** **2.76**	**Br** **2.96**	**Kr** **3.17**
5	**Rb** **0.70**	**Sr** **0.96**	**Y** **0.98**	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd** **1.73**	**In** **1.88**	**Sn** **2.02**	**Sb** **2.19**	**Te** **2.34**	**I** **2.50**	**Xe** **2.63**
6	**Cs** **0.69**	**Ba** **0.93**	**La** **0.92**	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg** **1.92**	**Tl** **1.96**	**Pb** **2.01**	**Bi** **2.06**	**Po**	**At**	**Rn**

Tom R. SANDERSON, 1983. Electronegativity and bond energy. Journal of the American Chemical Society 105(8):2259-2261. doi: 10.1021/ja00346a026

"super-atom" group electronegativity

Formula	$E_G=\Sigma_A V_A E_A/\Sigma V_A$	Method [1]
Group	Calculus (Revised Pauling scale)	Result
$-CH_3$	(4·2.55+3·2.20)/(4+3)	2.40
-CHO	(4·2.55+1·2.20+2·3.44)/(4+1+2)	2.75
-OH	(2·3.44+1·2.20)/(2+1)	3.03
$-OCH_3$	(2·3.44+1·2.40)/(2+1)	3.09

EA: Electronegativity of (super)atom;
VA: valence of (super)atom;
EG: group electronegativity.

[1] Wu HANQING, 1997. *Re-propose Organic and Inorganic Property Values and Group Electronegativity for Drug and Biological Molecules and Their Calculation through JavaScript and Application in QSAR Studies*. First International Electronic Conference on Synthetic Organic Chemistry (ECSOC-1), www.mdpi.org/ecsoc/, September 1-30, 1997.

Diudea-Silaghi group electronegativity

Formula	$E_{V,k} = \sqrt[k+\sum_j b_{v,j}]{(E_A)_v^{\,k} \prod_j (E_A)_j^{\,b_{v,j}}}$	Diudea-Silaghi [1]	
Group	Calculus (Sanderson scale)	Result	
$-CH_3$	$\sqrt[1+3]{(2.47)^1 \cdot ((2.31)^1 (2.31)^1 (2.31)^1)}$	2.349	
$-CHO$	$\sqrt[1+3]{(2.47)^1 \cdot ((2.31)^1 (3.46)^2)}$	2.875	
$-OH$	$\sqrt[1+1]{(3.46)^1 \cdot ((2.31)^1)}$	2.827	
$-OCH_3$	$\sqrt[1+1]{(3.46)^1 \cdot ((2.349)^1)}$	2.851	

$b_{v,j}$: bond order of v with j;
k: number of bonds of V from G to others ($\notin$G).

[1] Mircea V. DIUDEA, Ioan SILAGHI-DUMITRESCU, 1989. *Valence group electronegativity as a vertex discriminator*. Revue Roumaine de Chimie 34(5):1175-1182.

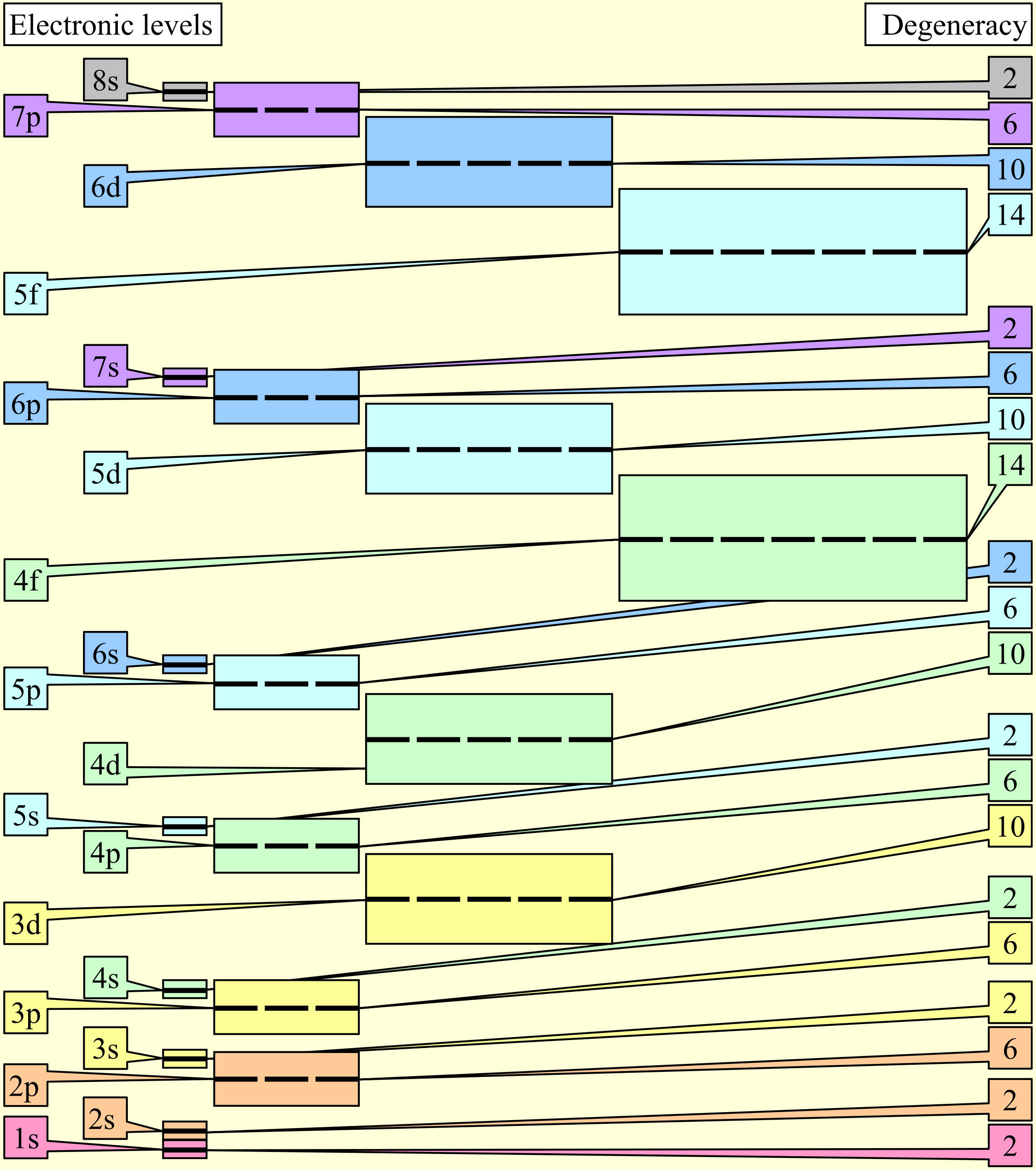
Groups – to do

Group	Group
-OF	>C=O
-ONO	-COOH
-OCl	$-CONH_2$
-OCN	-COCl
-OH	-CN
$-NO_2$	-CHO
>NH	$-CCl_3$
-NCO	-SCN
=NH	-SH
-NCS	$-C(CH_3)$
$-NH_2$	$-CH_3$
$>S(=O)_2$	>PH
>S=O	$-PH_2$
$-CF_3$	$-BH_2$
>C=O	>BH

Atomic structure

- "How many quantum numbers are necessary to describe a given system?" - has no universal answer; for every system seeking for the answer should be conducted and is the prerequisite of the complete analysis of the system. Obviously a quantified system requires at least one quantum number. *Chemical elements* can be described through their electronic structure using four quantum numbers: n - principal quantum number (shell): n = 0, 1, ...; l - angular quantum number (subshell): l = 0..n-1; m - magnetic quantum number (orbital): m = -l..l; s - spine quantum number (spin): s = ±½, a representative example for the deploying of the energy levels and filling of it with electrons being for the Mercury

Electronic levels



Electronic structure tree for Hg

Electronic shell				Order of
$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^{10}$ $4p^6$ $5s^2$ $4d^{10}$ $5p^6$ $6s^2$ $4f^{14}$ $5d^{10}$				filling (energy)
$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$ $4p^6$ $4d^{10}$ $4f^{14}$ $5s^2$ $5p^6$ $5d^{10}$ $5f^{14}$ $5g^{18}$ $6s^2$				appearance (quantum)
l (0..n-1)	m (-l..l)	s (±½)→		n
=0	=0	=±½	$1s^2$	=1
=0	=0	=±½	$2s^2$	=2
=1	=-1,0,1	=±½	$2p^6$	
=0	=0	=±½	$3s^2$	=3
=1	=-1,0,1	=±½	$3p^6$	
=2	=-2,-1,0,1,2	=±½	$3d^{10}$	
=0	=0	=±½	$4s^2$	=4
=1	=-1,0,1	=±½	$4p^6$	
=2	=-2,-1,0,1,2	=±½	$4d^{10}$	
=3	=-3,-2,-1,0,1,2,3	=±½	$4f^{14}$	
etc.				...

Questions & Responses

Which of the following are the electronic configurations of the chemical elements:

	0	Ar (Z=18): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$
	1	Ar (Z=18): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
	0	Hg (Z=80): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 5f^{14}\ 5g^{18}\ 6s^2$
	1	Hg (Z=80): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^{10}$
	0	Ag (Z=47): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^9$
	1	Ag (Z=47): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^1\ 4d^{10}$
	0	C (Z=8): $1s^2\ 2s^2\ 2p^6$
	1	C (Z=8): $1s^2\ 2s^2\ 2p^4$
	0	C (Z=6): $1s^2\ 2s^2\ 2p^2$

Atomic properties

- *Valence* is an atomic property (other atomic property: atomic number Z) and it reflects the tendency of elements to "stabilizes" their electronic structure; the path to stabilization tends to reach one of the following (meta)"stable" structures: s^2, p^3, p^6, d^5, d^{10}, etc. For example, at C - carbon (Z=6): $1s^2, 2s^2, 2p^2 \rightarrow 1s^2, 2s^2, 2p^6$:C^{4-} (CH_4). There are main ("preferred"), secondary ("rare") and elemental ("homoatomic" molecules) valences: H: +1 (HCl), -1 (LiH, BeH_2), 0 (H_2); O: -2 (H_2O, CaO), -1 (NaO-ONa), 0 (O_2); Cl: -1 (HCl), +1 ($HClO$), +3 ($HClO_2$), +5 ($HClO_3$), +7 ($HClO_4$). Following address locates a periodic system developed using a database and can be queried for valences:
  http://vl.academicdirect.ro/general_chemistry/periodic_system/ [1].
  Chemical combinations classifies in homoatomic and heteroatomic; also in binary, ternary, quaternary, etc. Following series gives representatives according with these classifications: O_2, O_3, H_2O (binary combination!), H_2SO_4.
  [1] Lorentz JÄNTSCHI, Delia M. GLIGOR, 2003. Periodic Systems of Elements Information (Software). Online: AcademicDirect. URL: http://vl.academicdirect.ro/general_chemistry/periodic_system/

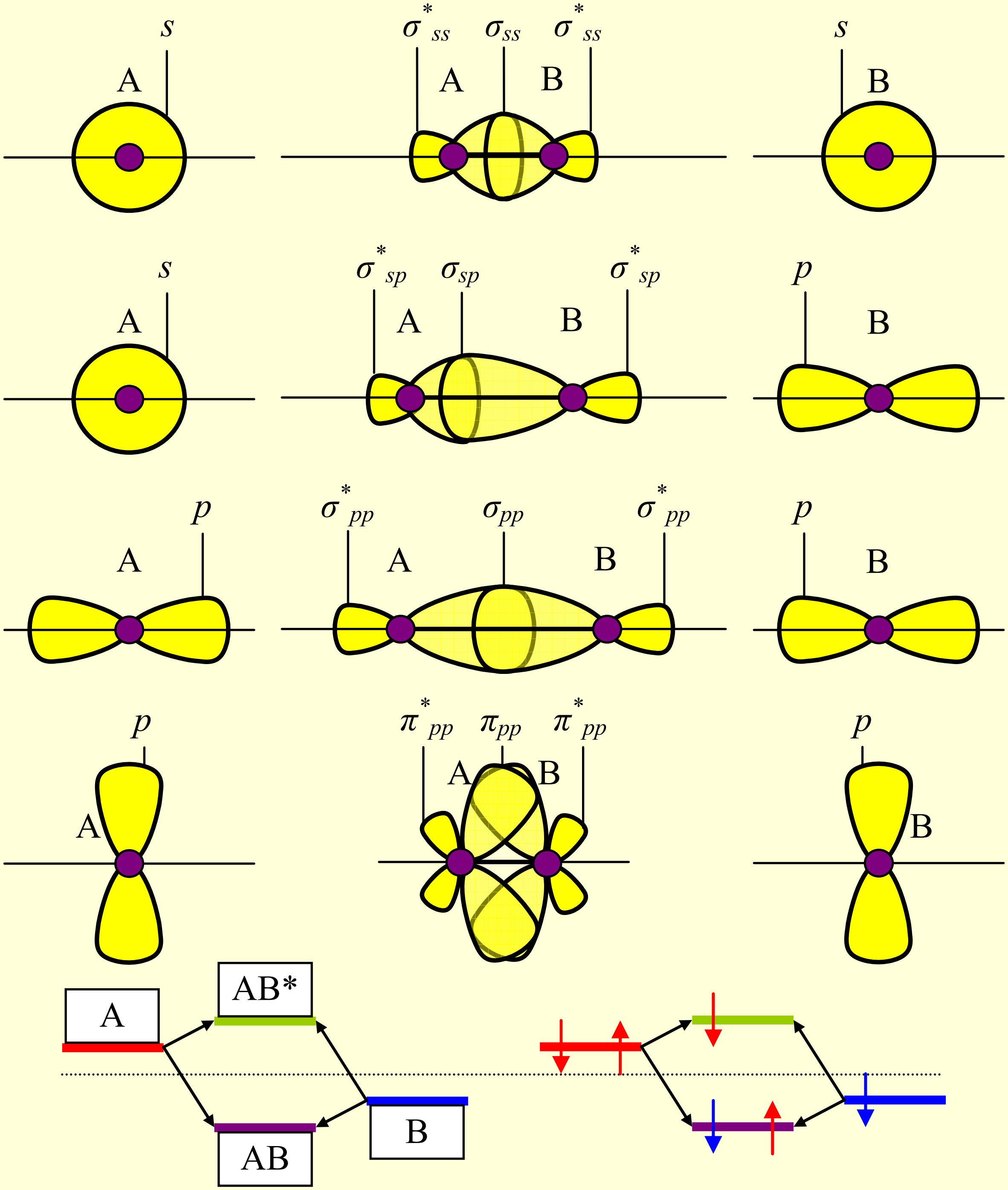
Questions & Responses

Identify which classifications are correctly given for chemical combinations:		
	0	H_2SO_4 - quaternary
	1	H_2SO_4 - heteroatomic
	0	H_2SO_4 - homoatomic
	1	H_2O - binary
	0	H_2O - homoatomic
	1	H_2O - heteroatomic
	0	O_2 - binary
	1	O_2 - homoatomic

Interaction models

- ***(covalent bond model)*** The covalent bond model is a representation of the chemical bond which assumes that every bond is created when two (by two) atoms are put together (by two by two atoms). It has as limit cases the *metallic bond* (Me - metal; Men molecule; n → ∞ metal network), *ionic bond* (A, B chemical species with - see below - different electronegativity; AB molecule; A^+B^- separating of the electric charges; A^+, B^- ions) and coordinative (such as: $CaCl_2$, Ca^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^0\ 4s^0$; $CaCl_2{\cdot}6H_2O$, Ca^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$ - antarcticite).
- ***(hybridization models)*** Hybridization models are able to explain the differences of the energies (at electronic orbital levels) when they join together in chemical bonds (see *Representation of hybridization process*). Hybridization conserves the total number of energy levels (orbital levels).

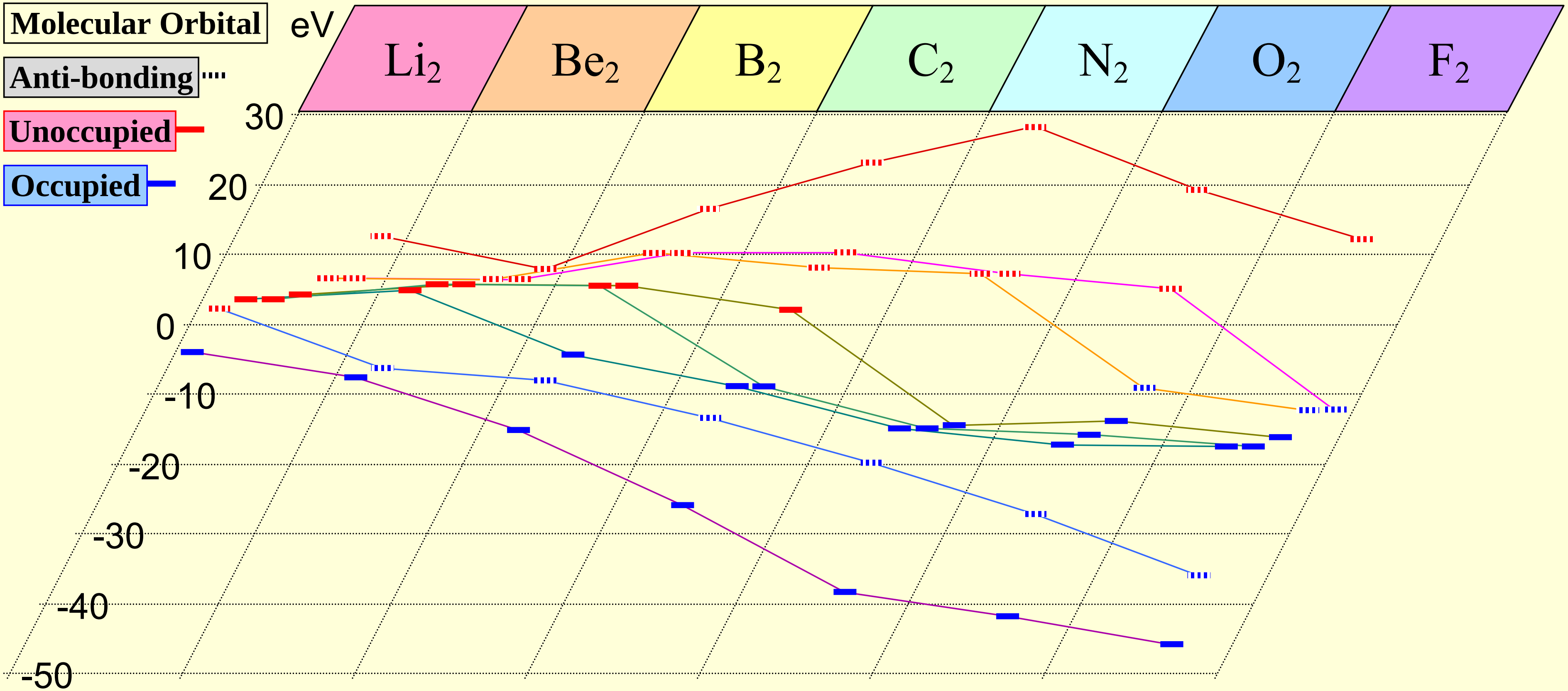
Hybridization process



Molecular orbital levels

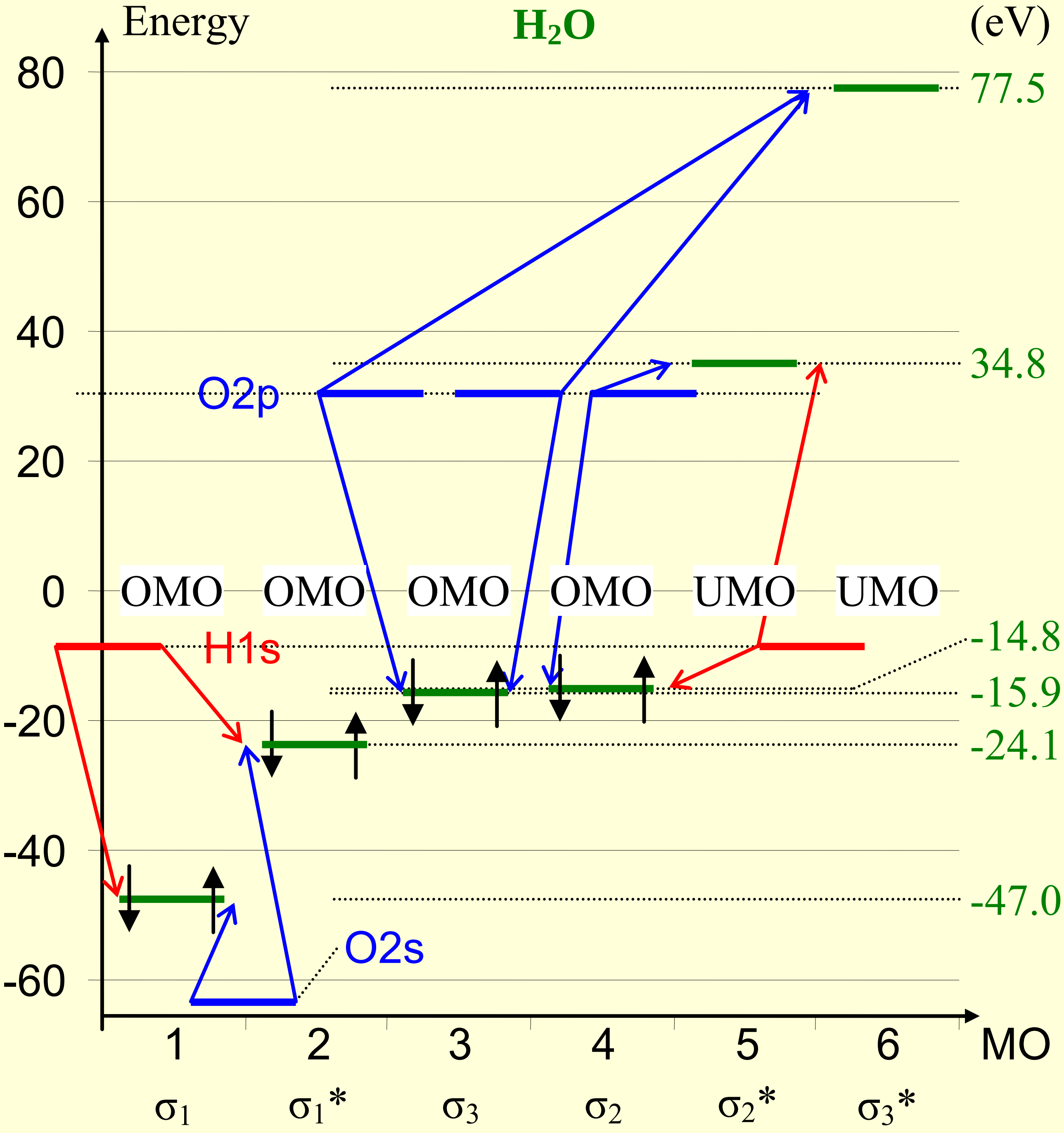
- Based on hybridisation the occurrence of molecular orbital levels is explained (see *Representation of hybridization process*). Under absence of energetic excitation (of a energy transfer to the molecule) filling with electrons of molecular energy levels is in increasing order of the energy of the levels (see *Diatomic homomolecules of 2nd period*). On molecular orbital forming basis and ordered filling of them with electrons the molecular stability are explained. A derived from model of the molecular orbital levels is the bond order. We count as bond order the difference between occupied "bond" orbital levels (lower energy split of the pair of orbital levels) and occupied "anti-bond" orbital levels (upper energy split of the pair of orbital levels). Bond order may take rational values, as in CC from C_6H_6: 9(bonds)/6(atoms) = $^3/_2$.

Diatomic molecules of 2nd period

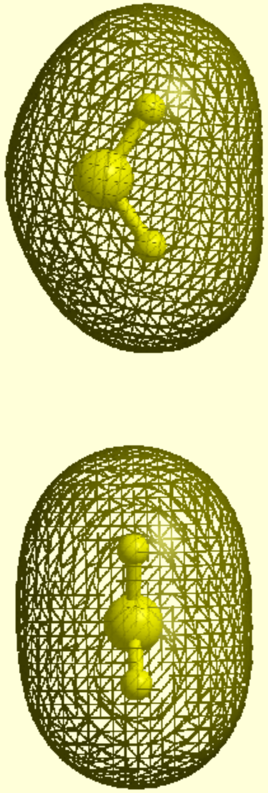


1	**0**	**1**	**2**	**3**	**2**	**1**	**Bond order**
2.7Å	**3.5Å**	**1.9Å**	**1.4Å**	**1.1Å**	**1.2Å**	**1.3Å**	**Distance**
1.1	**0.7**	**3.0**	**4.8**	**9.8**	**5.1**	**2.5**	**Energy (eV)**

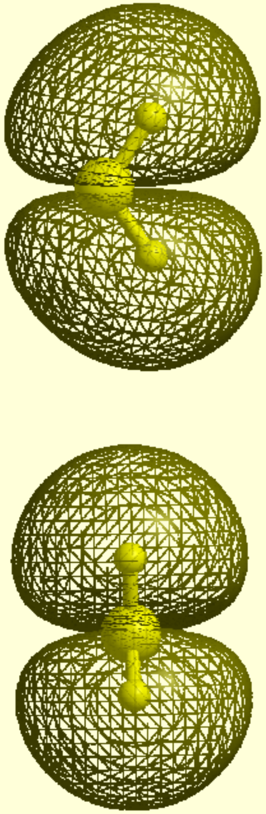
Molecular orbital & electron densities - water



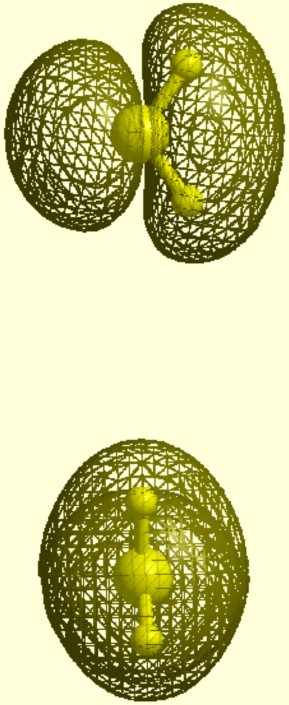
Molecular orbital & electron densities - water



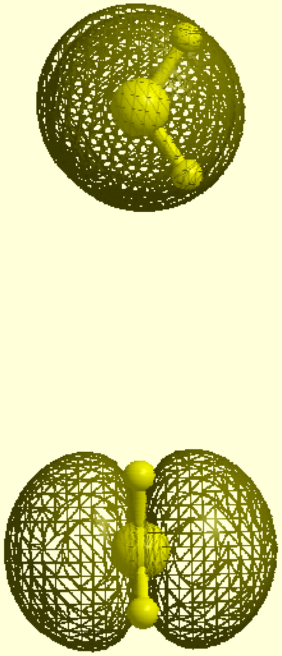
σ_1



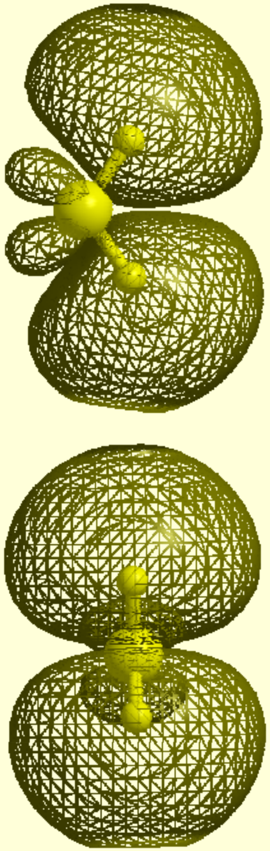
σ_1*



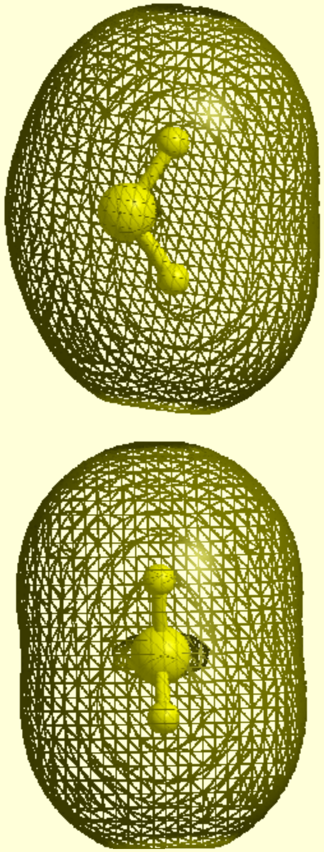
σ_3



σ_2



σ_2*

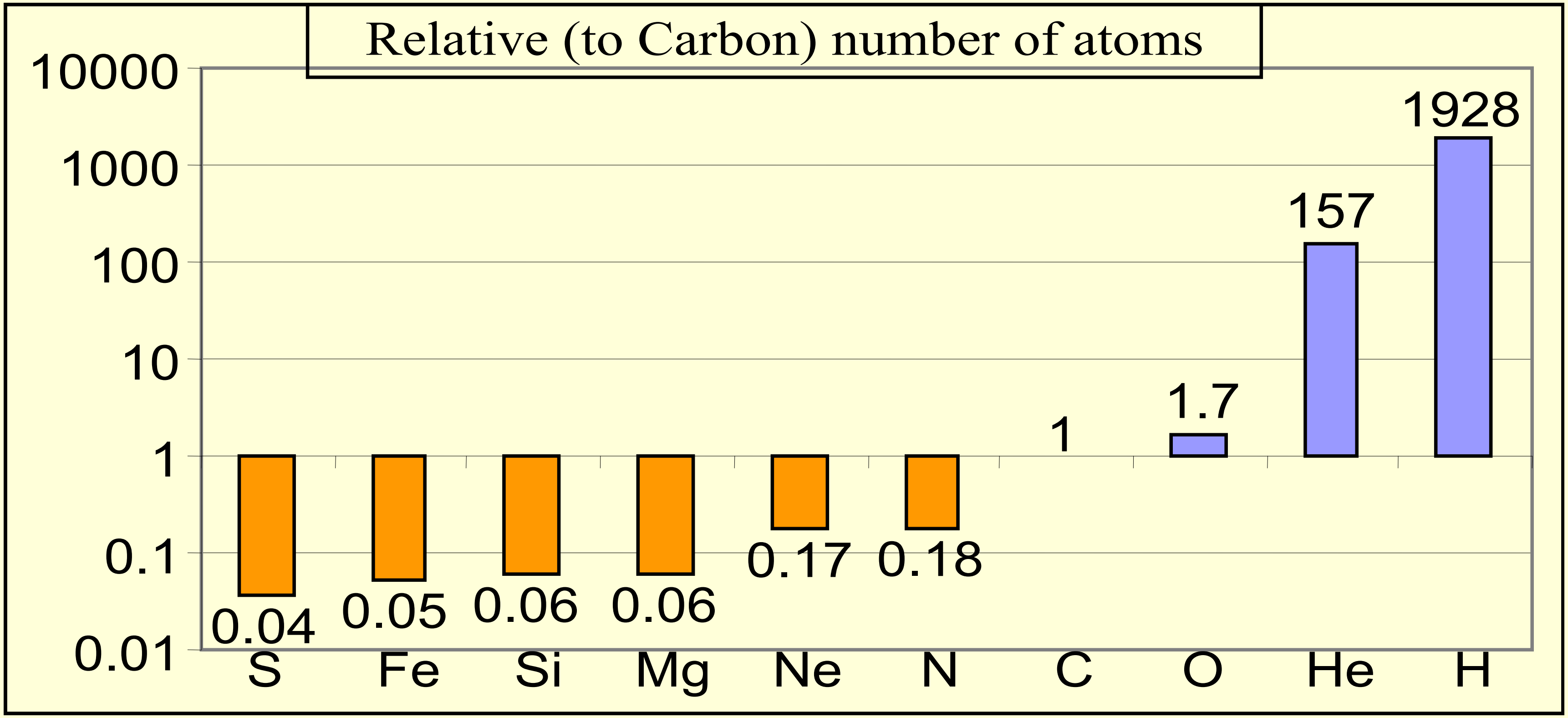


σ_3*

Course 2

Abundance of elements; chemical formulas; stoechiometry

Relative abundance of elements in the Galaxy*

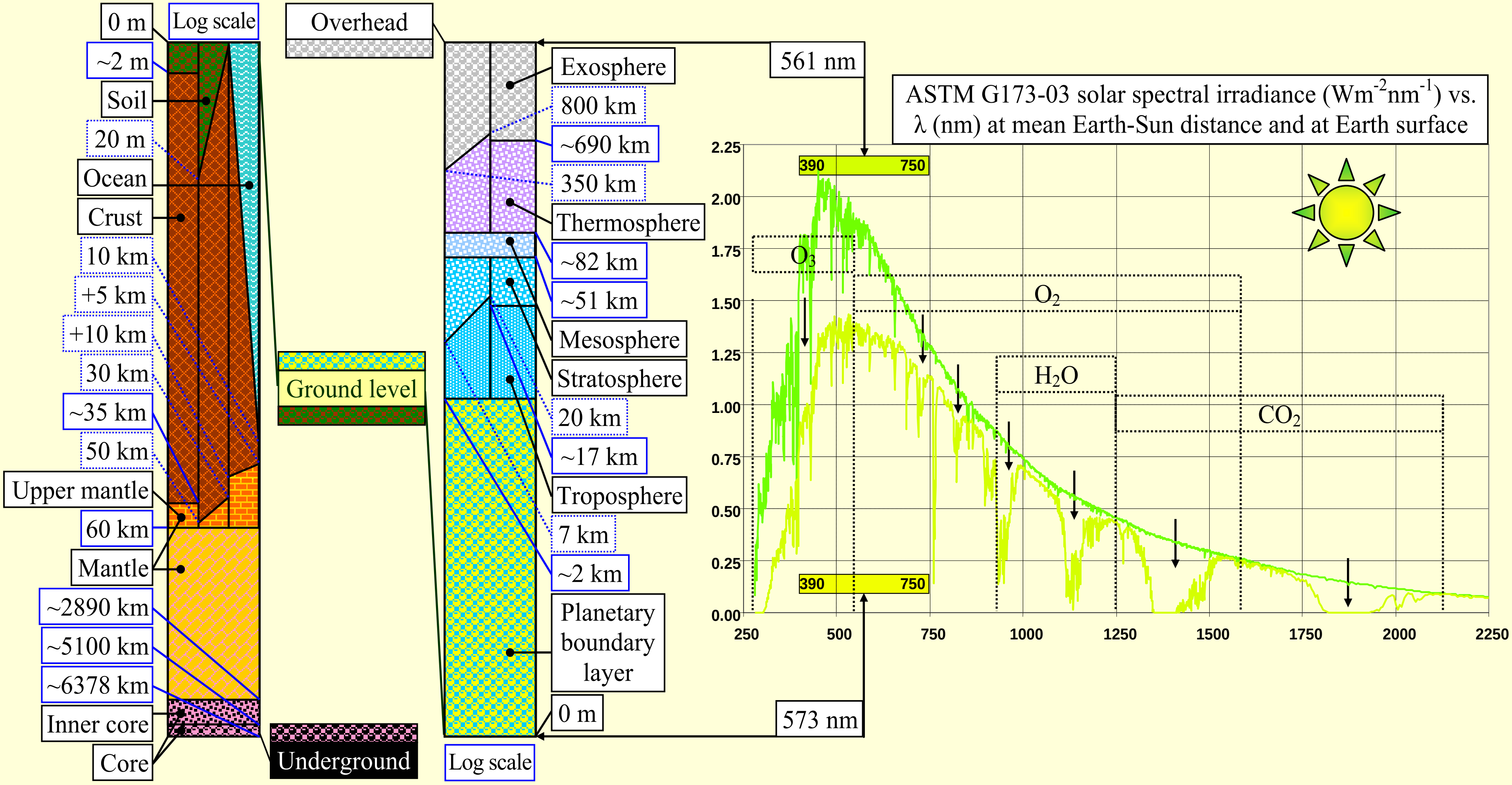


*spectroscopy measurements, adapted from [Croswell K, 1996. Alchemy of the Heavens]

Questions & Responses

The chemical elements are ordered by the abundance in the Galaxy as follows:		
	0	N > C
	0	C > O
	0	O > He
	0	He > H
	1	C > N
	1	O > C
	1	He > O
	1	H > He

Structure of the Earth and of the atmosphere

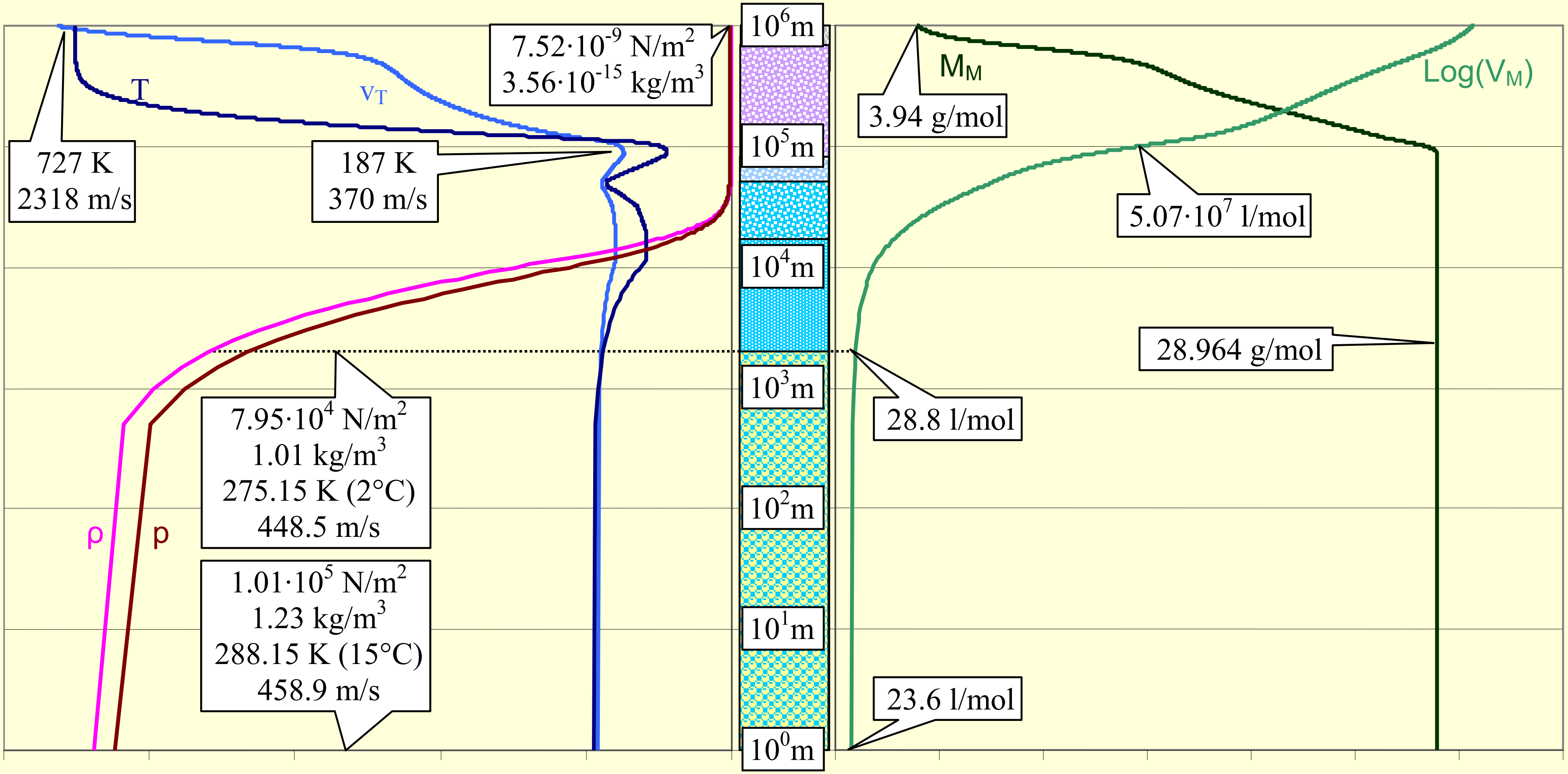


ASTM G173-03 solar spectral irradiance ($Wm^{-2}nm^{-1}$) vs. λ (nm) at mean Earth-Sun distance and at Earth surface

Questions & Responses

	When discussing the effects of the atmosphere to the solar radiation, we should know that:
1	The atmosphere absorbs some solar radiation
0	The visible range of the electromagnetic radiation ends to 390 nm
0	The visible range of the electromagnetic radiation starts from 750 nm
1	The visible range of the electromagnetic radiation is between 390 nm and 750 nm
0	The visible part of the solar radiation provides an average of 561 nm (yellow shifted to green) at the surface of the earth
0	The visible part of the solar radiation provides an average of 573 nm (yellow shifted to red) at entering in the atmosphere
1	The visible part of the solar radiation provides an average of 573 nm (yellow shifted to red) at the surface of the earth
1	The visible part of the solar radiation provides an average of 561 nm (yellow shifted to green) at entering in the atmosphere

Atmosphere



7.52·10^-9 N/m^2
3.56·10^-15 kg/m^3
10^6m
10^5m
10^4m
10^3m
10^2m
10^1m
10^0m
T
vT
727 K
2318 m/s
187 K
370 m/s
7.95·10^4 N/m^2
1.01 kg/m^3
275.15 K (2°C)
448.5 m/s
1.01·10^5 N/m^2
1.23 kg/m^3
288.15 K (15°C)
458.9 m/s
ρ
p
MM
3.94 g/mol
Log(VM)
5.07·10^7 l/mol
28.964 g/mol
28.8 l/mol
23.6 l/mol

Questions & Responses

When analysing the measurements of the properties of the atmosphere, someone may see that:	
0	In the upper atmosphere exists a part in which is in majority atomic hydrogen (H)
1	In the upper atmosphere exists a part in which is in majority atomic oxygen (O)
0	Biosphere domain of the atmosphere is correlated with minor changes in density (ρ) and pressure (p)
1	Biosphere domain of the atmosphere is correlated with minor changes in temperature (T) and thermal speed (v_T)
0	Biosphere domain of the atmosphere is correlated with minor changes in molar mass (M_M) and molar volume (V_M)
0	One of density (ρ) and pressure (p) carries information about the composition of the atmosphere
0	One of temperature (T) and thermal speed (v_T) carries information about the composition of the atmosphere
1	One of molar mass (M_M) and molar volume (V_M) carries information about the composition of the atmosphere

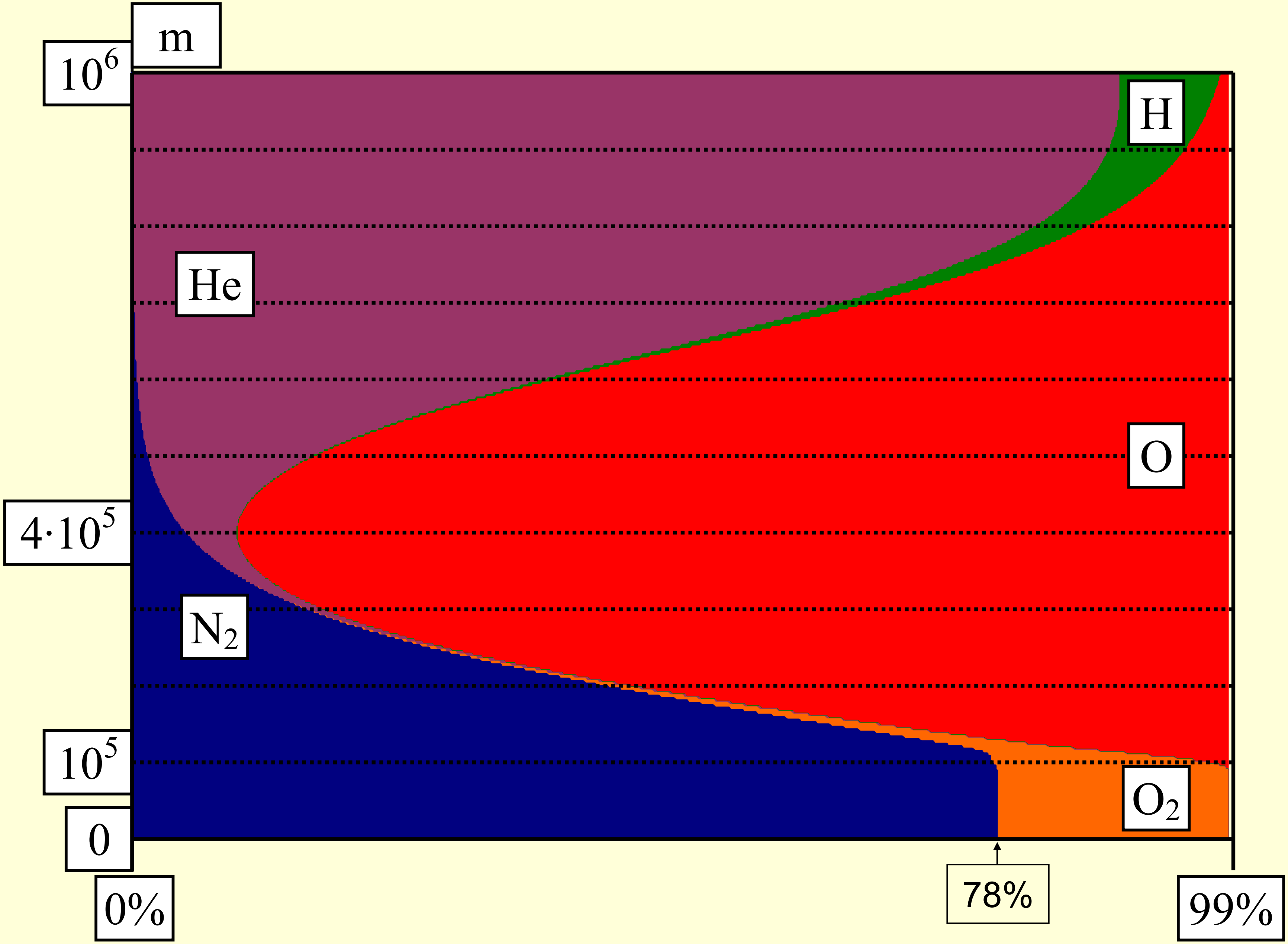
Spread of the elements in the atmosphere

- Gas shell surrounding the Earth is the atmosphere. Planetary boundary layer is formed mostly from nitrogen (78%) and oxygen (21%), along with others in small quantities (H_2O, Ar, CO_2, Ne, He, CH_4, Kr, H_2).

Questions & Responses

The atmospheric planetary boundary layer it has:		
	0	~ 20 km
	0	O_2 (78%), N_2 (21%), Others (1%)
	0	Oxygen (78%), Silicium (21%), Others (1%)
	0	Silicium (78%), Oxygen (21%), Others (1%)
	0	Oxygen (78%), Nitrogen (21%), Others (1%)
	1	~ 2 km
	1	N_2 (78%), O_2 (21%), Others (1%)
	1	Nitrogen (78%), Oxygen (21%), Others (1%)
	1	Gaseous state

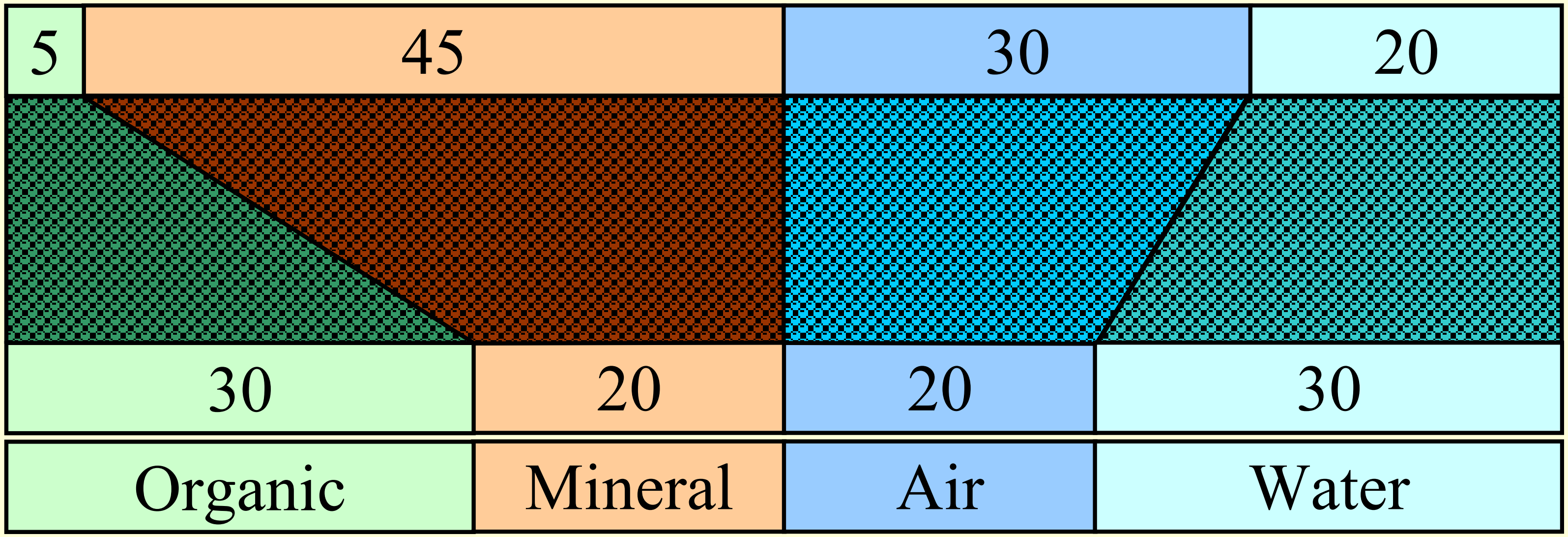
Atmosphere composition



Questions & Responses

		When analysing the measurements of the properties of the atmosphere, someone may see that:
	0	In the upper atmosphere exists a part in which is in majority atomic hydrogen (H)
	1	In the upper atmosphere exists a part in which is in majority atomic oxygen (O)
	0	Biosphere domain of the atmosphere is correlated with minor changes in density (ρ) and pressure (p)
	1	Biosphere domain of the atmosphere is correlated with minor changes in temperature (T) and thermal speed (v_T)
	0	Biosphere domain of the atmosphere is correlated with minor changes in molar mass (M_M) and molar volume (V_M)
	0	One of density (ρ) and pressure (p) carries information about the composition of the atmosphere
	0	One of temperature (T) and thermal speed (v_T) carries information about the composition of the atmosphere
	1	One of molar mass (M_M) and molar volume (V_M) carries information about the composition of the atmosphere

Topsoil composition



5 45 30 20

30 20 20 30

Organic Mineral Air Water

Organics for 1g of soil:

Bacteria: $[3\cdot10^6, 5\cdot10^8]$

Actinomycetes: $[10^6, 2\cdot10^7]$

Fungi: $[5\cdot10^3, 10^6]$

Yeast: $[10^3, 10^6]$

Protozoa: $[10^3, 5\cdot10^5]$

Algae: $[10^3, 5\cdot10^5]$

Nematodes: $[10^1, 5\cdot10^3]$

Typical minerals of soil:

SiO_2, $CaCO_3$

$MAlSi_3O_8$, M = Na, K, Ca

$KAlSi_3O_{10}(OH)_2$

$K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$

$MSiO_3$, M = Mg, Mn

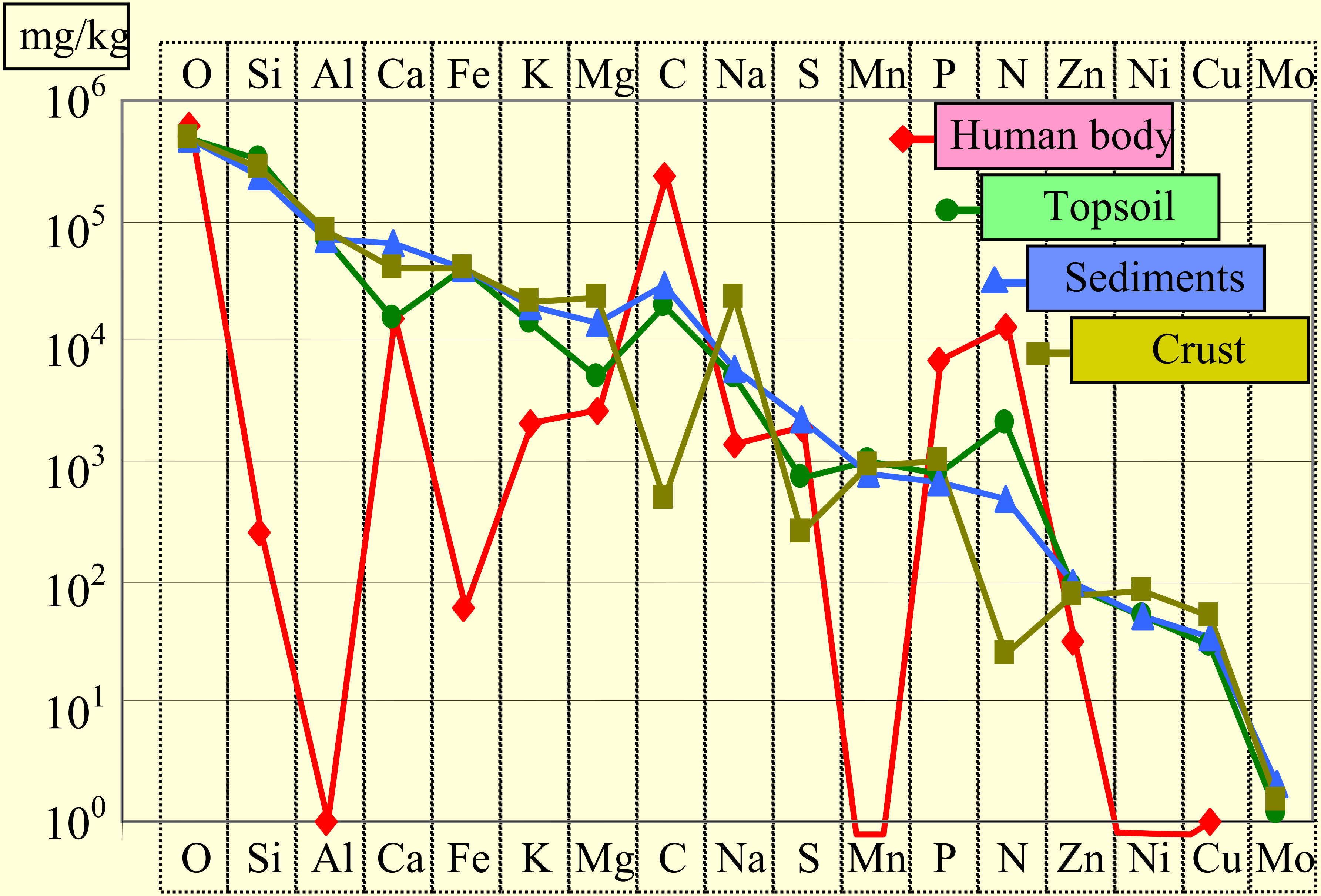
$(Mg,Fe)_2SiO_4$

$Ca_2Mg_5Si_8O_{22}(OH)_2$

Questions & Responses

When analysing the composition of the topsoil, someone may see that:		
	0	The solid (mineral + organic) part of it is much less than half
	0	The fluid (air + water) part of it is much less than half
	0	The solid (mineral + organic) part of it is much more than half
	0	The fluid (air + water) part of it is much more than half
	1	The solid (mineral + organic) part of it is about half
	1	The fluid (air + water) part of it is about half
	0	The mineral part of it is more than half
	1	The mineral part of it is less than half

Elemental composition at Earth's surface



% of elements in crust + upper mantle

Element	O	Si	Al	H	Na	Ca	Fe
% of atoms	59.4778	20.4663	6.2294	2.8963	2.5455	1.8774	1.8471
Σ%	59.48	79.94	86.17	89.07	91.62	93.49	95.34
Element	Mg	K	Ti	C	F	P	Mn
% of atoms	1.8016	1.3739	0.1896	0.1724	0.0871	0.0801	0.0376
Σ%	97.14	98.52	98.70	98.88	98.96	99.04	99.08
Element	S	Cl	V	Ba	N	Sr	Li
% of atoms	0.0323	0.0291	0.0077	0.0076	0.0074	0.0071	0.0059
Σ%	99.11	99.14	99.15	99.16	99.17	99.17	99.18
Element	Cr	Zr	Ni	Zn	Cu	B	Ce
% of atoms	0.0056	0.0045	0.0032	0.0025	0.0023	0.0019	0.0009
Σ%	99.18	99.19	99.19	99.19	99.20	99.20	99.20

In crust 15 elements, majority from the beginning of the periodic system, with low Z, are about 99.8%. Most spread elements in the crust: oxygen, silicon and aluminum, with over 82%.

Questions & Responses

By the number of moles the elements most spread in the crust are:		
	0	O, Na, H, Cl, S, Ca, Si (O > Na > H > Cl > S > Ca > Si)
	0	Si, Al, Fe, Na, Cu, Zn (Si > Al > Fe > Cu > Na > Zn)
	0	Si, Al, Fe, Cu, Zn (Si > Al > Fe > Cu > Zn)
	0	Si, Al, Fe, Cu (Si > Al > Fe > Cu)
	0	Si, Fe, Al (Si > Fe > Al)
	1	O, Si, Al (O > Si > Al)
	1	O, Si, Al, H (O > Si > Al > H)
	1	O, Si, Al, H, Na (O > Si > Al > H > Na)
	1	O, Si, Al, H, Na, Ca (O > Si > Al > H > Na > Ca
	1	O, Si, Al, H, Na, Ca, Fe (O > Si > Al > H > Na > Ca > Fe)

Observing space

- We may see the observing space as possessing a tree structure (see Structure of the observing space) expressing the belonging relations between the observables in deep picture being given for the Universe (as whole space of observation) and at surface (close to us as observers) being placed the chemical compounds - as form of representation of the matter with composition (of atoms) and relations (between them) well defined.

Structure of the observational space

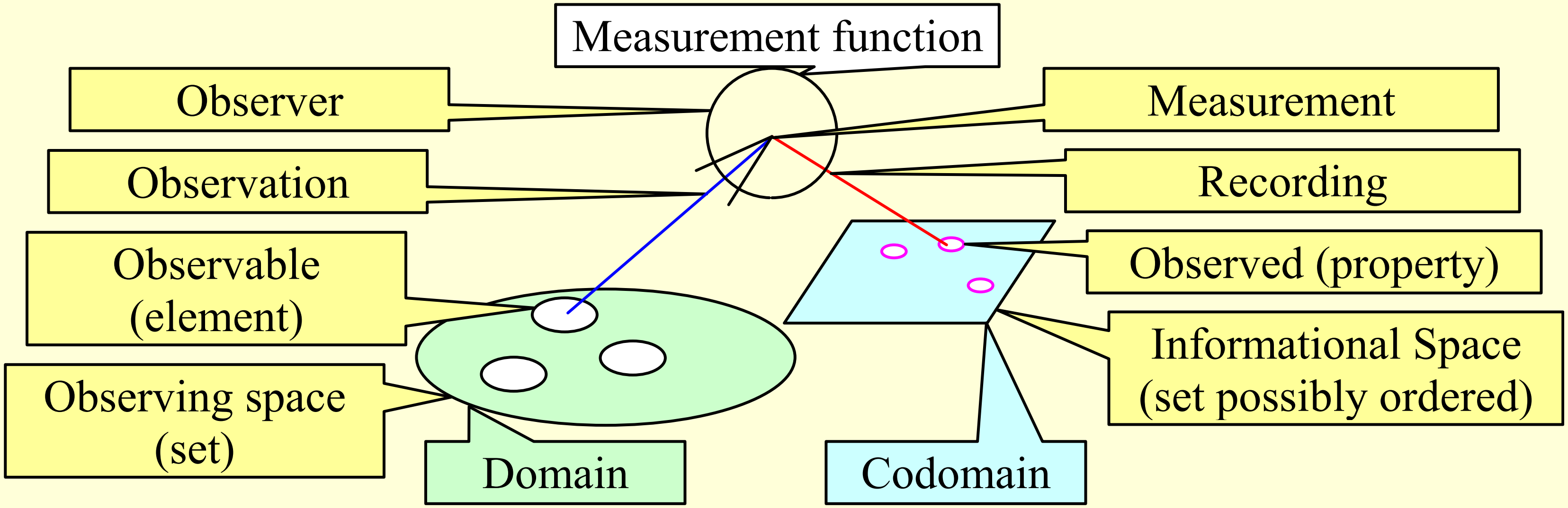
Structure	Property
-Universe	Whole observing space
-Radiant energy	Speed comparable with light
+Radiations such as β, γ	Differentiated through properties
-Matter	Whole not relativistic observables space
-Body	Speed much less than the light
-Materials ensemble	Variable and discontinue (chemical) composition
-Material	Variable and continue (chemical) composition
-Substance mixture	Well defined composition
+Heterogeneous substance	Variable (chemical) composition
-Solution	Solid or liquid aggregation state
+Alloy	Mixture of metals in solid or liquid aggregation state
-Homogenous substance	Constant (chemical) composition
+Chemical compound	Unique and well defined chemical structure

we may see that the observational space is intrinsic structured

Q
&
R

In relation to the observing space select from the following statements the true ones:		
	0	Chemical compounds have duplicitous and not well defined chemical structure
	1	Chemical compounds have unique and well defined chemical structure
	0	The homogeneous substances have variable chemical composition
	1	The homogeneous substances have constant chemical composition
	0	The substance mixtures doesn't have chemical composition
	1	The substance mixtures have well defined composition
	0	Materials doesn't have chemical composition
	1	Materials have variable and continue chemical composition
	0	Materials ensembles have constant and continue chemical composition
	1	Materials ensembles have variable and discontinue chemical composition
	0	A body has a speed comparable to the light
	1	A body has a speed much less than the light
	0	Matter is the whole relativistic observable space
	1	Matter is the whole non relativistic observable space
	0	The beta and gamma radiations are differentiated through speed
	1	The beta and gamma radiations are differentiated through properties
	0	Radiant energy has the speed comparable with sound
	1	Radiant energy has the speed comparable with light

Measurement vs. Mathematical



Measurement function

Observer

Measurement

Observation

Recording

Observable (element)

Observed (property)

Informational Space (set possibly ordered)

Observing space (set)

Domain

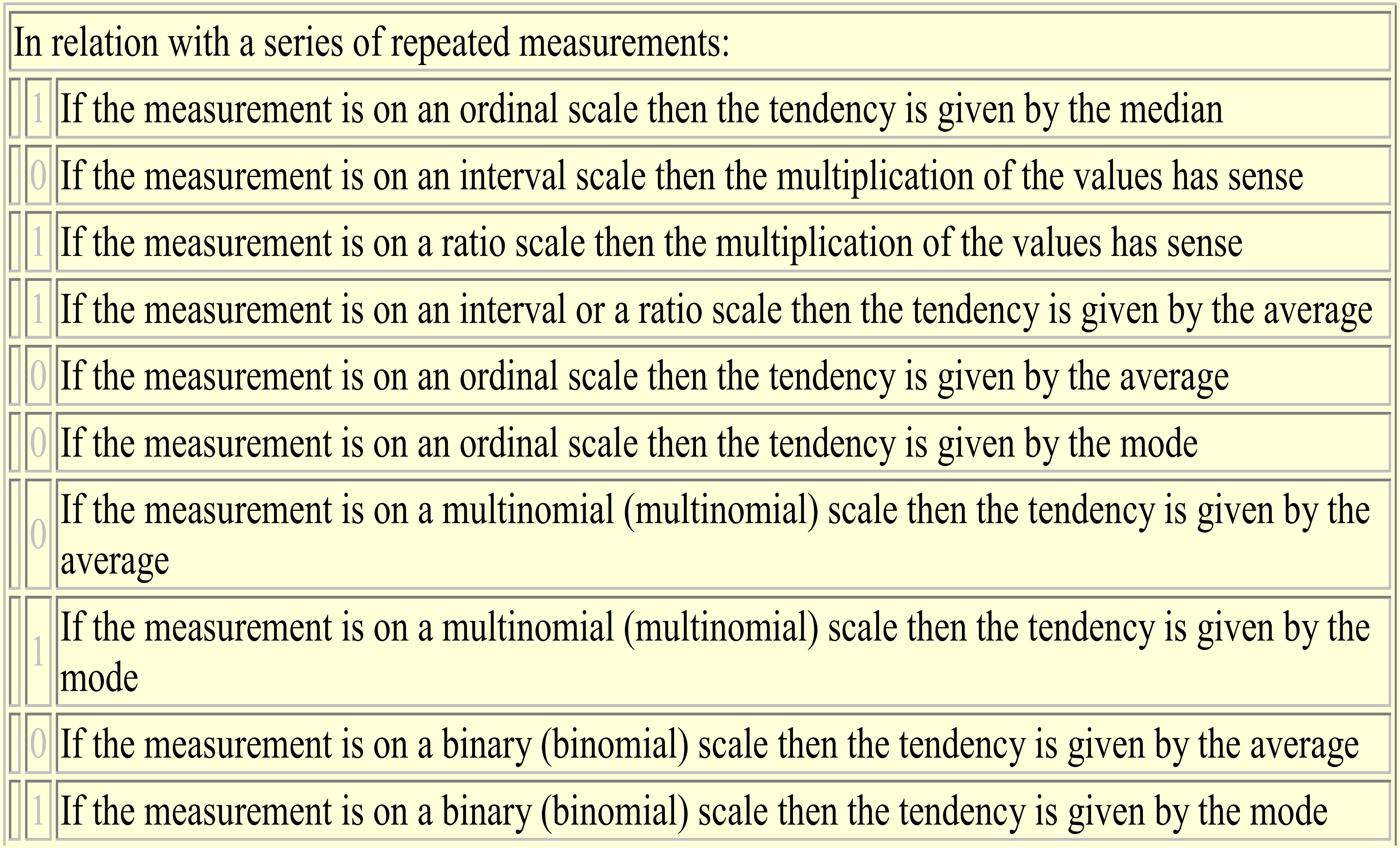
Codomain

f(·)	Mathematical function	SE, UQ
SE	Serial	$\exists b : (a,b) \in SE$
UQ	Uniquely	$(a,b), (a,c) \in UQ$ then $b \equiv c$

Measurement scales

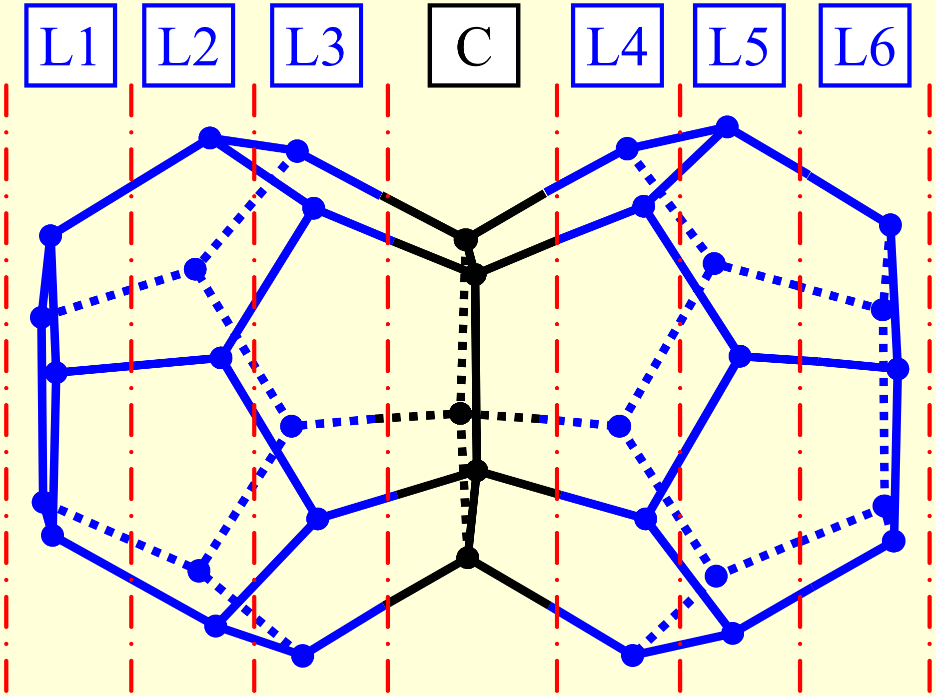
Scale	Type	Operations	Structure	Statistics	Examples
Binomial	Logical	"=", "!"	Boolean algebra	Mode, Fisher Exact	Dead/Alive Sides of a coin
(multi) Nomi(n)al	Discrete	"="	Standard set	Mode, Chi squared	ABO blood group system Living organisms classification
Ordinal	Discrete	"=", "<"	Commutative algebra	Median, Ranking	Number of atoms in molecule
Interval	Continue	"≤", "-"	Affine space (one dimensional)	Mean, StDev, Correlation, Regression, ANOVA	Temperature scale Distance scale Time scale Energy scale
Ratio	Continue	"≤", "-", "*"	Vector space (one dimensional)	GeoMean, HarMean, CV, Logarithm	Sweetness relative to sucrose pH

Questions & Responses



	In relation with a series of repeated measurements:
1	If the measurement is on an ordinal scale then the tendency is given by the median
0	If the measurement is on an interval scale then the multiplication of the values has sense
1	If the measurement is on a ratio scale then the multiplication of the values has sense
1	If the measurement is on an interval or a ratio scale then the tendency is given by the average
0	If the measurement is on an ordinal scale then the tendency is given by the average
0	If the measurement is on an ordinal scale then the tendency is given by the mode
0	If the measurement is on a multinomial (multinomial) scale then the tendency is given by the average
1	If the measurement is on a multinomial (multinomial) scale then the tendency is given by the mode
0	If the measurement is on a binary (binomial) scale then the tendency is given by the average
1	If the measurement is on a binary (binomial) scale then the tendency is given by the mode

Nanostructure design



- Layers: 6
- Levels: 3
- L1, …, L6: Boron, Nitrogen, Carbon
- All combinations: 729
- Distinct structures: 378 labeling isomorphism

Full factorial analysis:

- 2 out of 3 levels are independent e.g. B and C or B and N or C and N;

Factors set

nL	"*"	C^nL_"*"	3-1^"*"	"+"	Meaning
6	0	1	1	1	Free term
6	1	6	2	12	"Lx"
6	2	15	4	60	"Lx*Ly"
6	3	20	8	160	…
6	4	15	16	240	
6	5	6	32	192	
6	6	1	64	64	
Full factorial analysis terms				729	Total

Questions & Responses

Factorial analysis:

0	Requires that the multinomial variables to be converted to ordinal variables
1	Requires that the multinomial variables to be converted to binary variables
0	May be incomplete, in which case the experiment are included in all possible
0	It enables the establishment of inequalities between quantitative variables and quantitative variables
0	It can be full, in which case explains partly the phenomena subjected to the experiment
1	It can be full, in which case explains entirely the phenomena subjected to the experiment
1	It can be full, in which case in the experiment are included in all possible variants
0	Not requires the design of the experiment
1	Requires the design of the experiment
1	It enables the establishment of relationships between qualitative variables and quantitative variables

Restricted Hartree-Fock 3-21G*

- Energy Hartrees
- Properties Spartan ’10
  - MolVol – Molecular volume $Å^3$
  - SurfA – Surface area $Å^2$
  - Ovality – Ovality dimensionless 1.234
  - HOMO – Highest Occupied Molecular Orbital Energy eV
  - LUMO – Lowest Unoccupied Molecular Orbital Energy eV
  - Estimated polarizability: $*10^{-30}$ m^3
  - Lumo+Homo* eV; *:electronegativity= -HOMO + LUMO /2
  - Lumo-Homo** eV; **: hardness= -HOMO - LUMO/2
- Do the decomposition of the property by `atom type` factors!

Factor analysis original software

- Detect groups of equivalent factors - Symmetry
- Detect groups of irrelevant factors - Zero’s
- Leave-one-out on factors reducing of the complexity of the factorial analysis

Results** - different distinct factors!!

Property	Distinct*	Grp.	Zero	Property	Distinct*	Grp.	Zero
DipoleT_0	376	352		Lumo-Homo_0	353	375	
DipoleT_1	377	351		Lumo-Homo_1	331	397	
DipoleT_2	377	351		Lumo-Homo_2	372	356	
EnergyHF_0	131	510	87	MolVol_0	175	512	41
EnergyHF_1	139	507	82	MolVol_1	167	530	31
EnergyHF_2	346	382		MolVol_2	372	356	
HOMO_0	337	389	2	Ovality_0	46	516	166
HOMO_1	320	408		Ovality_1	51	590	87
HOMO_2	367	361		Ovality_2	56	645	27
LUMO_0	318	410		Polariz_0	349	379	
LUMO_1	300	428		Polariz_1	316	412	
LUMO_2	367	361		Polariz_2	371	357	
Lumo+Homo_0	355	373		SurfA_0	221	477	30
Lumo+Homo_1	324	404		SurfA_1	202	520	6
Lumo+Homo_2	356	370	2	SurfA_2	368	360	

"_0": Boron and Nitrogen as factors; Carbon as reference
"_1": Carbon and Boron as factors; Nitrogen as reference
"_2": Nitrogen and Carbon as factors; Boron as reference

**from 378 observations
& 729 full design records
*'expected' = 378

Turning back to chemistry

Structure	Property
-Universe	Whole observing space
-Radiant energy	Speed comparable with light
+Radiations such as β, γ	Differentiated through properties
-Matter	Whole not relativistic observables space
-Body	Speed much less than the light
-Materials ensemble	Variable and discontinue (chemical) composition
-Material	Variable and continue (chemical) composition
-Substance mixture	Well defined composition
+Heterogeneous substance	Variable (chemical) composition
-Solution	Solid or liquid aggregation state
+Alloy	Mixture of metals in solid or liquid aggregation state
-Homogenous substance	Constant (chemical) composition
+Chemical compound	Unique and well defined chemical structure

Only the chemical compound has well defined structure

Questions & Responses

The chemical composition:	
0	Varies when passing from one state of aggregation to another
0	It is well defined for a material
1	It is well defined for a pure substance
0	It is incompletely defined by the empirical formula
1	It is completely defined by the empirical formula
1	Defines a class of chemical compounds that share the same combination ratio of each element
0	Uniquely defines a chemical compound
1	It is defined by the ratio combination of each element in the compound

Pure substances

- Almost all elements exists in nature only as combinations. Exceptions are the noble gases and metals.
- Proportion of each element in a compound is well defined by its oxidation state and we may relate it with the oxidation numbers. Exception to this rule are the alloys.
- A pure substance is a substance with well defined chemical composition. The chemical composition is defined by the ratio of each element in the compound. We name empirical formula the set of lowest numbers being in the ratio of each element in the compound. Sometimes empirical formulas are enough, sometimes not.

Questions & Responses

Almost all the elements occur in nature only in the form of combinations. Exceptions are:		
	0	F
	0	Ca
	0	K
	0	Na
	0	N
	0	Ni
	1	Pt
	1	Ag
	1	Au
	1	Ar
	1	Ne
	1	He

Chemical formulas

- ***Empirical formulas*** express the relative number of atoms from each element in the compound. Coming from experiment, if we determined the (relative) mass of each element, we can use the atomic masses of the elements to obtain the empirical formula. For instance if a substance contains 36.1% Ca and 63.9% Cl then because M(Ca) = 40.08 and M(Cl) = 35.453 the ratio between elements is Ca : Cl = 36.1/40.8 : 63.9/35.453 ~ 0.90 : 1.80 = 1 : 2 and thus the empirical formula is $CaCl_2$. Other examples of empirical formulas: P_2O_5 (P:O = 2:5), CH (C:H = 1:1), CH_2 (C:H = 1:2), Cl_2PN (Cl:P:N = 2:1:1).

Questions & Responses

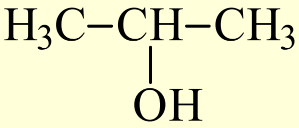
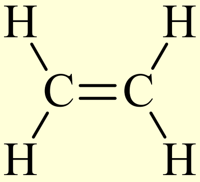
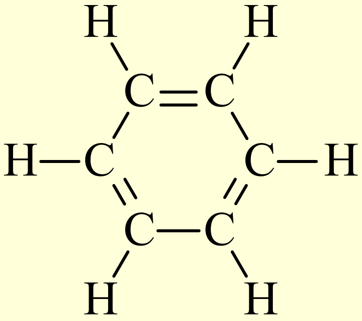
Chemical formulas are:

	0	Integral formulas
	0	Irrational formulas
	0	Calculation formulas
	1	Structural formulas
	1	Rational formulas
	0	Molar formulas
	1	Molecular formulas
	1	Empirical (gross) formulas

Molecular formulas

- ***Molecular formulas*** give in full the number of atoms from each element for one piece (molecule) of the substance. We may recover the molecular formula from empirical formula when we know the molecular mass. Molecular formula is a multiple of empirical formula. Examples for molecular formula are: $CaCl_2$ $((CaCl_2)_1)$ P_4O_{10} $((P_2O_5)_2)$, C_2H_2 $((CH)_2)$, C_6H_6 $((CH)_6)$, $Cl_6P_3N_3$ $((Cl_2PN)_3)$. Again, sometimes molecular formula provides not enough information to uniquely determine a compound.

Rational and structural formulas

Rational	1-propanole	2-propanole	ethyl-methyl-ether
Rationales for C_3H_8O	$H_3C{-}CH_2{-}CH_2{-}OH$	 $H_3C{-}\underset{\displaystyle OH}{\underset{\vert}{CH}}{-}CH_3$	$CH_3{-}O{-}CH_2{-}CH_3$
Structural	ethene (ethylene)	benzene	acetylene
			$H{-}C{\equiv}C{-}H$

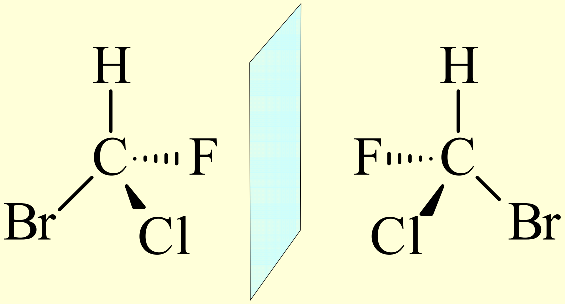
Structure isomers. Two or more compounds are structural isomers when possess same molecular formula and different structural formulas (see above). Nonane (C_9H_{20}) have 35 isomers (http://ph.academicdirect.org/CCPNI_2007.pdf).

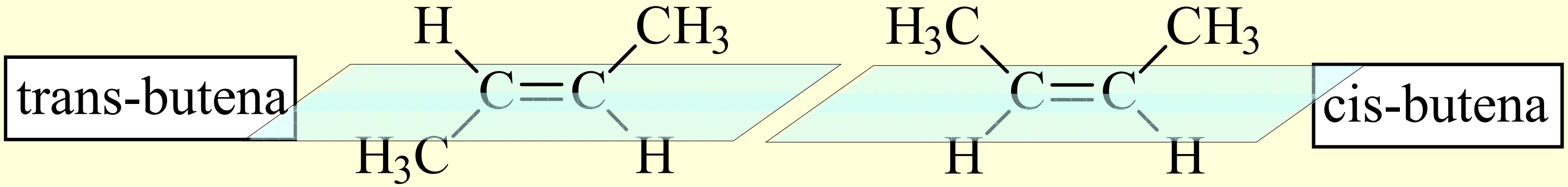
Questions & Responses

In connection with the empirical, molecular, structural and rational formulas:		
	0	Compounds with different molecular formulas can have the same structural formula
	1	Compounds with different structural formulas can have the same molecular formula
	0	Compounds with different empirical formulas can have the same structural formula
	1	Compounds with different structural formulas can have the same empirical formula
	0	Compounds with different empirical formulas can have the same rational formula
	1	Compounds with different rational formulas can have the same empirical formula
	0	Compounds with different molecular formulas can have the same structural formula
	1	Compounds with different structural formulas can have the same molecular formula
	0	Compounds with different molecular formulas can have the same rational formula
	1	Compounds with different rational formulas can have the same molecular formula
	0	Compounds with different empirical formulas can have the same molecular formula
	1	Compounds with different molecular formulas can have the same empirical formula

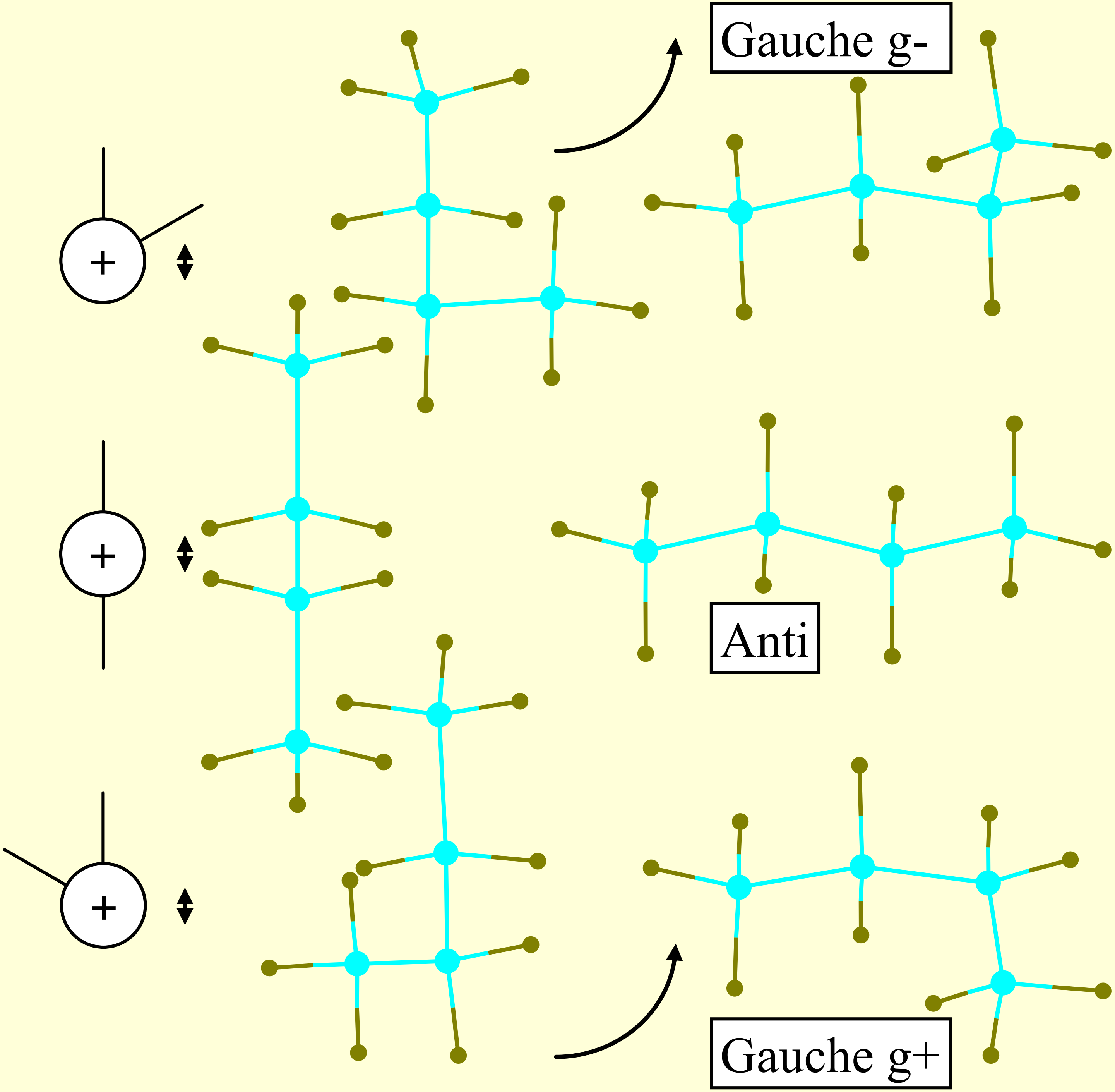
Geometry isomers

- Two (or more) compounds are geometrical isomers when has same structural formula and different geometries. Particular cases are classified as follows:
  - Enantiomers; example: CHClBrF
  - Diastereoisomers:
    - Cis-trans isomers; example:
    - Conformers; example - butane "Gauche g-" & "Gauche g+“





- Rotamers: example - butane "Anti"

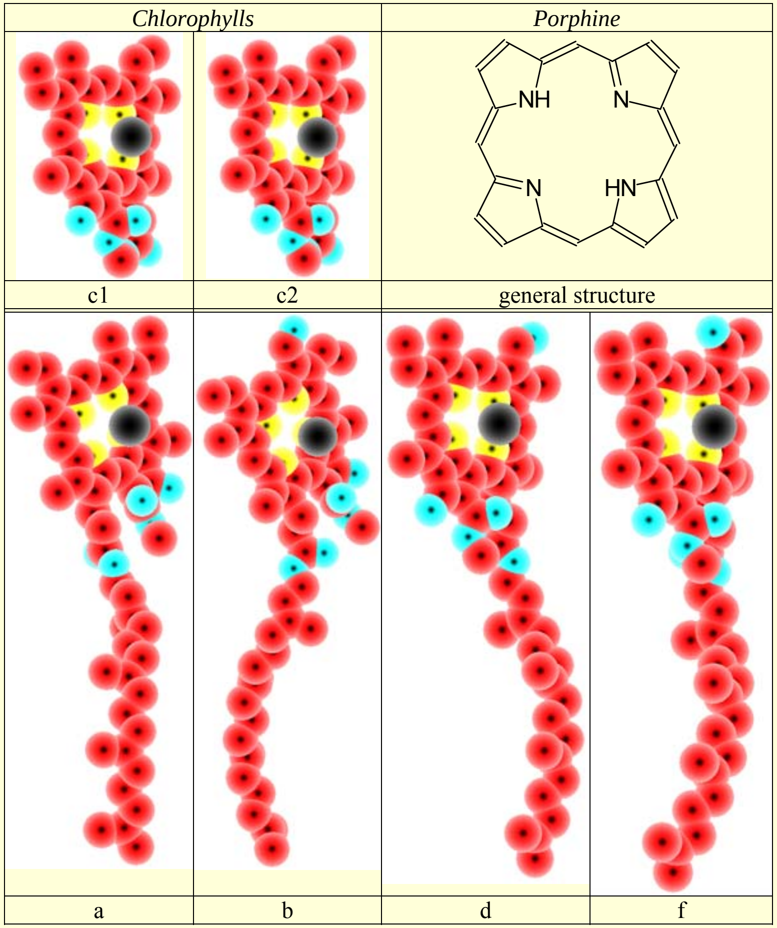


Gauche g-

Anti

Gauche g+

Representation levels



Chlorophyll	Ref.	Molecular formula	Present in	$\rho_{e,HOMO}\cdot\Sigma H_{1,UMO}$ & Spread [1]	
a	[2]	$C_{55}H_{72}O_5N_4Mg$	Universal	1.84	****
b	[3]	$C_{55}H_{70}O_6N_4Mg$	Many plants	1.54	***
d	[4]	$C_{54}H_{70}O_6N_4Mg$	Cyanobacteria	1.38	**
c1	[5]	$C_{35}H_{30}O_5N_4Mg$	Different algae	1.33	**
c2		$C_{35}H_{28}O_5N_4Mg$	Different algae	1.38	**
f	[6]	$C_{55}H_{70}O_6N_4Mg$	Cyanobacteria	1.21	*

Spread of chlorophylls

---

[1] Lorentz JÄNTSCHI, Sorana D. BOLBOACĂ, Mugur C. BĂLAN, Radu E. SESTRAŞ, 2011. Chlorophylls - natural solar cells. BUASVM. Agriculture, 68(1):181-187.

[2] James B. CONANT, Emma M. DIETZ, Carroll F. BAILEY, S. E. Kamerling, 1931. Studies in the chlorophyll series. V. The structure of chlorophyll a. Journal of the American Chemical Society 53(6):2382-2393.

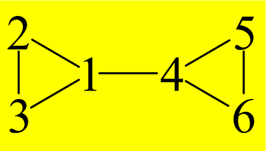
[3] James B. CONANT, Emma M. DIETZ, Tyrrell H. WERNER, 1931. Studies in the chlorophyll series. VIII. The structure of chlorophyll b. Journal of the American Chemical Society 53(12):4436-4448.

[4] Hideaki MIYASHITA, Hisato IKEMOTO, Norihide KURANO, Kyoko ADACHI, Mitsuo CHIHARA, Shigeto MIYACHI, 1996. Chlorophyll d as a major pigment. Nature 383(6599):402.

[5] Harold H. STRAIN, Benjamin T. COPE, Geraldine N. McDONALD, Walter A. SVEC, Joseph J. KATZ, 1971. Chlorophylls c1 and c2. Phytochemistry 10(5):1109-1114.

[6] Min CHEN, Martin SCHLIEP, Robert D. WILLOWS, ZhengLi CAI, Brett A. NEILAN, Hugo SCHEER, 2010. A red-shifted chlorophyll. Science 329(5997):1318-1319.

Molecular topology - graph fragments



[Sz]	1	2	3	4	5	6
1		1	1	1 2	1 2 3	1 2 3
2	2		2	1 2	1 2 3	1 2 3
3	3 4 5 6	3 4 5 6		1 2 3	1 2 3	1 2 3
4	4 5 6	4 5 6	4 5 6		1 2 3 4	1 2 3 4
5	4 5 6	4 5 6	5 6	5		5
6	4 5 6	4 5 6	5 6	6	6	

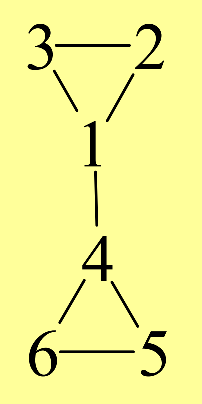
[cM]	1	2	3	4	5	6
1		2	3 4 5 6	4 5 6	5	6
2	1		3 4 5 6	4 5 6	5	6
3	1	2		4 5 6	5	6
4	1	2	1 2 3		5	6
5	1	2	1 2 3	1 2 3 4		6
6	1	2	1 2 3	1 2 3 4	5	

[Mx]	1	2	3	4	5	6
1		1 3 4 5 6	1 2	1 2 3	1 2 3 4 6	1 2 3 4 5
2	2 3 4 5 6		1 2	1 2 3	1 2 3 4 6	1 2 3 4 5
3	2 3 4 5 6	1 3 4 5 6		1 2 3	1 2 3 4 6	1 2 3 4 5
4	2 3 4 5 6	1 3 4 5 6	4 5 6		1 2 3 4 6	1 2 3 4 5
5	2 3 4 5 6	1 3 4 5 6	4 5 6	5 6		1 2 3 4 5
6	2 3 4 5 6	1 3 4 5 6	4 5 6	5 6	1 2 3 4 6	

[Cy]	1	2	3	4	5	6
1		1 2 3	1 2 3			
2	1 2 3		1 2 3			
3	1 2 3	1 2 3				
4					4 5 6	4 5 6
5				4 5 6		4 5 6
6				4 5 6	4 5 6	

[Cf]	1	2	3	4	5	6
1		1	1	1 2	1 2	1 2
2	2		2	1 2	1 2	1 2
3	3 4 5 6	3 4 5 6		1 2 3	1 2 3	1 2 3
4	4 5 6	4 5 6	4 5 6		1 2 3 4	1 2 3 4
5	5 6	5 6	5 6	5		5
6	5 6	5 6	5 6	6	6	

Molecular topology - graph polynomials

<table>
<tr><th>Graph [G]</th><th>Matrix ([M])</th><th>Polynomial</th><th>Characteristic</th></tr>
<tr><td rowspan="7"></td><td>Distance</td><td>$CP(Di;x)=8x^3+8x^2+14x^1+6x^0$</td><td rowspan="7">
<table>
<tr><td>[Ch]</td><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td></tr>
<tr><td>1</td><td>x</td><td>-1</td><td>-1</td><td>0</td><td>0</td><td>0</td></tr>
<tr><td>2</td><td>-1</td><td>x</td><td>-1</td><td>0</td><td>0</td><td>0</td></tr>
<tr><td>3</td><td>-1</td><td>-1</td><td>x</td><td>-1</td><td>0</td><td>0</td></tr>
<tr><td>4</td><td>0</td><td>0</td><td>-1</td><td>x</td><td>-1</td><td>-1</td></tr>
<tr><td>5</td><td>0</td><td>0</td><td>0</td><td>-1</td><td>x</td><td>-1</td></tr>
<tr><td>6</td><td>0</td><td>0</td><td>0</td><td>-1</td><td>-1</td><td>x</td></tr>
</table>
</td></tr>
<tr><td>Maximal</td><td>$CP(Mx;x)=20x^5+6x^3+4x^2+6x^0$</td></tr>
<tr><td>Complement of maximal</td><td>$CP(cM;x)=4x^4+6x^3+20x^1+6x^0$</td></tr>
<tr><td>Szeged (unsymmetrical)</td><td>$CP(Sz;x)=4x^4+14x^3+4x^2+8x^1+6x^0$</td></tr>
<tr><td>Cluj (fragmental)</td><td>$CP(Cf;x)=4x^4+6x^3+12x^2+8x^1+6x^0$</td></tr>
<tr><td>Cycles (always symmetrical)</td><td>$CP(Cy;x)=12x^3+24x^0$</td></tr>
<tr><td>- (adjacency)</td><td>$\varphi(G;x)=1x^6-7x^4-4x^3+11x^2+12x^1+3x^0$</td></tr>
</table>

http://l.academicdirect.org/Fundamentals/Graphs/polynomials/

http://l.academicdirect.org/Fundamentals/Graphs/cycles_count/

http://l.academicdirect.org/Fundamentals/Graphs/indices/

http://l.academicdirect.org/Fundamentals/Graphs/terminal_paths/

http://l.academicdirect.org/Fundamentals/Graphs/vertex_cutting/

Molecular geometry – theory levels

- ***Molecular mechanics*** uses the Newtonian mechanics to model molecular systems and its main application is energy optimization [1].
- The ***empirical or semi-empirical methods***, including Austin Model 1 (AM1 [2]), CFF [3], Del-Re [4], Parameterized Model (PM3 [5],[6], PM6 [7]), RM1 [8], Gasteiger [9],[10], Hückel [11],[12],[13],[14], Pullman [15], Optimized Potentials for Liquid Simulations (OPLS [16]), MM+, Assisted Model Building with Energy Refinement (Amber [17]) and Merck Molecular Force Field (MMFF [18],[19],[20],[21],[22]), are widely implemented in software, including MOPAC [23], Gaussian [24], SPARTAN [25], HyperChem [26], ChemBioOffice [27], and MolecularModellingPro [28], due to their speed.

[1] K. I. Ramachandran, Gopakumar DEEPA, Krishnan NAMBOORI, 2008. Computational Chemistry and Molecular Modeling: Principles and Applications. Berlin: Springer.

[2] Michael J. S. DEWAR, Eve G. ZOEBISCH, Eamonn F. HEALY, James J. P. STEWART, 1985. Development and use of quantum mechanical molecular models. 76. AM1: a new general purpose quantum mechanical molecular model. Journal of the American Chemical Society 107(13):3902-3909.

[3] Jon R. MAPLE, Jeong M. HWANG, Thomas P. STOCKFISCH, Uri DINUR, Marvin WALDMAN, Carl S. EWIG, Arnold T. HAGLER, 1994. Derivation of class II force fields. I. Methodology and quantum force field for the alkyl functional group and alkane molecules. Journal of Computational Chemistry 15(2):162-182.

[4] G. del RE, B. Pullman, T. Yonezawa, 1963. Electronic structure of the α-amino acids of proteins: I. Charge distributions and proton chemical shifts. Biochimica et Biophysica Acta 75:153-182.

[5] James J. P. STEWART, 1989. Optimization of parameters for semiempirical methods I. Method. Journal of Computational Chemistry 10(2):209-220.

[6] James J. P. STEWART, 1989. Optimization of parameters for semiempirical methods II. Applications. Journal of Computational Chemistry 10(2):221-264.

[7] James J. P. STEWART, 2007. Optimization of Parameters for Semiempirical Methods V: Modification of NDDO Approximations and Application to 70 Elements. Journal of Molecular Modeling 13(12):1173-1213.

[8] Gerd B. ROCHA, Ricardo O. FREIRE, Alfredo M. SIMAS, James J. P. STEWART, 2006. RM1: A reparameterization of AM1 for H, C, N, O, P, S, F, Cl, Br, and I. Journal of Computational Chemistry 27(10):1101-1111.

[9] Johann GASTEIGER, Mario MARSILI, 1980. Iterative partial equalization of orbital electronegativity - a rapid access to atomic charges. Tetrahedron 36(22):3219-3228.

[10] Johann GASTEIGER, Mario MARSILI, 1978. A new model for calculating atomic charges in molecules. Tetrahedron Letters 19(34):3181-3184.

[11] Erich HÜCKEL, 1931. Quantentheoretische Beiträge zum Benzolproblem - I. Die Elektronenkonfiguration des Benzols und verwandter Verbindungen. Zeitschrift für Physik 70 (3-4):204-286.

[12] Erich HÜCKEL, 1931. Quantentheoretische Beitrage zum Benzolproblem - II. Quantentheorie der induzierten Polaritaten. Zeitschrift für Physik 72(5-6):310-337.

[13] Erich HÜCKEL, 1932. Quantentheoretische Beitrage zum Problem der aromatischen und ungesattigten Verbindungen. III. Zeitschrift für Physik 76(9-10):628-648.

[14] Erich HÜCKEL, 1933. Die freien Radikale der organischen Chemie - Quantentheoretische Beitr¨age zum Problem der aromatischen und ungesättigten Verbindungen. IV. Zeitschrift für Physik 83(9-10):632-668.

[15] H. Berthod, C. Giessner-Prettre, A. Pullman, 1967. Sur les rôles respectifs des électrons σ et π dans les propriétés des dérivés halogénés des molécules conjuguées. Application à l'étude de l'uracile et du fluorouracile. Theor. Chim. Acta. 8(3):212-222.

[16] William L. JORGENSEN, Julian TIRADO-RIVES, 1988. The OPLS [optimized potentials for liquid simulations] potential functions for proteins, energy minimizations for crystals of cyclic peptides and crambin. Journal of the American Chemical Society 110(6):1657-1666.

[17] Scott J. WEINER, Peter A. KOLLMAN, David A. CASE, Chandra U. SINGH, Caterina GHIO, Guliano ALAGONA, Salvatore PROFETA, Paul WEINER, 1984. A new force field for molecular mechanical simulation of nucleic acids and proteins. Journal of the American Chemical Society 106, 765-784.

[18] Thomas A. HALGREN, 1996. Merck molecular force field. II. MMFF94 van der Waals and electrostatic parameters for intermolecular interactions. Journal of Computational Chemistry 17(5-6):520-552.

[19] Thomas A. HALGREN, 1996. Merck molecular force field. III. Molecular geometries and vibrational frequencies for MMFF94. Journal of Computational Chemistry 17(5-6):553-586.

[20] Thomas A. HALGREN, 1996. Merck molecular force field. IV. Conformational energies and geometries for MMFF94. Journal of Computational Chemistry 17(5-6):587-615.

[21] Thomas A. HALGREN, Merck molecular force field. V. Extension of MMFF94 using experimental data, additional computational data, and empirical rules. Journal of Computational Chemistry 17 (1996) 616-641.

[22] Thomas A. HALGREN, 1996. Merck molecular force field. I. Basis, form, scope, parameterization, and performance of MMFF94. Journal of Computational Chemistry 17(5-6):490-519.

[23] David YOUNG, 2001. Appendix A (A.3.2 p.342, MOPAC) In: Computational Chemistry, New York: Wiley-Interscience.

[24] ***, 2004. Publisher's Note: Sir John A. POPLE, 1925-2004. Journal of Computational Chemistry 25(9):v-viii.

[25] David YOUNG, 2001. Appendix A (A.1.6 p.330, SPARTAN) In: Computational Chemistry, New York: Wiley-Interscience.

[26] Hypercube, 2002. HyperChem7 (software). Website: http://www.hyper.com/

[27] CambridgeSoft, 2010. ChemBioOffice2010 (software). Website: http://www.cambridgesoft.com/software/chembiooffice/

[28] ChemSW, 2007. MolecularModellingPro (software). Web: http://www.chemistry-software.com/modelling/13052.htm

Molecular geometry – theory levels

- A series of ***ab initio methods*** were developed (for example STO-3G, 3-21G, 6-31G*, 6-31G**, Gradient, MP2, Hamiltonian, Huckel, CNDO, INDO, etc. [62]) although, the time-consuming calculations is a major barrier in their utilization. A very good software (which I recommend) for ***ab initio calculations*** is Massively Parallel Quantum Chemistry Program (abbreviated as MPQC). The MPQC program computes properties of atoms and molecules from first principles using the time independent Schrödinger equation [1]. The version 2.3.1 released on 2006-03-22 was used [2] under a FreeBSD operating system platform.

- [1] Joseph P. KENNY, Curtis L. JANSSEN, Edward F. VALEEV, Theresa L. WINDUS, 2008. Components for integral evaluation in quantum chemistry. Journal of Computational Chemistry 29(4):562-577.
- [2] Michael BANCK, Mike COLVIN, Curtis JANSSEN, Joe KENNY, Matt LEININGER, Ida NIELSEN, Ed SEIDL, Edward VALEEV (P.I.), Toon VERSTRAELEN, 2006. MPQC-2.3.1: The Massively Parallel Quantum Chemistry Program (software, open source). Website: http://www.mpqc.org/

Massively Parallel Quantum Chemistry Program (mpqc) & SAPF

No	CID	Conv. Cycles	mol. no atoms	HOMO (eV)	LUMO (eV)	GAP (eV)	SCF (Hartrees)	Nucl_Rep (Hartrees)
1	5994	18	53	-0.3580	0.1145	0.4725	-962.4	2074.8
2	107845	26	47	-0.2982	0.0766	0.3748	-995.9	1948.6
3	250948	58	61	-0.3257	0.0864	0.4121	-1264.8	2991.8
4	5757	61	44	-0.2948	0.1441	0.4390	-845.3	1623.4
5	9904	17	46	-0.3551	0.1170	0.4721	-846.5	1675.9
6	6446	21	53	-0.3547	0.1196	0.4743	-1098.3	2395.5
7	5858	23	52	-0.3549	0.1184	0.4734	-924.6	1954.8
8	227107	13	52	-0.3508	0.1040	0.4548	-1383.5	2279.2
9	13327	12	54	-0.3513	0.1033	0.4546	-1496.2	2525.9
10	538883	26	51	-0.3589	0.0969	0.4558	-998.2	2129.5
11	5281034	21	56	-0.3360	0.1102	0.4462	-1038.4	2285.3

From:

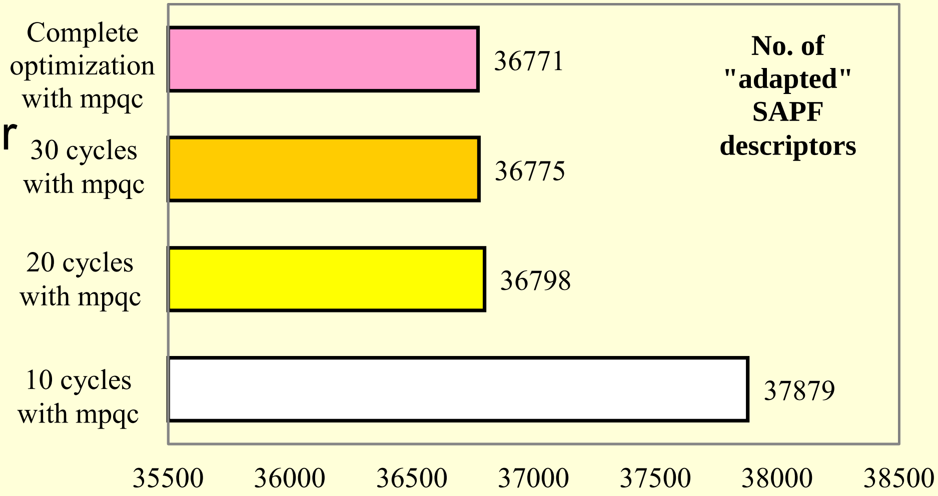
Quantum Mechanics Study on a Series of Steroids Relating Separation with Structure

Radu E. SESTRAŞ,
Lorentz JÄNTSCHI,
Sorana D. BOLBOACĂ
(accepted paper)

mpqc optimization: CLHF 6-31G* (ab-initio)

SAPF adaptation: For hRf = retardation factor

Adaptation	Min/Max	Value
Absolute variance of the descriptor value relative to the measured property	minimum	0.02
Deviation from normality relative to measured property	maximum	2.00
Determination between descriptor value and measured property	minimum	0.02



Course 3

Minerals
Physical and chemical properties
Chemical reactions

Minerals

Mineral class	Examples
Native	Diamond, coal, S, Au, Ag, Cu, Pt, Pd
Halogenated	NaCl (also known as salt, common salt, table salt or halite), KCl, CaF_2, $KCl \cdot MgCl_2 \cdot 6H_2O$
Oxides and hydroxides	Al_2O_3, AlO(OH), $Al(OH)_3$, Fe_2O_3, FeO, Fe_3O_4, MnO_2, TiO_2, SnO_2, SiO_2, UO_2, U_3O_8
Sulfides, arsenides	FeS_2, PbS, ZnS, HgS, CuS, Sb_2S_3, Bi_2S_3, MoS_2, $CuFeS_2$, NiAs, CoAsS
Carbonated	$CaCO_3$, $MgCO_3$, $CaCO_3 \cdot MgCO_3$, $FeCO_3$, $MnCO_3$, $Cu_2(CO_3)(OH)_2$, $Cu_3(CO_3)_2(OH)_2$
Nitrates	$NaNO_3$, KNO_3

US National Museum of Natural History images (October 2005)

Questions & Responses

Typical examples of minerals by classes of minerals are:

0	Nichelates: $NaNO_3$, KNO_3
0	Oxides and hydroxides: $CaCO_3$, $MgCO_3$, $CaCO_3 \cdot MgCO_3$, $Cu_2(CO_3)(OH)_2$
1	Carbonates: $CaCO_3$, $MgCO_3$, $CaCO_3 \cdot MgCO_3$, $Cu_2(CO_3)(OH)_2$
1	Oxides and hydroxides: Al_2O_3, $AlO(OH)$, $Al(OH)_3$
0	Selenides: FeS_2, PbS, ZnS, HgS, CuS, Sb_2S_3, Bi_2S_3, MoS_2, $CuFeS_2$, NiAs, CoAsS
1	Sulfides and arsenides: FeS_2, PbS, ZnS, HgS, CuS, Sb_2S_3, Bi_2S_3, MoS_2, $CuFeS_2$, NiAs, CoAsS
0	Halogenated: FeS_2, PbS, ZnS, HgS, CuS, Sb_2S_3, Bi_2S_3, MoS_2, $CuFeS_2$, NiAs, CoAsS
1	Halogenated: NaCl, KCl, CaF_2, $KCl \cdot MgCl_2 \cdot 6H_2O$
0	Fossil: Diamond, coal, S, Au, Ag, Cu, Pt, Pd
1	Native: Diamond, coal, S, Au, Ag, Cu, Pt, Pd

Zeolites

$MAl_2Si_3O_{10}\cdot 2H_2O$

$M = Na_2, K_2, Ca, Mg$

Beryl ($Be_3Al_2(SiO_3)_6$)

Heliodor (some V replaces Al)	🟨
Emerald ($Be_3Al_2(SiO_3)_6$)	🟩
Riesling (some V & Fe replaces Al)	🟩
Aquamarine (some Fe replaces Al)	🟦
Morganite (some Mn replaces Al)	🟪

Corundum (Al_2O_3)

Sapphire

Sapphire

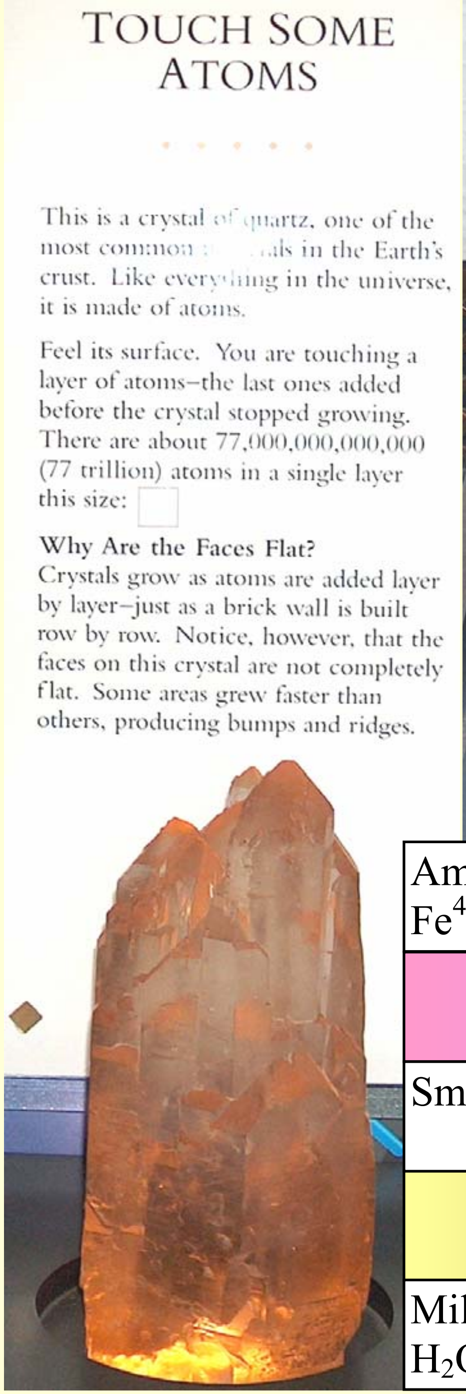
Sapphire

Sapphire

Ruby

Corundum is a crystalline form of Al_2O_3 (blue) with traces of iron (green), vanadium (yellow), titanium (orange) and chromium (red)

Quartz (SiO_2)

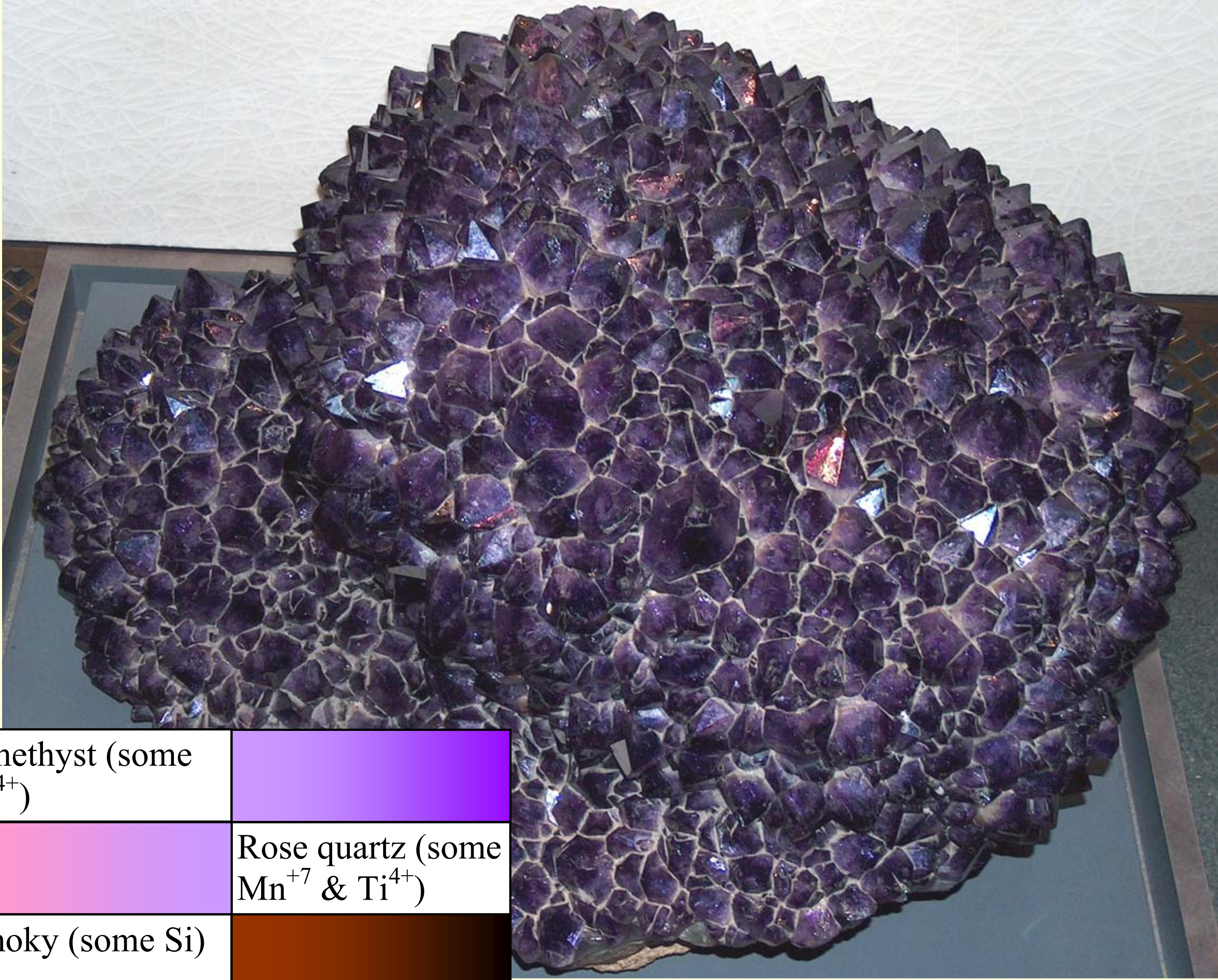


TOUCH SOME ATOMS

This is a crystal of quartz, one of the most common minerals in the Earth's crust. Like everything in the universe, it is made of atoms.

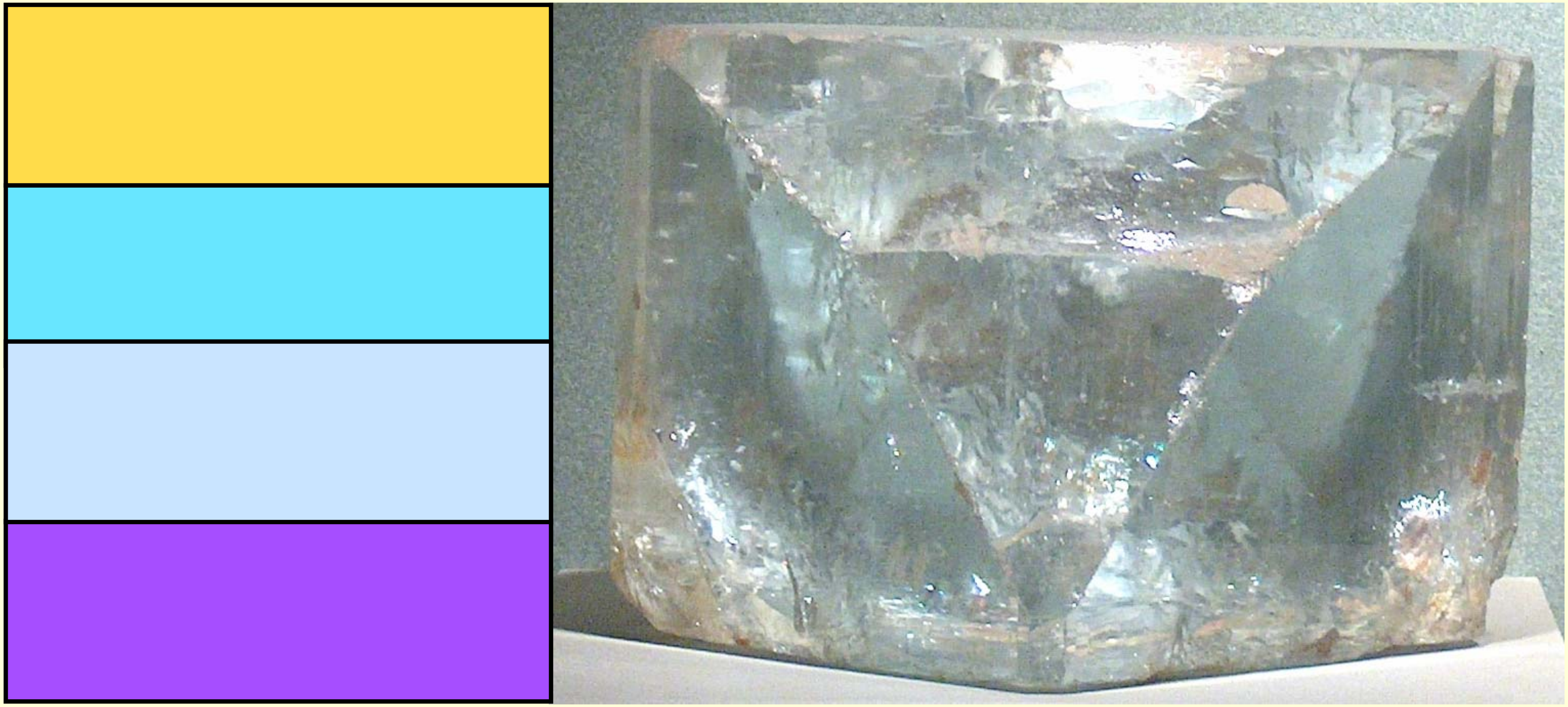
Feel its surface. You are touching a layer of atoms—the last ones added before the crystal stopped growing. There are about 77,000,000,000,000 (77 trillion) atoms in a single layer this size: ☐

Why Are the Faces Flat?
Crystals grow as atoms are added layer by layer—just as a brick wall is built row by row. Notice, however, that the faces on this crystal are not completely flat. Some areas grew faster than others, producing bumps and ridges.



Amethyst (some Fe^{4+})	🟪
🟪	Rose quartz (some Mn^{+7} & Ti^{4+})
Smoky (some Si)	🟫
🟨	Citrine (some Fe^{3+})
Milky (some CO_2, H_2O)	⬜

Topaz ($Al_2SiO_4(F,OH)_2$)



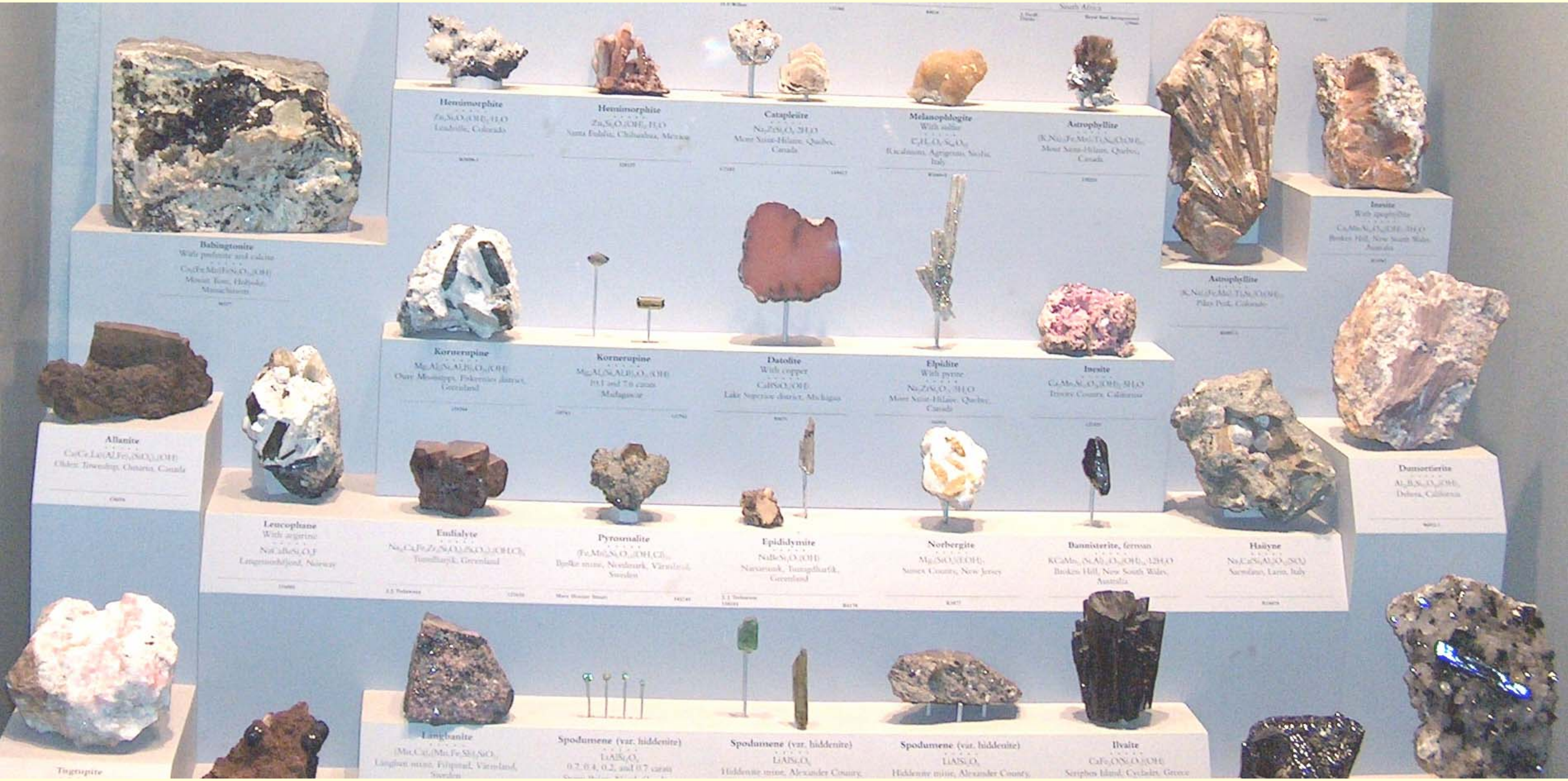
Native & S^{2-}

O^{2-} & CO_3^{2-}

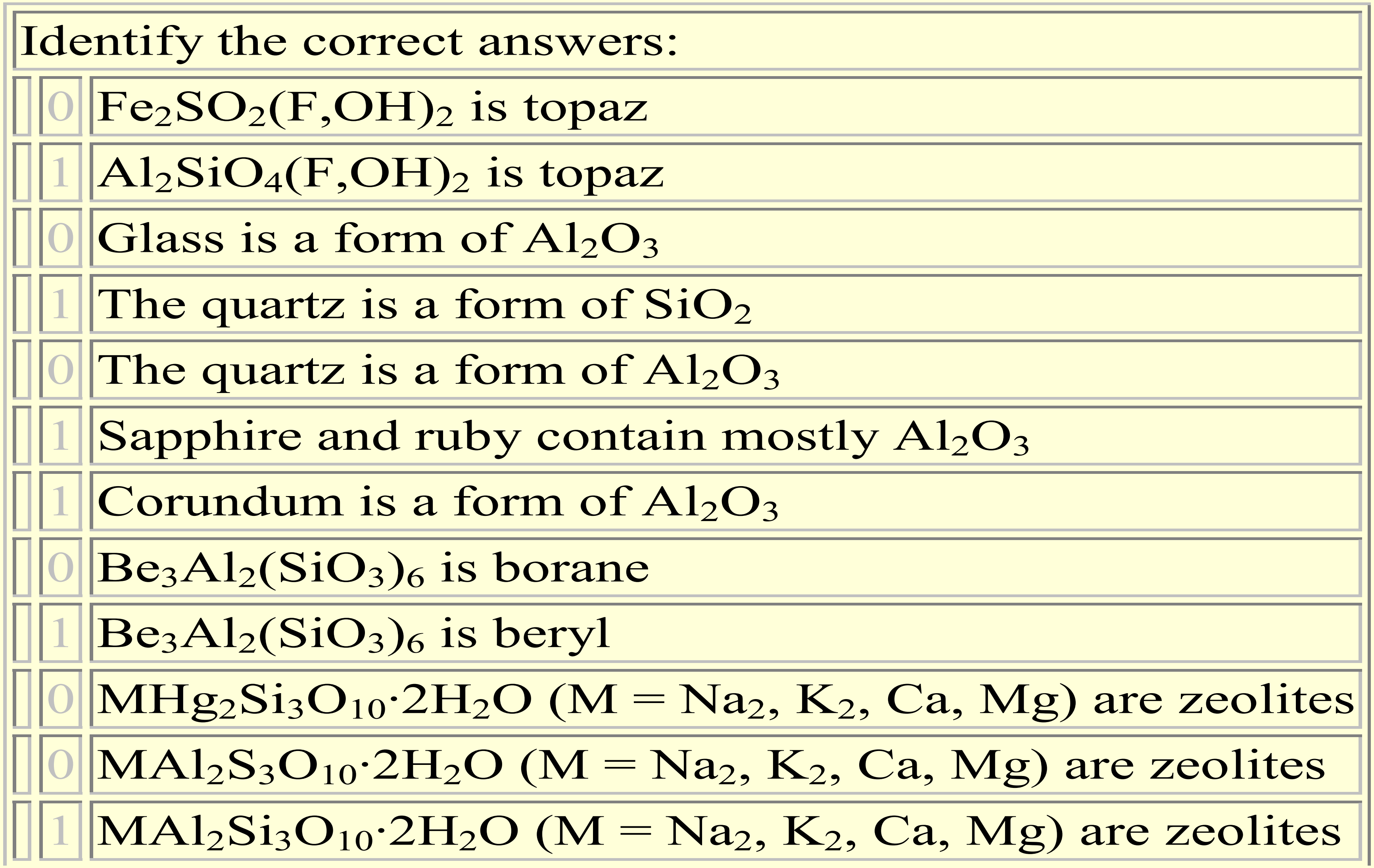
X^- & SO_4^{2-}

PO_4^{3-}, AsO_4^{3-}, VO_4^{3-}

SiO_4^{4-}


Hemimorphite
Hemimorphite
Catapleiite
Melanophlogite
Astrophyllite
Babingtonite
Inesite
Astrophyllite
Kornerupine
Kornerupine
Datolite
Elpidite
Inesite
Allanite
Dumortierite
Leucophane
Eudialyte
Pyrosmalite
Epididymite
Norbergite
Bannisterite, ferroan
Haüyne
Langbanite
Spodumene (var. hiddenite)
Spodumene (var. hiddenite)
Spodumene (var. hiddenite)
Ilvaite
Tugtupite

Questions & Responses



		Identify the correct answers:
	0	$Fe_2SO_2(F,OH)_2$ is topaz
	1	$Al_2SiO_4(F,OH)_2$ is topaz
	0	Glass is a form of Al_2O_3
	1	The quartz is a form of SiO_2
	0	The quartz is a form of Al_2O_3
	1	Sapphire and ruby contain mostly Al_2O_3
	1	Corundum is a form of Al_2O_3
	0	$Be_3Al_2(SiO_3)_6$ is borane
	1	$Be_3Al_2(SiO_3)_6$ is beryl
	0	$MHg_2Si_3O_{10}\cdot 2H_2O$ (M = Na_2, K_2, Ca, Mg) are zeolites
	0	$MAl_2S_3O_{10}\cdot 2H_2O$ (M = Na_2, K_2, Ca, Mg) are zeolites
	1	$MAl_2Si_3O_{10}\cdot 2H_2O$ (M = Na_2, K_2, Ca, Mg) are zeolites

Physical and chemical properties

Activation Energies Environmental Fate Isoelectric Point Activity Coefficients Equilibrium Constants Kinetic Data Adsorption and Adsorption Coefficients Expansion Coefficient Lattice Energies Antoine Coefficients and Constants Explosive Properties Log P Atomic Mass Constant Exposure Limits Luminescence Atomic Radius Extinction Coefficient Melting Point Avogadro's Constant Flammability Molar Absorptivity Bioconcentration Factor Flash Point Molecular Weight Biodegradation Free Energy NFPA Chemical Hazard Labelling Bohr Radius Freezing Point Octanol/Water Partition Coefficient Boiling Point Friction Coefficient Optical Rotation Boltzmann Constant Fundamental Physical Constants Oxidation-Reduction Potentials Bond Energies G-Factors

Sarah Shannon Stevenson

Science and Engineering Library

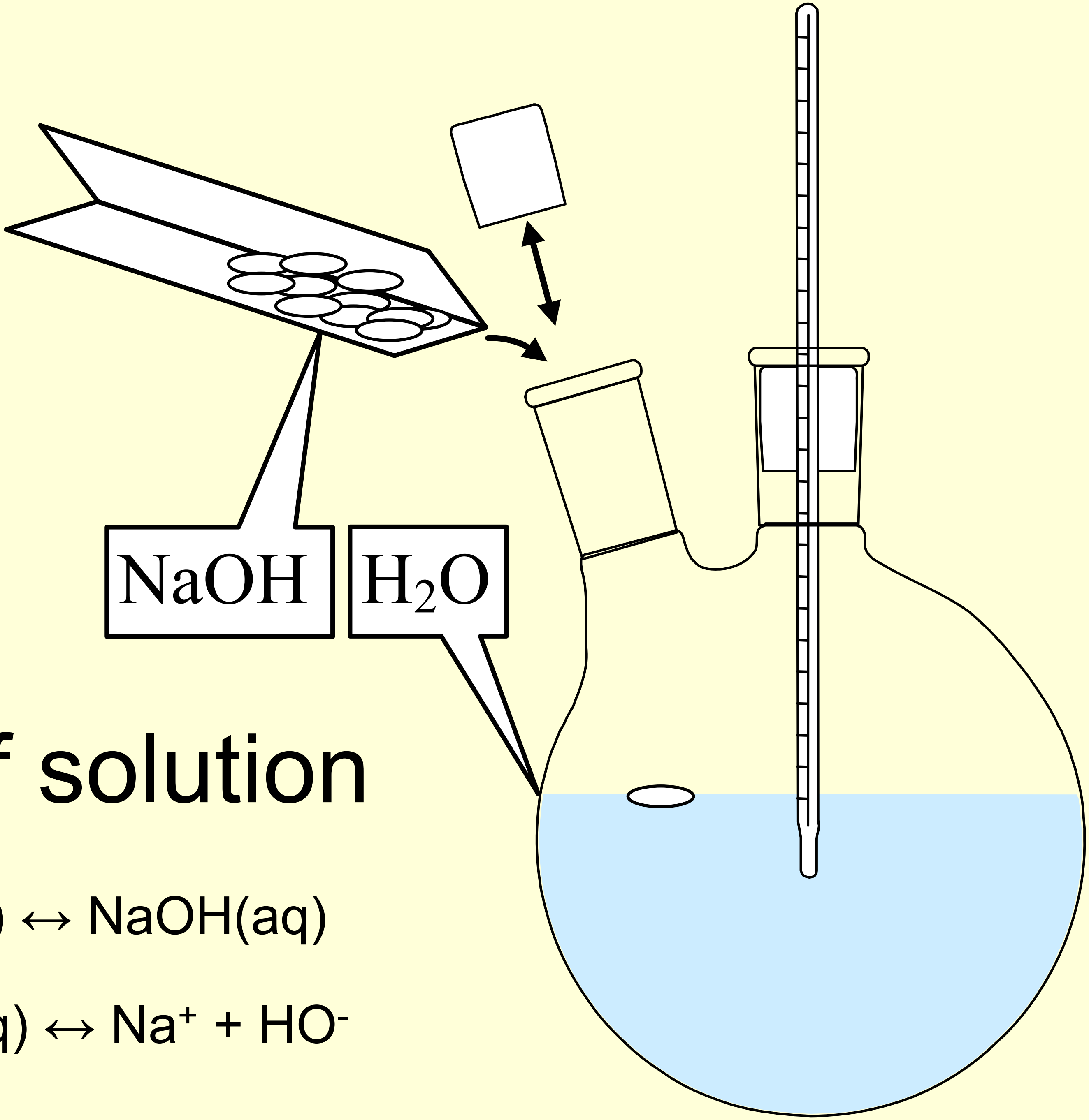
Jean & Alexander Heard Library ∗ Vanderbilt University

Oxidation States Bond Lengths/Bond Angles Gas Law Ozone Depletion Potential Compressibility Gibbs Free Energy Partition Coefficients Conductivity Global Warming Potential Phase Diagrams Conversion factors Half Life Physical Properties, General Corrosion Hazard Ratings, Code and Reactions pK Critical Properties Heat Capacity Proton Affinity Crystal Structure and Space Groups Heat of Combustion Radii Debye-Huckel Coefficients Heat of Dilution Rate Coefficients Decomposition Rate Heat of Formation Rate Constants Degradation Heat of Fusion Refractive Index Density Heat of Hydration Solubility Dielectric Constant Heat of Ionization Space Group Diffusion (Molecular) Heat of Mixing Specific Gravity Dipole Moment Heat of Neutralization Specific Heat Dissociation Constant

Heat of Polymerization Specific Rotation Distribution Coefficient Heat of Reaction Stability Constants Electrical Conductivity Heat of Solution Surface Tension Electrical Resistivity Heat of Sublimation Tensile Strength Electrode Potentials Heat of Transformation Thermal Conductivity Electron Affinity Heat of Transition Thermal Diffusivity Electron Binding Energies Heat of Vaporization Thermal Expansion Electron Configuration Henry's Law Constants and Coefficients Thermodynamic Properties Electronegativity Internuclear Distance Vapor Pressure Enthalpy Ionization Constant Virial Coefficient Enthalpy of... Ionization Energy Viscosity Entropy Ionization Heat Young's Modulus Ionization Potential

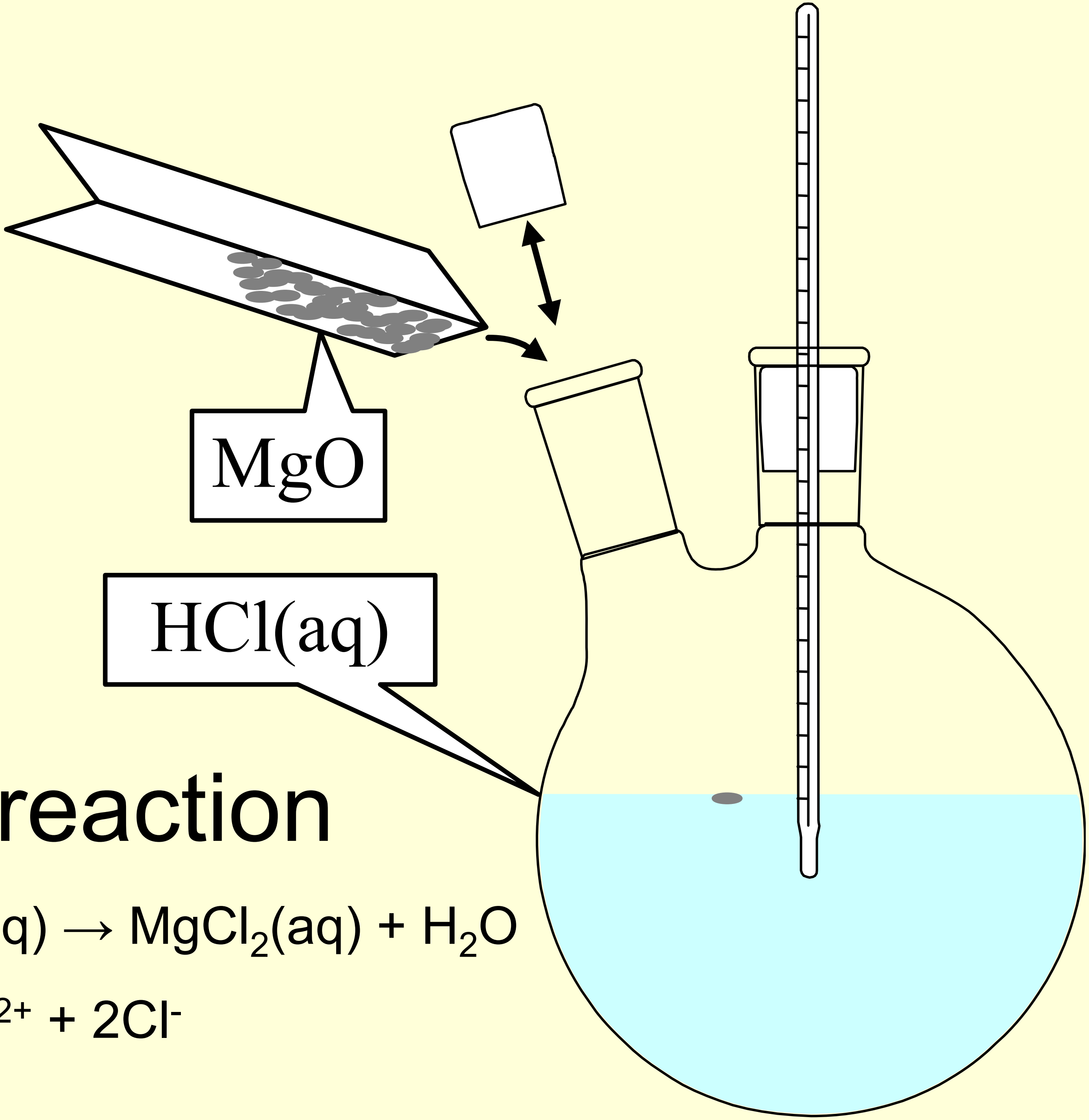
Sarah Shannon Stevenson
Science and Engineering Library
Jean & Alexander Heard Library * Vanderbilt University

Heat of solution



$\mathrm{NaOH(s)} \leftrightarrow \mathrm{NaOH(aq)}$

$\mathrm{NaOH(aq)} \leftrightarrow \mathrm{Na^+ + HO^-}$



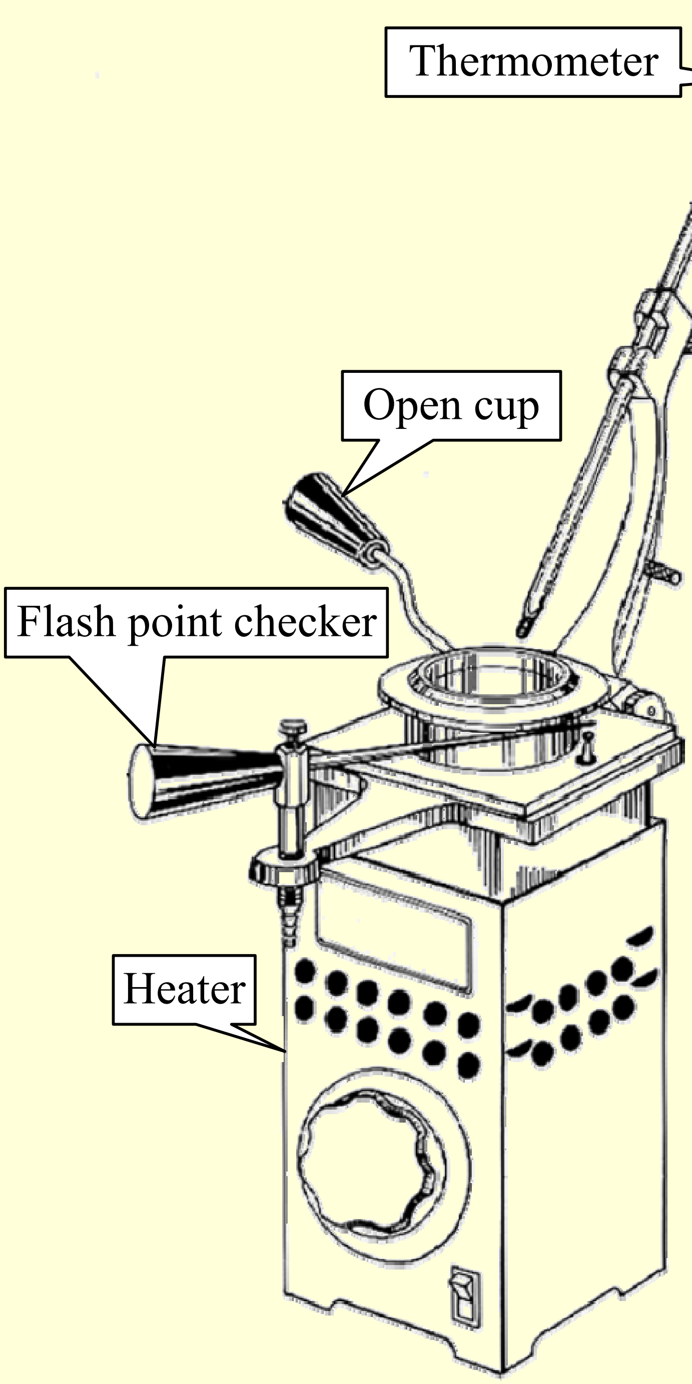
Heat of reaction

$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O$

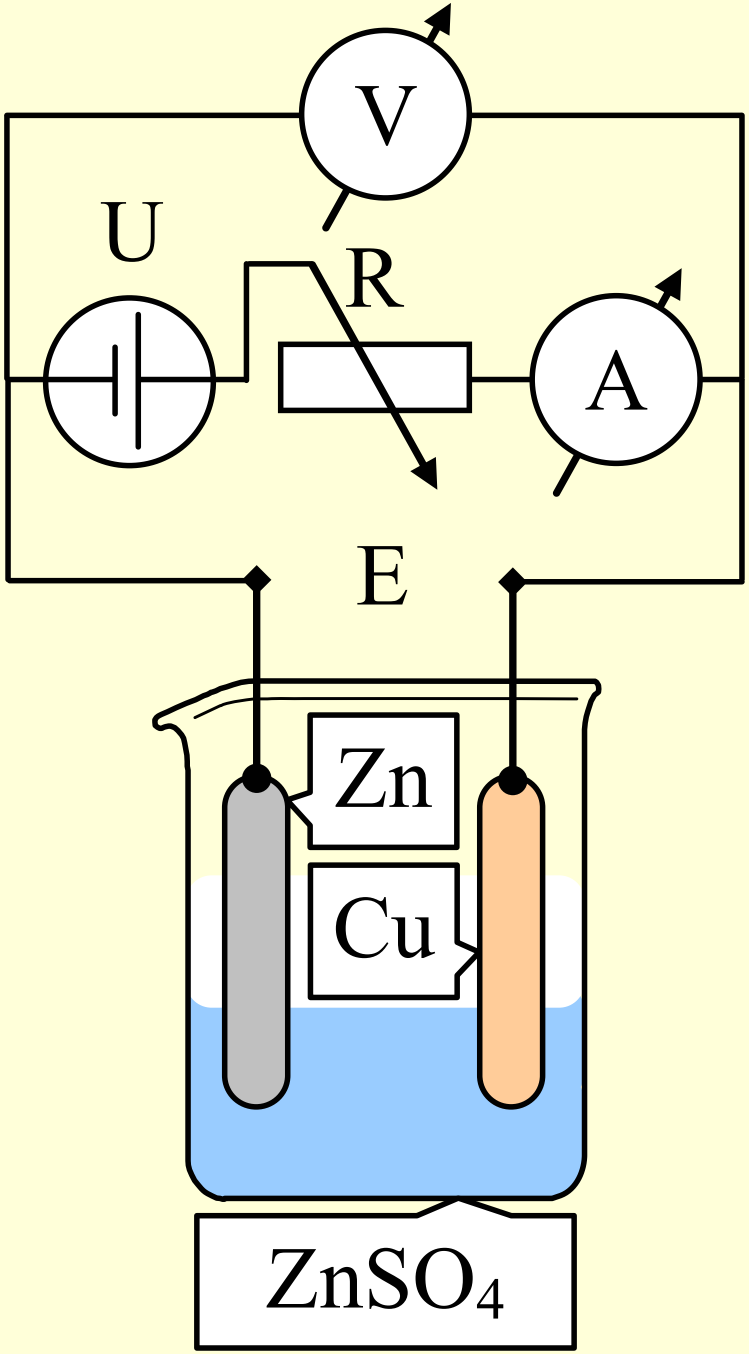
$MgCl_2(aq) \leftrightarrow Mg^{2+} + 2Cl^-$

Flash point

“open cup” method



Electrode potential



Closing circuit method

Chemical reactions

- The simplest reactions are of forming of compounds from elements. For instance: $C + S \rightarrow CS_2$
- Terms in the left of „→” are the reactants and terms in the right of „→” are products
- A problem is to establish the coefficients – the ratio between the participants; for the above example: $C + 2S \rightarrow CS_2$
- Other case is when reactants are homomolecues. For instance: $H_2 + O_2 \rightarrow H_2O$ and with coefficients: $H_2 + ½O_2 \rightarrow H_2O$
- If are imposed that all coefficients be integers, then: $2H_2 + O_2 \rightarrow 2H_2O$
- Establishing the coefficients of the reactions are the subject of stoechiometry.

Questions & Responses (see & Course4)

		For the reaction $H_2 + O_2 \longrightarrow H_2O$:
	1	It is possible that: $H_2(g) + O_2(g) \longrightarrow H_2O(g)$
	1	It is possible that: $H_2(g) + O_2(g) \longrightarrow H_2O(l)$
	0	H_2O is reactant
	1	H_2O is product of reaction
	1	H_2 and O_2 are reactants
	0	H_2 and O_2 are products of reaction
	0	The correct coefficients are 1 (H_2), 2 (O_2), 2 (H_2O)
	0	The correct coefficients are 1 (H_2), 1 (O_2), 1 (H_2O)
	0	The correct coefficients are 1 (H_2), 2 (O_2), 1 (H_2O)
	1	The correct coefficients are 2 (H_2), 1 (O_2), 2 (H_2O)

Conservation laws

- Stoechiometry is based on conservation laws – for the electrons and for the atoms.
- Electrons conservation: in a reaction the total number of electrons given by the atoms (or atom groups) equals with the total number of the electrons taken by the atoms. Exception is when electrical current is involved (subject of electrochemistry) when partial reactions not obey this principle, but the global reactions obey.
- Atoms number conservation: in a reaction the number of atoms from each species which enters in the reaction is equal to the number of atoms which result from the reaction. Exception is for nuclear reactions and in this case only the total rest mass is conserved.

Questions & Responses

Which of the following apply in determining coefficients of a chemical reaction:	
1	Coefficients are the smallest natural numbers satisfying the conservation of the number of atoms
0	Law transforming the mass into energy
0	The total number of protons given by the atoms is equal to the total number of protons taken by the atoms
0	The total number of neutrons given by the atoms is equal to the total number of neutrons taken by the atoms
1	The total number of electrons given by the atoms is equal to the total number of electrons taken by the atoms
1	For each type of atoms sum total number of atoms in the reactants is equal to the sum of the total number of atoms in the reaction products
0	Law of conservation of the number of neutrons
0	Law of conservation of the number of protons
1	Electron number conservation law
1	Law of conservation of the number of atoms

Algebraic method

- Are labeled as unknowns the coefficients of the reaction:

$$a\cdot KMnO_4 + b\cdot HCl \rightarrow c\cdot KCl + d\cdot MnCl_2 + e\cdot H_2O + f\cdot Cl_2$$

- It considers only the atoms number conservation. Please see that we have 5 equations and 6 unknowns; let us express all depending on one of them. Let be “e” the independent one. Then (after calculation):

$$\begin{cases} (K) & a = c \\ (Mn) & a = d \\ (O) & 4a = e \\ (H) & b = 2e \\ (Cl) & b = c + 2d + 2f \end{cases}$$

$$a = e/4;\ b = 2e;\ c = e/4;$$

$$d = e/4;\ e = e;\ f = 5e/8,$$

- Let be placed it in the initial equation:

$$({}^{e}/_{4})KMnO_4+(2e)HCl \rightarrow ({}^{e}/_{4})KCl+({}^{e}/_{4})MnCl_2+(e)H_2O+({}^{5e}/_{8})Cl_2$$

- The coefficients are natural expressed when are integers and do not have a common divisor greater than 1. A simple arithmetic give thus e = 8 as unique solution.

Coefficients of reactions: algebraic method

App for: $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$

Alg0. reaction: $(a)Cu + (b)HNO_3 \rightarrow (c)Cu(NO_3)_2 + (d)NO + (e)H_2O$

Alg1. assumptions: a, b, c, d, e natural not null numbers;

Alg2. conservation laws: (Cu): $a=c$; (N): $b=2c+d$; (H): $b=2e$; (O): $3b=6c+d+e$;

Alg3. system of equations; going with consecutive substitutions: $\boxed{c=a}$; $b=2a+d$; $b=2e$; $3b=6a+d+e$; $\boxed{b=2e}$; $2e=2a+d$; $6e=6a+d+e$; $\boxed{d=2e-2a}$; $6e=6a+2e-2a+e$; $\boxed{3e=4a}$ $\rightarrow$ $e=4$, $a=3$; $d=2$, $b=8$, $c=3$

Alg4. reaction: $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$ ☑

Oxidation state; oxidation number

- An often used concept is the oxidation number (O.N.) and is equal with the negative number of electrons required that the atom (or group of atoms; species) to be taken to become neutral. Is a formal concept, because charged species it exists only in certain environmental conditions. Along with this concept are used too the concept of oxidation (when during reaction electrons are taken) and of reduction (when electrons are given). Oxidation decreases O.N. and reduction increases O.N.

Rules establishing the oxidation state

- Electronegativity (elements, groups) and chemical activity (metals) provide a set of priority rules:

1. When are molecules of same element (homomolecules) the oxidation state is 0 (for instance Li in solid state, F_2, O_2, etc.);
2. Alkali (Li, Na, K, Rb, Cs, Fr) have oxidation state +1;
3. Fluorine have -1;
4. Oxygen have -2; exception is with F (ex. OF_6), peroxids (ex. NaO–ONa, Na_2O_2) and superoxids (ex. KO_2);
5. Hydrogen have +1; exception: hydrides of more chemical active metals (Li, K, Ca, Na, Fe, Zn, etc.);
6. Alkaline earth metals (Be, Mg, Ca, Sr, Ba, Ra) have +2;
7. Halogens (Cl, Br, I, At) have -1; electronegativity based rule
8. For covalent bonds of Carbon (organic compounds) belonging of the electrons again is established on electronegativity; a special case here – delocalized bonds as in benzene – conventionally fractional number accepted (9/6=1.5 for C in benzene).

Oxidation numbers method - steps

- Writing of the molecular formulas for reactants and products;
- Identification of the O.N. changed during reaction;
- Writing of the equations for oxidation and reduction;
- Electronic balance – electrons conservation;
- Atoms balance – number of atoms conservation;
- At the end of this steps coefficients are identified.

- Example: Hydrochloric acid reaction with kalium permanganate (source of chlorine in the lab). Steps:
- Reactants: $KMnO_4$, HCl; Products: KCl, $MnCl_2$, H_2O, Cl_2;
- Oxidation numbers:

$KMnO_4$ O.N.(K) = +1; O.N.(O) = -2; O.N.(Mn) = +7;
HCl O.N.(Cl) = -1; O.N.(H) = +1;
KCl O.N.(Cl) = -1; O.N.(K) = +1;
$MnCl_2$ O.N.(Cl) = -1; O.N.(Mn) = +2;
H_2O O.N.(H) = +1; O.N.(O) = -2;
Cl_2 O.N.(Cl) = 0;

- The elements changing its oxidation state are Cl (-1 → 0) and Mn (+7 → +2)
- Cl is oxidized, Mn is reduced; the changes in their oxidation state are expressed by:
- $Cl^{-1} - 1e^{-} \rightarrow Cl^{0}$
- $Mn^{+7} + 5e^{-} \rightarrow Mn^{+2}$
- Because the final state of Cl is as Cl_2 we should express this in the partial reaction too:
- $2Cl^{-1} - 2e^{-} \rightarrow Cl_2^{0}$
- $Mn^{+7} + 5e^{-} \rightarrow Mn^{+2}$

- Electrons balance: we must find the least common multiple of electrons given and taken; here is 10; the reactions are multiplied so that the electrons balance be accomplished:
- $5\cdot \big|\quad 2Cl^{-1} - 2e^{-} \rightarrow Cl_{2}0$
- $2\cdot \big|\quad Mn^{+7} + 5e^{-} \rightarrow Mn^{+2}$
- These two divisors becomes the coefficients of the implied species:

$\mathbf{2}\cdot KMnO_4 + (\mathbf{?})\cdot HCl \rightarrow (\mathbf{?})\cdot KCl + \mathbf{2}\cdot MnCl_2 + H_2O + \mathbf{5}\cdot Cl_2$

- Interrogation denotes that till now we do not possess enough information - in fact more exactly first “?” is (10+x+4) when the second “?” is (x). A remark: even at previous stage the atom conservation principle were applied (for manganese and here for chlorine). Same principle applies for the rest of atoms.

- It is easily to observe that following the known values we are able to provide values for the unknown ones.
- Thus, for K: 2·K (reactants) ⇒ 2·K (products), thus:

$$\mathbf{2}\cdot \mathrm{KMnO_4} + \mathbf{(?)}\cdot \mathrm{HCl} \rightarrow \mathbf{2}\cdot \mathrm{KCl} + \mathbf{2}\cdot \mathrm{MnCl_2} + \mathrm{H_2O} + \mathbf{5}\cdot \mathrm{Cl_2}$$

- For Cl: 2+2·2+5·2 (products) ⇒ 16 (Cl, in reactants) and:

$$\mathbf{2}\cdot \mathrm{KMnO_4} + \mathbf{16}\cdot \mathrm{HCl} \rightarrow \mathbf{2}\cdot \mathrm{KCl} + \mathbf{2}\cdot \mathrm{MnCl_2} + \mathrm{H_2O} + \mathbf{5}\cdot \mathrm{Cl_2}$$

- For H: 16·H (reactants) ⇒ 8·H_2 (in products):

$$\mathbf{2}\cdot \mathrm{KMnO_4} + \mathbf{16}\cdot \mathrm{HCl} \rightarrow \mathbf{2}\cdot \mathrm{KCl} + \mathbf{2}\cdot \mathrm{MnCl_2} + \mathbf{8}\cdot \mathrm{H_2O} + \mathbf{5}\cdot \mathrm{Cl_2}$$

- Only O remained. If the algorithm were correctly applied, then with oxygen we are able to check the balance. Indeed, 2·4 O in reactants and 8 O in products.
- This final remark lead us to rationalize that the sistem of equations applying both principles is over-determined – contains more equations than necessary. It may be considered that the number of atoms conservation is enough (electrons conservation provide one equation more). True.

Coefficients of reactions: oxidation numbers method

App for: $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$

ON0. assumptions: $Cu=Cu^0$; $HNO_3=H^+(NO_3)^-=H^+N^{5+}(O^{2-})_3$; $NO=N^{2+}O^{2-}$; $Cu(NO_3)_2=Cu^{2+}((NO_3)^-)_2$;

ON1. changes (reactants → products): $\boxed{Cu: Cu^0 \rightarrow Cu^{2+}}$; $\boxed{N(\text{in NO produced}): N^{5+} \rightarrow N^{2+}}$;

ON2. coefficients (conserving no. of e$^-$): $3Cu^0 - 3\cdot 2e^- + 2N^{5+} \rightarrow 3Cu^{2+} + 2N^{2+} - 2\cdot 3e^-$;

ON3. reaction: $(\boxed{3})Cu + (\boxed{2}+?)HNO_3 \rightarrow (\boxed{3})Cu(NO_3)_2 + (\boxed{2})NO + (?)H_2O$;

ON4. unknowns (x,y): $(3)Cu + (2+x)HNO_3 \rightarrow (3)Cu(NO_3)_2 + (2)NO + (y)H_2O$;

ON5. conserving no. of N atoms: $2+x = 3\cdot 2 + 2 \rightarrow \boxed{x = 6}$;

ON6. reaction: $(\boxed{3})Cu + (\boxed{2}+\boxed{6})HNO_3 \rightarrow (\boxed{3})Cu(NO_3)_2 + (\boxed{2})NO + (?)H_2O$;

ON7. unknown (y): $(\boxed{3})Cu + (\boxed{2}+\boxed{6})HNO_3 \rightarrow (\boxed{3})Cu(NO_3)_2 + (\boxed{2})NO + (y)H_2O$;

ON8. conserving no. of O atoms: $8\cdot 3 = 3\cdot 6 + 2 + y \rightarrow \boxed{y = 4}$;

ON9. reaction: $(\boxed{3})Cu + (\boxed{2}+\boxed{6})HNO_3 \rightarrow (\boxed{3})Cu(NO_3)_2 + (\boxed{2})NO + (\boxed{4})H_2O$;

ON10. checking (for no. of H atoms): $8 = 4\cdot 2$; ☑

Ion – electron method

- Exploits the fact that most of the reactions occurs in aqueous environment when dissociation occurs.
- Both reactants and products are existing ions and molecular species in solutions. Two partial balanced equations are written. Steps:
- Identification of the oxidant and of the conjugate reducer;
- Writing and balancing of the partial reactions;
- Charge equalizing between these partial reactions;
- Summing of the partial reactions. Example:

Premises: $HNO_{3(aq)} \rightleftharpoons H^{+}_{(aq)} + NO_3{}^{-}{}_{(aq)}$; $Cu(NO_3)_{2(aq)} \rightleftharpoons Cu^{2+}_{(aq)} + 2NO_3{}^{-}{}_{(aq)}$;
Partial reactions (half-reactions, in aq., implies H^+, e^-, H_2O):
÷ $HNO_3 + (3H^+ + 3e^-) \rightarrow NO + 2H_2O$;
÷ $Cu^0 + H_2O \rightarrow Cu^{2+} + (2e^- + 2H^+)$;
÷ $3Cu^0 + 2HNO_3\ (+6e^-) \rightarrow 3Cu^{2+} + 2NO\ (+6e^-)$;
Global reaction: $(3)Cu + (2+x)HNO_3 \rightarrow (3)Cu(NO_3)_2 + (2)NO + (y)H_2O$;
Continues with identification of the unknowns algebraically.

Coefficients of reactions: ion-electron method

App for: $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$

IE0. assumptions: $HNO_{3(aq)} \rightleftharpoons H^+_{(aq)} + NO_3^-{}_{(aq)}$; $Cu(NO_3)_{2(aq)} \rightleftharpoons Cu^{2+}_{(aq)} + 2NO_3^-{}_{(aq)}$;

IE1. half-reactions (aqueous, implies presence of H^+, e^-, H_2O):

$$HNO_3 + (3H^+ + 3e^-) \rightarrow NO + 2H_2O;$$

$$Cu^0 + H_2O \rightarrow Cu^{2+} + (2e^- + 2H^+);$$

$$3Cu^0 + 2HNO_3\ (+6e^-) \rightarrow 3Cu^{2+} + 2NO\ (+6e^-);$$

IE2. reaction: $(3)Cu + (2+x)HNO_3 \rightarrow (3)Cu(NO_3)_2 + (2)NO + (y)H_2O$;

IE3. go to ON5;

Applications: equalize following reactions

$AgNO_3 + H_2O + I_2 \rightarrow AgI + AgIO_3 + HNO_3$

$Cr_2(SO_4)_3 + NaOH + Br_2 \rightarrow Na_2CrO_4 + NaBr + Na_2SO_4 + H_2O$

$Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$

$H_2CrO_4 + NO + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

$H_2SeO_3 + FeSO_4 + H_2SO_4 \rightarrow Se + Fe_2(SO_4)_3 + H_2O$

$HNO_3 + FeSO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + NO + H_2O$

$K_2Cr_2O_7 + FeSO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

$K_2Cr_2O_7 + H_2S + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + S + H_2O$

$K_2Cr_2O_7 + HNO_2 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + HNO_3 + H_2O$

$K_2Cr_2O_7 + KBr + H_2SO_4 \rightarrow Br_2 + K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

Course 4

Hydrogen, Oxygen, Water

Hydrogen

http://l.academicdirect.org/Education/Training/Mendeleev/ ↵

SELECT * FROM `MendeleevSystem` WHERE 1 AND (0 OR `Number` = '1')

Symbol: H

Discovery: Hydrogen was first recognized as an element by Cavendish in 1766, and named by Lavoisier.

Appearance Hydrogen is a colourless gas.

Source Hydrogen is found in the sun and most of the stars, and is easily the most abundant element in the universe. The planet Jupiter is composed mostly of hydrogen, and there is a theory that in the interior of the planet the pressure is so great that metallic hydrogen is formed from solid molecular hydrogen. On this planet, hydrogen is found in the greatest quantities in water, but is present in the atmosphere only in small amounts - less than 1 part per million by volume. Hydrogen is prepared commercially by several methods; electrolysis of water, decomposition of hydrocarbons, displacement from acids by certain metals, action of steam on heated carbon, and action of sodium or potassium hydroxide on aluminum.

Uses Large quantities are used in the Haber Process (the production of ammonia for agricultural use) and for the hydrogenation of oils to form fats. It has several other uses, including welding and the reduction of metallic ores, and liquid hydrogen is important in cryogenics and superconductivity studies as its melting point is just above absolute zero.

...

- $1s^1$ configuration and ionization stability implies that the hydrogen to form, in most of the cases, ***covalent bonds***.
- Ions H^+ & $:H^-$ are unstable – chemical this fact are expressed with the term ‘very reactive’
- Thus, due to the intense electrostatic field surrounding the proton, the proton it cannot exist alone in same solution with polar molecules, or species which can be polarized – it reacts instantly with them.
- In water, H+ ion stabilizes becoming *hydronium* ion - H_3O^+, and in ammonia become *ammonium* ion, NH_4^+, the coordinative bond being due to a pair of NH_3 unbonded electrons.
- Formal: $H^+ + H_2O \rightarrow H_3O^+$, $\Delta H = -1093\ kJ \cdot mol^{-1}$
- Actually exists more than one hydronium species containing 3-12 water molecules, most likely being: $(H_2O)_4H^+$, but for simplicity all are written as H_3O^+

Q
&
R

In connection with the hydrogen ions:		
	0	The most probable value of n in $(H_2O)_nH^+$ is 8
	1	The most probable value of n in $(H_2O)_nH^+$ is 4
	0	In ammonia H^- ions stabilizes becoming NH_4^-
	1	In ammonia H^+ ions stabilizes becoming NH_4^+
	0	In water H^- ions stabilizes becoming $(H_2O)_nH^-$
	1	In water H^+ ions stabilizes becoming $(H_2O)_nH^+$
	0	H^- ions very low reactive
	1	H^- ions very reactive
	1	H^- ions are instable
	0	H^- ions are stable
	0	H^+ ions very low reactive
	1	H^+ ions very reactive
	1	H^+ ions are instable
	0	H^+ ions are stable

- Hydrogen have three isotopes : protium, deuterium, and tritium: ${}_{1}^{1}H$, ${}_{1}^{2}H$ (noted D) şi ${}_{1}^{3}H$ (noted T). Of course the mass of D is twice of the mass of protium and the mass of tritium is three times than of protium. 99.985% from crust's hydrogen is protium and only 0.015% is deuterium. This is the reason for which the atomic mass of the hydrogen is fractional (1.008). Heaviest isotope - tritium - is β^- radioactive, having the halving time $T_{1/2} = 12.26$ years, passing to helium. It can be used without danger as *radioactive tracer* – shows the manner in which a succession of chemical reactions or technological stages are deployed.

Q
&
R

In connection with isotopes of hydrogen:		
	0	p is radioactive having $T_{1/2} = 12.26$ years
	0	D is radioactive having $T_{1/2} = 12.26$ years
	1	T is radioactive having $T_{1/2} = 12.26$ years
	0	$3*M(T) = 2*M(D)$
	0	$3*M(T) = M(p)$
	0	$2*M(D) = M(p)$
	1	$2*M(T) = 3*M(D)$
	1	$M(T) = 3*M(p)$
	1	$M(D) = 2*M(p)$
	0	$T = {}^{30}{}_{15}H$ is tritium
	0	$D = {}^{20}{}_{10}H$ is deuterium
	0	$p = {}^{10}{}_{5}H$ is protium
	1	$T = {}^{3}{}_{1}H$ is tritium
	1	$D = {}^{2}{}_{1}H$ is deuterium
	1	$p = {}^{1}{}_{1}H$ is protium

Obtaining of the hydrogen

- From low-mass hydrocarbons. In the industrial processes of gasoline refining, hydrogen is the secondary product. Thus, during synthesis of the octane, C_8H_{18}, starting from small molecules, hydrogen are obtained too:

$$2C_2H_6 + C_4H_8 \rightarrow C_8H_{18} + H_2$$

- Other procedure is to crack hydrocarbons – breaking of the larger to smaller hydrocarbons – it results hydrogen and unsaturated hydrocarbons. For instance:

$$C_{12}H_{26} \rightarrow C_5H_{10} + C_4H_8 + C_3H_6 + H_2$$

- Other methods uses along with hydrocarbons, water vapors and catalysts. Thus, for methane:

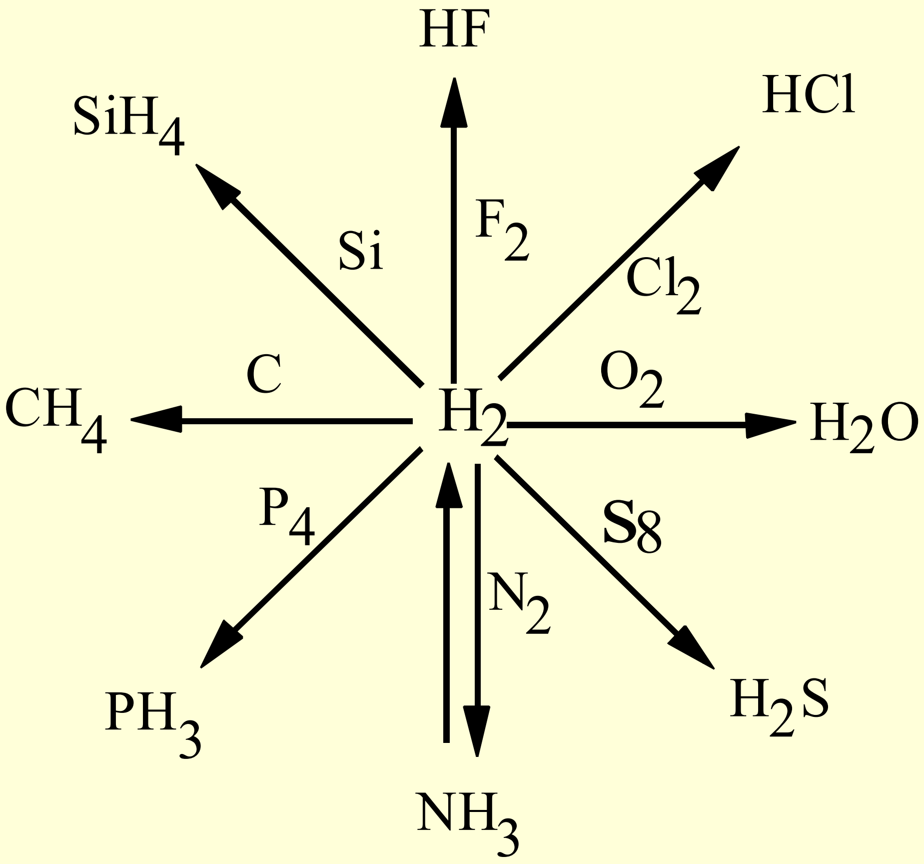
$$CH_4 + H_2O \rightarrow CO + 3H_2$$

- Product ($CO + H_2$ mixture) is known as *gas of synthesis* because can be used as raw material in a series of industrial syntheses, such as of the methyl alcohol (or methanol). With a second catalytic reaction the carbon oxide may be converted with water vapors to carbon dioxide and hydrogen – phenomena being known as the reaction of water gas:

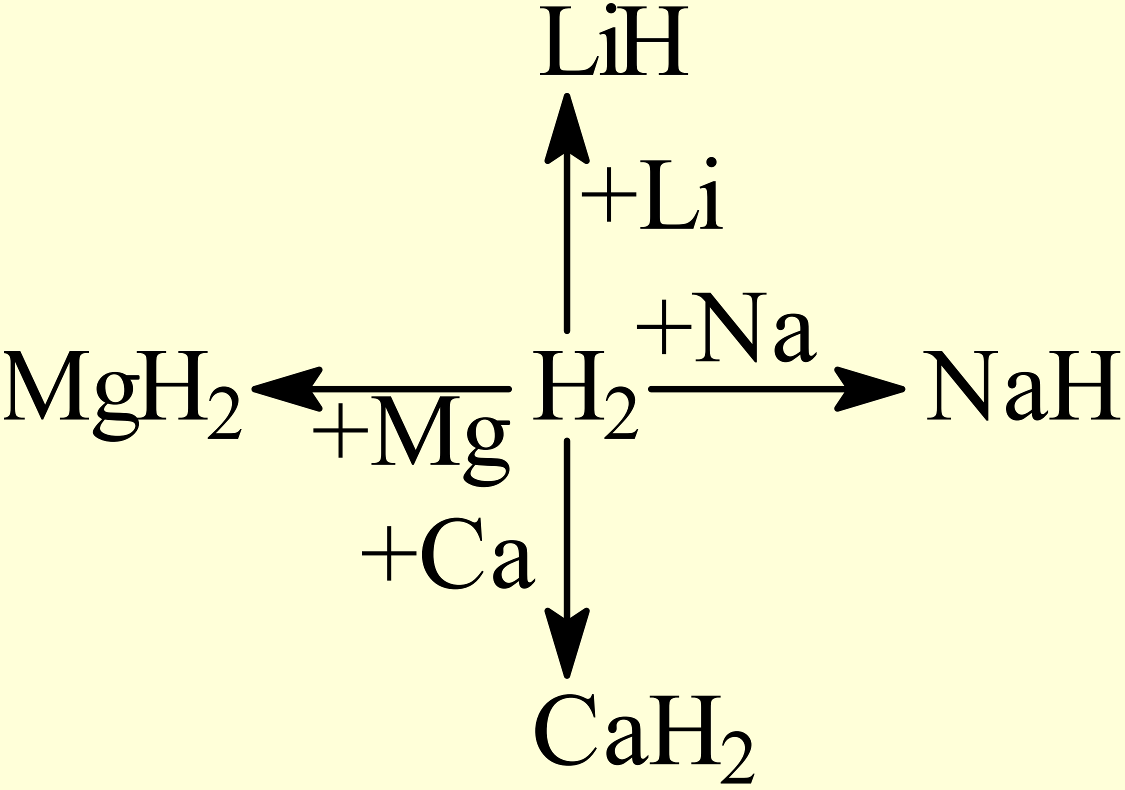
$$CO + H_2O \, _{Fe/Cu}\!\rightarrow_{500°C} \, CO_2 + H_2$$

Fe/Cu - fer activated with copper.

Chemical properties of hydrogen. Reactions with nonmetals

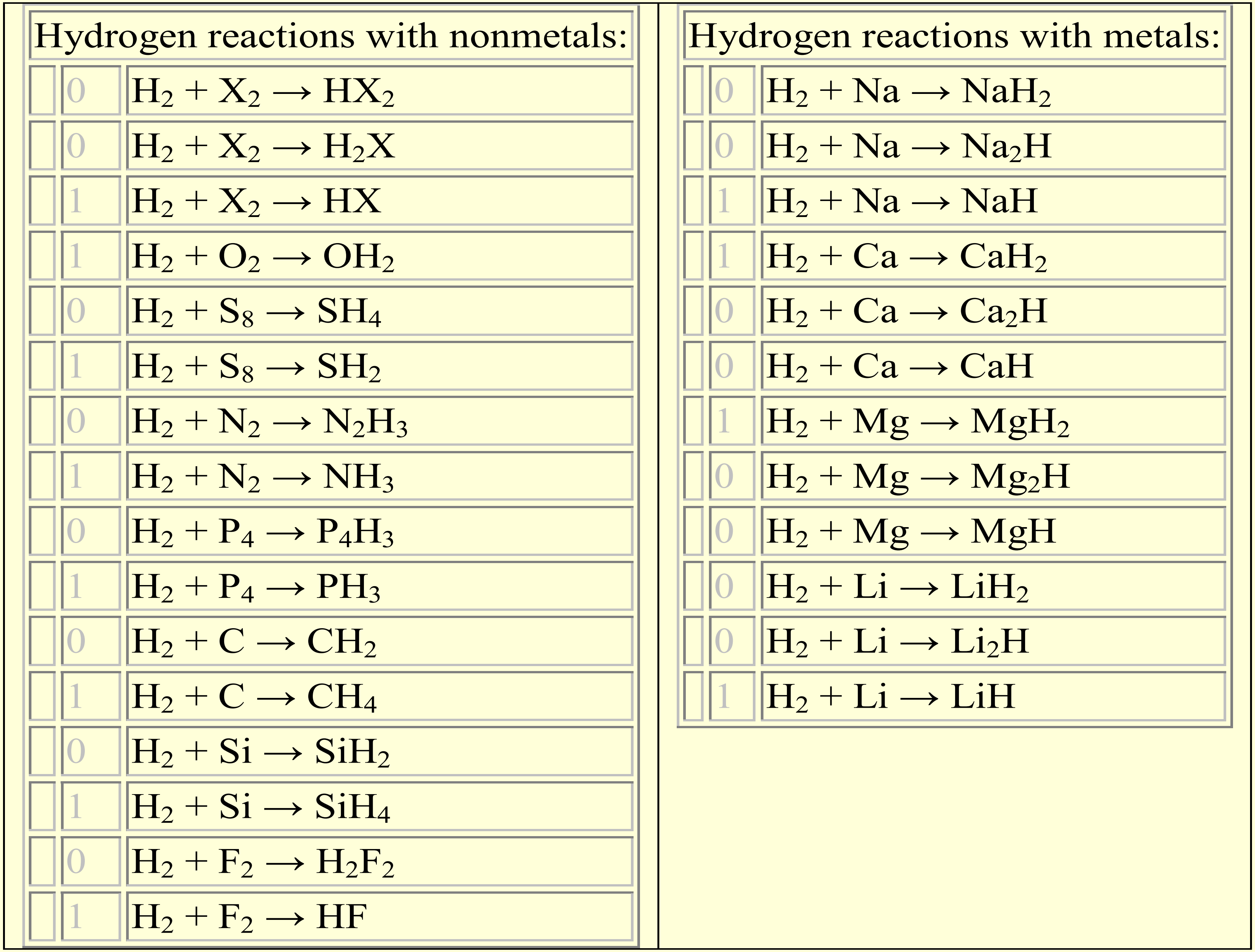


Chemical properties of hydrogen. Reactions with metals



With other metals does not react, but may associate, through specific interactions, to give interstitial metallic hydrides, very similarly to alloys

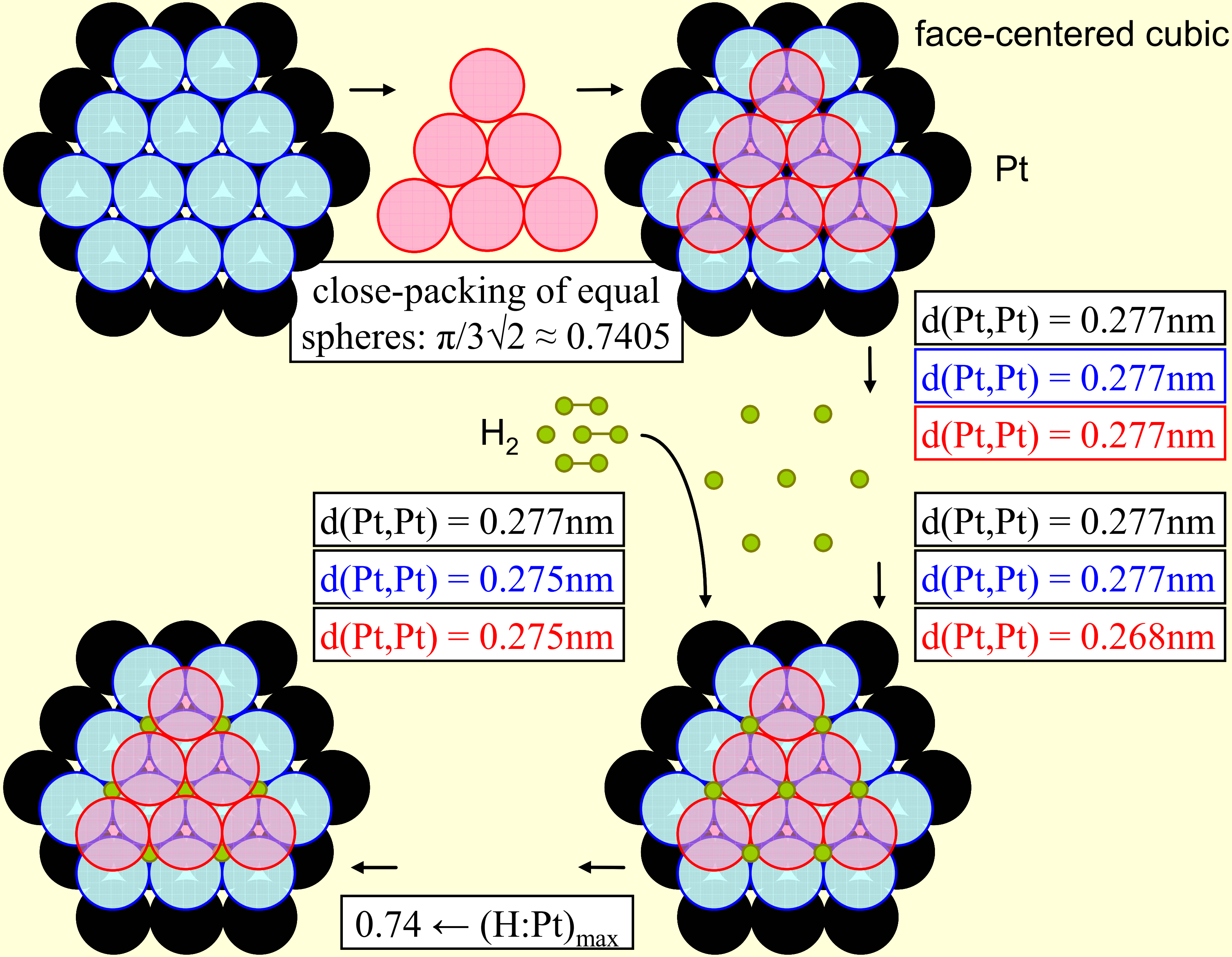
Q
&
R



		Hydrogen reactions with nonmetals:
	0	$H_2 + X_2 \rightarrow HX_2$
	0	$H_2 + X_2 \rightarrow H_2X$
	1	$H_2 + X_2 \rightarrow HX$
	1	$H_2 + O_2 \rightarrow OH_2$
	0	$H_2 + S_8 \rightarrow SH_4$
	1	$H_2 + S_8 \rightarrow SH_2$
	0	$H_2 + N_2 \rightarrow N_2H_3$
	1	$H_2 + N_2 \rightarrow NH_3$
	0	$H_2 + P_4 \rightarrow P_4H_3$
	1	$H_2 + P_4 \rightarrow PH_3$
	0	$H_2 + C \rightarrow CH_2$
	1	$H_2 + C \rightarrow CH_4$
	0	$H_2 + Si \rightarrow SiH_2$
	1	$H_2 + Si \rightarrow SiH_4$
	0	$H_2 + F_2 \rightarrow H_2F_2$
	1	$H_2 + F_2 \rightarrow HF$

		Hydrogen reactions with metals:
	0	$H_2 + Na \rightarrow NaH_2$
	0	$H_2 + Na \rightarrow Na_2H$
	1	$H_2 + Na \rightarrow NaH$
	1	$H_2 + Ca \rightarrow CaH_2$
	0	$H_2 + Ca \rightarrow Ca_2H$
	0	$H_2 + Ca \rightarrow CaH$
	1	$H_2 + Mg \rightarrow MgH_2$
	0	$H_2 + Mg \rightarrow Mg_2H$
	0	$H_2 + Mg \rightarrow MgH$
	0	$H_2 + Li \rightarrow LiH_2$
	0	$H_2 + Li \rightarrow Li_2H$
	1	$H_2 + Li \rightarrow LiH$

H absorption on Pt



face-centered cubic

Pt

close-packing of equal spheres: $\pi/3\sqrt{2} \approx 0.7405$

d(Pt,Pt) = 0.277nm
d(Pt,Pt) = 0.277nm
d(Pt,Pt) = 0.277nm

H_2

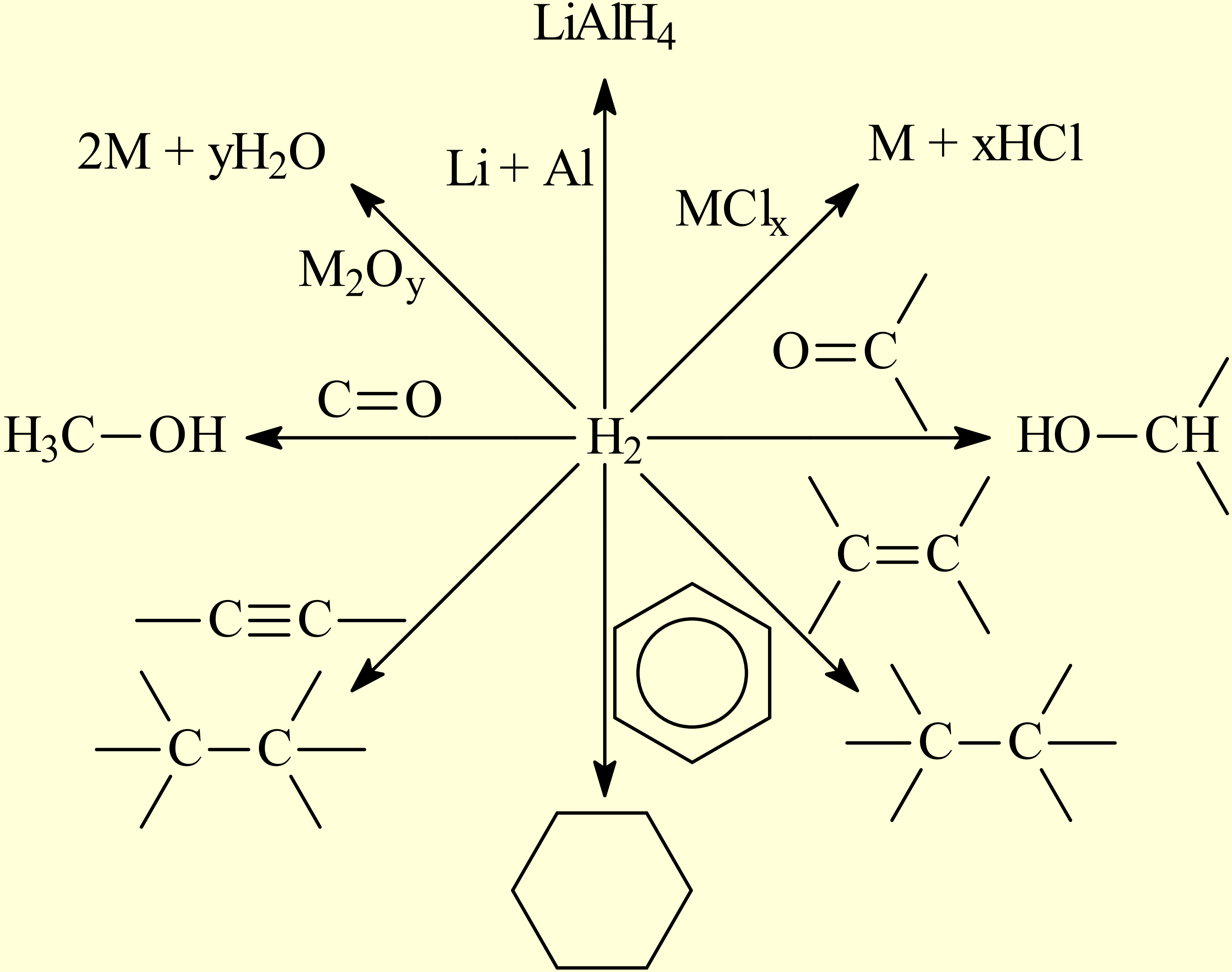
d(Pt,Pt) = 0.277nm
d(Pt,Pt) = 0.275nm
d(Pt,Pt) = 0.275nm

d(Pt,Pt) = 0.277nm
d(Pt,Pt) = 0.277nm
d(Pt,Pt) = 0.268nm

$0.74 \leftarrow (\mathrm{H:Pt})_{max}$

Reduction character of the hydrogen

- With many combinations, organic included, hydrogen have a reduction character, similarly with the one from the reaction with nonmetals (oxidants). Due to this character, hydrogen is industrially used in the reaction for copper (or other metals) reduction: $Cu^{2+}_{(aq)} + H_{2(g)} = Cu_{(s)} + 2H^{+}_{(aq)}$
- Thus, after extracting as cooper sulfate of the cooper from ore, though bubbling of hydrogen, metalic cooper may be separated. About 1/3 from all industrial hydrogen is used for such kind of reductions. The necessary condition for this reduction is that the redox potential ($\varepsilon°$) of the metal to be positive.
- Also, a large number of oxides can be reduced with hydrogen to metals, by using a high temperature, and thus serving to the obtaining of the metals. For instance, wolfram trioxide reduces to metal via: $WO_3 + 3H_2 \rightarrow W + 3H_2O$


LiAlH$_4$
Li + Al
2M + yH$_2$O
M$_2$O$_y$
M + xHCl
MCl$_x$
H$_2$
C═O
H$_3$C—OH
O═C
HO—CH
C═C
—C≡C—
C—C
C—C

Q & R

Hydrogen reducing character is manifested in:		
	1	$H_2 + Li + Al \longrightarrow LiAlH_4$
	0	$^y/_2H_2 + MX_y \longrightarrow MH + X_2$
	1	$^y/_2H_2 + MX_y \longrightarrow M + yHX$
	0	$H_2 + M_2O_y \longrightarrow 2MH + {}^y/_2O_2$
	1	$H_2 + M_2O_y \longrightarrow 2M + yH_2O$
	0	$H_2 + HC{\equiv}CH \longrightarrow H_2C\text{-}CH_2$
	0	$H_2 + HC{\equiv}CH \longrightarrow H_4C\text{-}CH_4$
	1	$H_2 + HC{\equiv}CH \longrightarrow H_3C\text{-}CH_3$
	0	$H_2 + H_2C{=}CH_2 \longrightarrow HC{\equiv}CH$
	1	$H_2 + H_2C{=}CH_2 \longrightarrow H_3C\text{-}CH_3$
	0	$H_2 + H_2C{=}O \longrightarrow CO_2 + H_2O$
	1	$H_2 + H_2C{=}O \longrightarrow H_3C\text{-}OH$

- On another hand, a large quantity of hydrogen is used in the alimentary industry for hydrogenation of vegetable oils (they have a isolated double bond in a saturated chain, R, from a fatty acid (R-COOH):

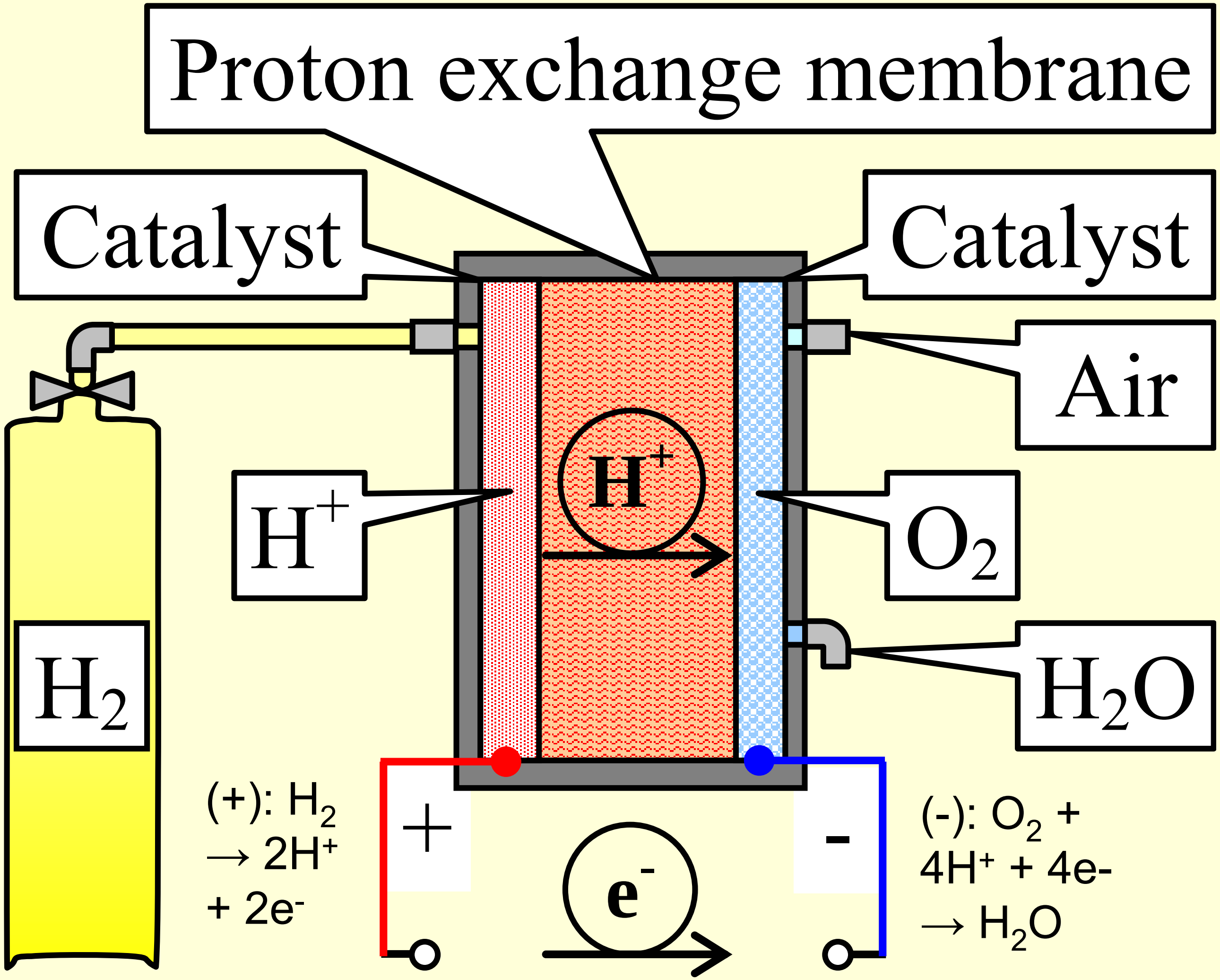
$$H_2 + \ldots\text{-}CH_2\text{-}CH= CH\text{-}CH_2\text{-} \ldots \rightarrow \ldots\text{-}CH_2\text{-}CH_2 – CH_2\text{-}CH_2\text{-}\cdots$$

- The process is a reduction too. Due to this treatment the oils (liquid fats), containing double bonds, become solid fats (margarine) due to the fact that din cauza faptului că, embedding better, the interactions between chains are stronger
- Hydrogen is used in the industry practice due to the catalytic hydrogenation reactions; one important is hydrogenation of nitrogen, carbon oxide and natural oils:
  - nitrogen (Haber procedure);
  - Carbon oxide: $CO + 2H_2 \rightarrow CH_3OH$ (methanol);
  - Unsaturated oils to saturated ones for margarine.
- All below mentioned reactions are with catalysts and using energetic conditions.

Alternative sources of energy

- Polymer Electrolyte Membrane Fuel Cell (PEMFC)
- Solid Electrolyte Cell Fuel or Ion Exchange Membrane Fuel Cell (IEMFC)
- The anodes are expensive because of platinum. One thus seeks to decrease the quantities of Pt used: large progress was made making pass the content of 4 mg/cm^2 to 0.1 mg/cm^2 but it would seem that one cannot decrease still much this content.

Hydrogen fuel cell



(+): $H_2 \rightarrow 2H^+ + 2e^-$

(-): $O_2 + 4H^+ + 4e^- \rightarrow H_2O$

The negative ions (electrons) are retained by the catalyst of H^+ (usually Platinum) at anode.

Only H^+ are mobile and free to transport the positive load through the membrane consisting of an organic compound.

At the surface of cathode (usually Nickel) water are produced.

Oxygen

- Oxygen is the first element of group 16 and have the following electronic configuration $2s^22p^4$; is the second element by the electronegativity, after fluorine
- Oxygen is the most spread in the nature (46.59%) in air in free state (20.9% volume), în water (88.89%) and in crust being part of the most rocks and ores (46.6%).
- Existence of the oxygen makes happen the occurrence of the superior life forms on Earth. Oceans cover ¾ of the Earth surface. In crust, oxygen are found as oxy-salts – silicates and alumino-silicates, carbonates, sulfates, nitrates, nad as oxides.
- It has 3 isotopes: ^{16}O (99.759%), ^{17}O (0.0374%), ^{18}O (0.239%). Through fractioned distilling of water till 97% we may concentrate ^{18}O and 4% ^{17}O. ^{18}O uses as tracer in the reactions involving oxygen. ^{17}O has nuclear spine and may serve in (magnetic) resonance studies, for instance to make distinction between the complex fixed water and the water from solution: $Co(NH^3)_5 \cdot H_2O$.

Questions & Responses

	The oxygen:
0	Is ~5% from crust (~4.7%$_{\text{mass}}$, ~6%$_{\text{at}}$)
1	Is ~50% from crust (~47%$_{\text{mass}}$, ~60%$_{\text{at}}$)
0	Is ~10%$_{\text{mass}}$ from water
1	Is ~90%$_{\text{mass}}$ from water
0	Is ~80%$_{\text{vol}}$ from air
1	Is ~20%$_{\text{vol}}$ from air
0	Is a relatively low spread in the environment (~5%)
1	Is the most spread element in the environment (~50%)
0	Is the first element by electronegativity before fluorine
1	Is the second element by electronegativity after fluorine
0	Is the second element of Group 16
1	Is the first element of Group 16

Q & R

Oxygen is found in:

0	One of its 2 isotopic states: ^{7}O and ^{8}O
1	One of its 3 isotopic states: ^{16}O, ^{17}O, and ^{18}O
0	In middle parts of the atmosphere (stratosphere, mesosphere) as homoatomic molecules of tetraoxygen (O_4)
1	In middle parts of the atmosphere (stratosphere, mesosphere) as homoatomic molecules of trioxygen (O_3)
1	In lower parts of the atmosphere (planetary boundary layer, troposphere), as homoatomic molecules of dioxygen (O_2)
0	In upper parts of the atmosphere (thermosphere and exosphere), as homoatomic molecules of dioxygen (O_2)
0	In lower parts of the atmosphere (planetary boundary layer, troposphere, stratosphere, mesosphere), in atomic form (O)
1	In upper parts of the atmosphere (thermosphere and exosphere), in atomic form (O)
0	In crust, as oxy-salts: silicides, alumino-silicides, carbonides, sulfides, and nitrides
1	In crust, as oxy-salts: silicates, alumino-silicates, carbonates, sulfates, nitrates, and as oxides
0	Water of the oceans, covering $^{1}/_{4}$ of the Earth's surface
1	Water of the oceans, covering $^{3}/_{4}$ of the Earth's surface

- **Allotropic states.** Oxygen has two allotropic states: O_2 – di-oxygen, and O_3 – tri-oxygenor ozone.
- Reaction of forming O_3 from O_2 is endothermic and its reverse is exothermic:

$$3O_2 \rightarrow 2O_3 \qquad \Delta H = +8.1\ \text{kJ}\cdot\text{mol}^{-1}$$

$$2O_3 \rightarrow 3O_2 \qquad \Delta H = -142\ \text{kJ}\cdot\text{mol}^{-1}$$

- O_3 results also from thermal dissociation of O_2 at over 1500°C, when O_2 dissociates in 2 atoms of O with which O_2 leads to O_3.
- The action of the ultraviolet radiation (UV) on O_2 produces traces of O_3 in the upper atmosphere (stratosphere). Highest concentration of ozone are about 25Km altitude. The presence of the ozone is of vital importance for protecting Earth’s surface on excessive exposure to UV radiations.

Q & R

Related to the ozone:	
0	The presence of the ozone is of vital importance for protecting Earth's surface on excessive exposure to X radiations
1	The presence of the ozone is of vital importance for protecting Earth's surface on excessive exposure to UV radiations
1	Highest concentration of ozone is at about 25000 m altitude
0	Highest concentration of ozone is at about 2500 m altitude
0	Lowest concentration of ozone is at about 25 km altitude
1	Highest concentration of ozone is at about 25 km altitude
0	The action of the IR radiation on O_3 produces traces of O_2 in exosphere
1	The action of the UV radiation on O_2 produces traces of O_3 in stratosphere

Methods obtaining O_2

Industrial

- **Fractioned distilling of liquid air**. O_2 have b.p. = -182.9 °C and N_2 have b.p. = -195.7 °C, and thus may be easily separated one to each other. Oxygen are kept in steel tubes at pressures of about 150 atm.
- **Acidic or alkaline water electrolysis.** For instance NaOH 15-20% solutions, by using cathode of Fe and anode of graphite. At cathode are separated H_2 and at anode are separated O_2.

In lab

- Small quantities of O_2 can be obtained from thermal decomposition of some combinations*:*
- - oxides: $2HgO \rightarrow O_2 + 2Hg$, $3MnO_2 \rightarrow O_2 + Mn_3O_4$
- - peroxides: $2BaO_2 \rightarrow O_2 + 2BaO$
- - salts: $KClO_3 \rightarrow {}^3/_2O_2 + KCl$, $2KMnO_4 \rightarrow O_2 + MnO_2 + K_2MnO_4$
- Other way is from some redox reactions, such as:

$$4MnO_4^- + 12H^+ \rightarrow 5O_2 + 4Mn^{2+} + 6H_2O$$

Q & R

	In connection with the production and use of the oxygen:
0	The green plants, using light do: $C_x(H_2O)_y + (x+{}^{y}/_{2})O_2 \rightarrow xCO_2 + yH_2O$
0	Breathing organisms, producing energy do: $xCO_2 + yH_2O \rightarrow C_x(H_2O)_y + (x+{}^{y}/_{2})O_2$
1	Breathing organisms, producing energy do: $C_x(H_2O)_y + (x+{}^{y}/_{2})O_2 \rightarrow xCO_2 + yH_2O$
1	The green plants, using light do: $xCO_2 + yH_2O \rightarrow C_x(H_2O)_y + (x+{}^{y}/_{2})O_2$
0	$4AlBr_3 + 3O_2 \rightarrow 6Br_2O + 4Al$
1	$4AlBr_3 + 3O_2 \rightarrow 6Br_2 + 2Al_2O_3$
0	$4HX + O_2 \rightarrow 2X_2 + 2H_2O$, $X = F$
1	$4HX + O_2 \rightarrow 2X_2 + 2H_2O$, $X = Cl, Br, I$
0	Combustion of fossil coils and hydrocarbons is a secondary source of heating (~25% in 2014)
1	Combustion of fossil coils and hydrocarbons is the main source of heating (~75% in 2014)
0	Oxygen can be obtained by distilling the water
1	Oxygen can be obtained by distilling the air

Ionomolecular species of oxygen

	O_2^+	O_2	O_2^-	O_2^{2-}
Name	cation	dioxygen	superoxide	peroxide
Bond order	2.5	2.0	1.5	1.0
$d_{O\text{-}O}$ (nm)	0.112	0.121	0.135	0.148
Binding energy (KJ·mol^{-1})	641	493	0	210

Burns

- Some elements reacts energetically with oxygen with releasing of a lot of heat and light (live burns). These reactions are even more violent in pure O_2 than are in air. From nonmetals, phosphorus, carbon and sulfur burns easily in O_2, and between metals Mg, Al, Fe (when are heat to incandescence).
- Burn of fossil coals and of hydrocarbons is the main source of heating.
- Burn of H_2 or hydrocarbons with O_2 or air is a explosive reaction (the mechanism is of chain-reaction type, through free atoms and radicals, with a initiation phase with spark or flame).

- Oxidation of the halides to elementary halogen:

$$SiCl_4 + O_2 \rightarrow 2Cl_2 + SiO_2$$

$$MgCl_2 + O_2 \rightarrow Cl_2 + 2MgO$$

$$2AlBr_3 + {}^3/_2O_2 \rightarrow 3Br_2 + Al_2O_3$$

- Oxidation of sulfides (roasting), metallurgy important:

$$2FeS + {}^7/_2O_2 \rightarrow Fe_2O_3 + 2SO_2$$

$$ZnS + {}^3/_2O_2 \rightarrow ZnO + SO_2$$

- Oxidation of inferior oxides:

$$CO + {}^1/_2O_2 \rightarrow CO_2$$

$$2FeO + {}^1/_2O_2 \rightarrow Fe_2O_3$$

$$SO_2 + {}^1/_2O_2 \rightarrow SO_3 \text{ (with catalysts)}$$

$$NO + {}^1/_2O_2 \rightarrow NO_2$$

- Oxidation of covalent hydrides (of nonmetals):

$$2HX + {}^1/_2O_2 \rightarrow X_2 + H_2O,\ X = Cl, Br, I$$

$$SH_2 + {}^1/_2O_2 \rightarrow S + H_2O$$

$$2NH_3 + {}^3/_2O_2 \rightarrow N_2 + 3H_2O$$

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2O$$

- In water, there are many possible reactions of chemical dissolving of oxygen:

$$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O,\ \varepsilon_0 = +1.229\ V$$

$$O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^-,\ \varepsilon_0 = +0.401\ V$$

$$O_2 + 2H^+ + 2e^- \leftrightarrow H_2O_2,\ \varepsilon_0 = +0.682\ V$$

$$O_2 + H_2O + 2e^- \leftrightarrow OH^- + HO_2^-,\ \varepsilon_0 = -0.076\ V$$

Oxygen biochemistry

- Existence of the oxygen in terrestrial atmosphere is essential for life on Earth. Most of the oxygen from atmosphere are produced during photosynthesis process by green plants, in which the chlorophyll converts the solar energy into the chemical energy – synthesizing sugars:

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

- This is a endothermic reaction which may occur only in the presence of the light. Living organisms consumes the oxygen from atmosphere as in following reaction:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

Oxides

- Ionic, covalent-ionic, and covalent
- **Ionic:**
  - Elements from groups 1 and 2 provides oxides with predominant ionic bonds
  - Metals of the d and f blocks, in lower oxidation states, lead to ionic oxides, having a alkali character; crystallizes in ionic networks
  - O^{2-} ion exists only in solid state;
  - In water presence hydrolyses: $O^{2-} + H_2O \rightarrow 2OH^-$

- **Covalent:**
  - Are the oxides of the nonmetals and have a acidic character
  - The molecules are simple, for instance CO, CO_2, NO, NO_2, SO_2, SO_3
  - Some transitionally metals may have covalent character in their higher oxidation states
  - Soluble ones in water provide acids: $SO_2 + H_2O = H_2SO_3$
  - Insoluble ones reacts with alkali providing salts:

$$Sb_2O_5 + 2OH^- + 5H_2O = 2[Sb(OH)_6]^-$$

- **Covalent-ionic:**
  - When combines with the rest of the elements
  - Have intermediary properties (amphoters):

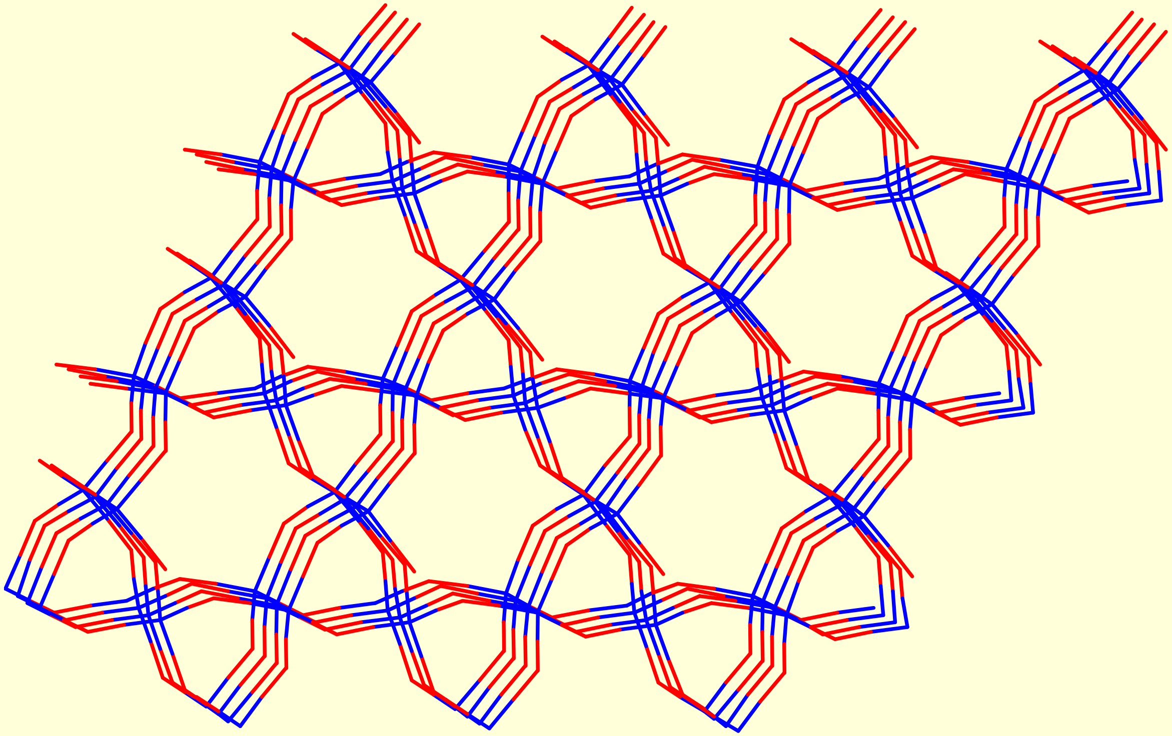
$$Al_2O_3 + 6H^+ = 2Al^{3+} + 3H_2O$$

$$Al_2O_3 + 2OH^- + 3H_2O = 2[Al(OH)_4]^-$$

(α)-Quartz structure

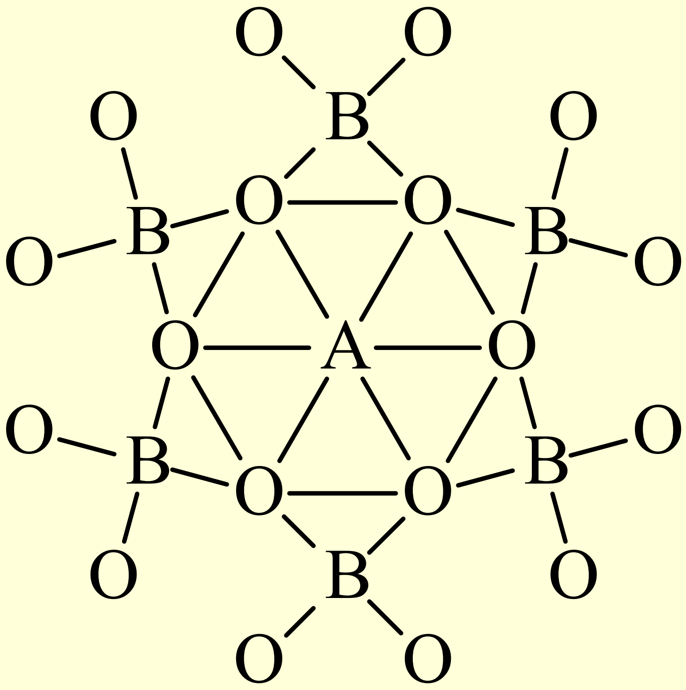
- Belongs to the family of di-coordinated oxygen. These oxids, with general formula R_2O, have angular molecules. The angle between the two R-O bonds depends on R. For instance, the angle increases here:

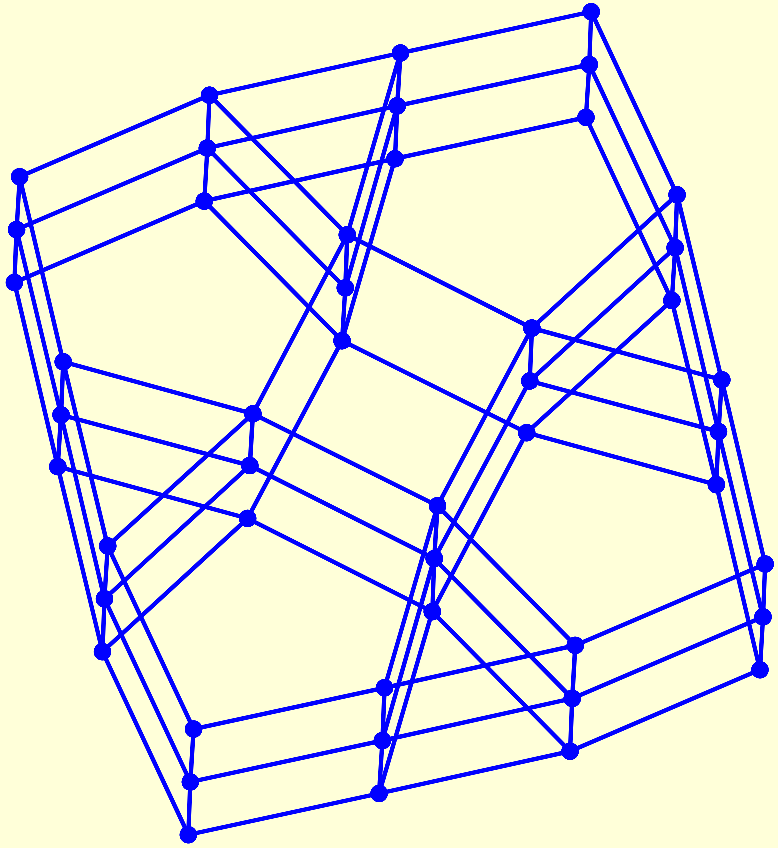
$$H_2O < (CH_3)_2O < Si\text{-}O\text{-}Si \text{ (quartz)}.$$



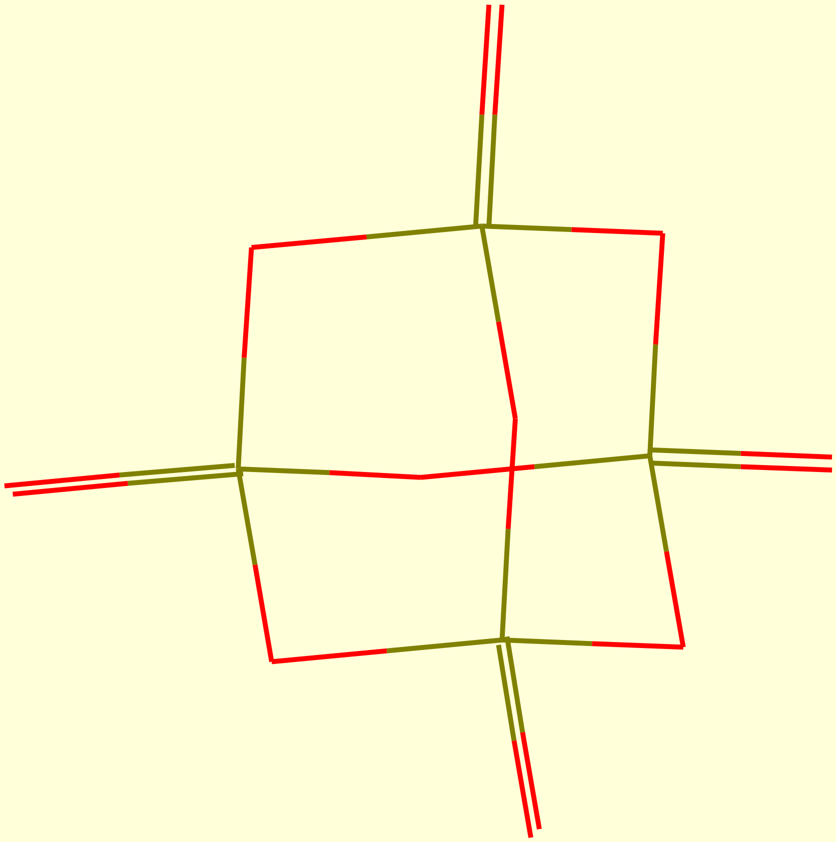
Bronzes

- Cathegory of non-stoechiometric compounds with perovskitic structure with general formula: A_xBO_3 where B: W, Mo, Nb, Ta, V and A: Li, Na, K, Pr.
- Structure of tetragonal tungsten bronzes:

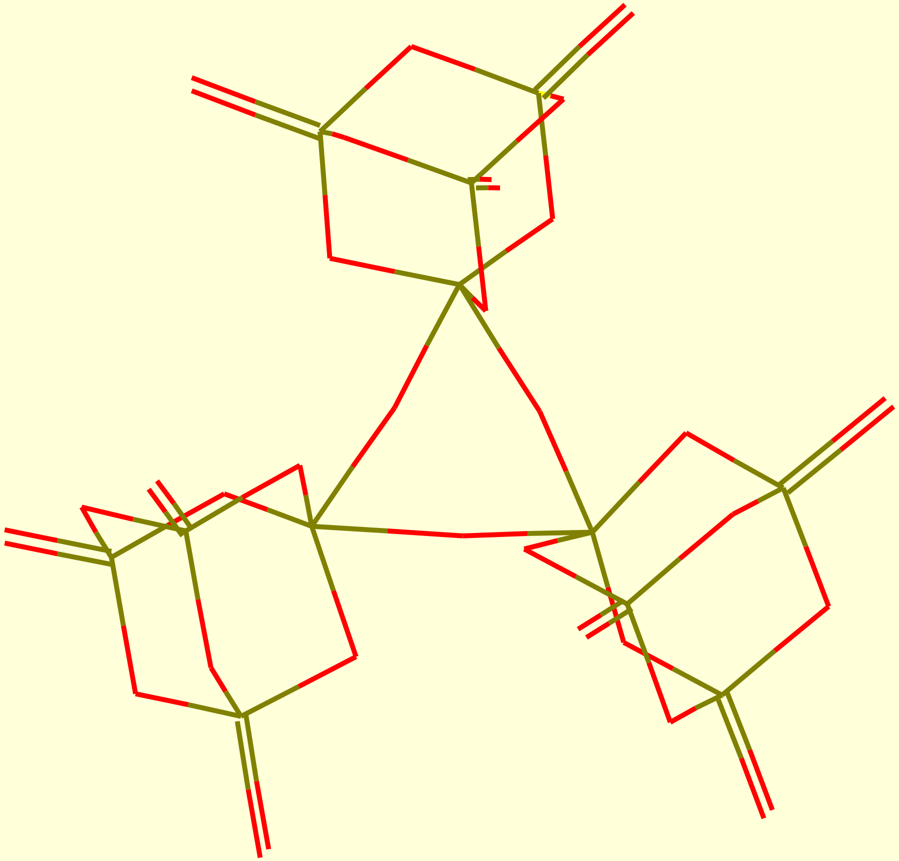




Phosphorus oxides

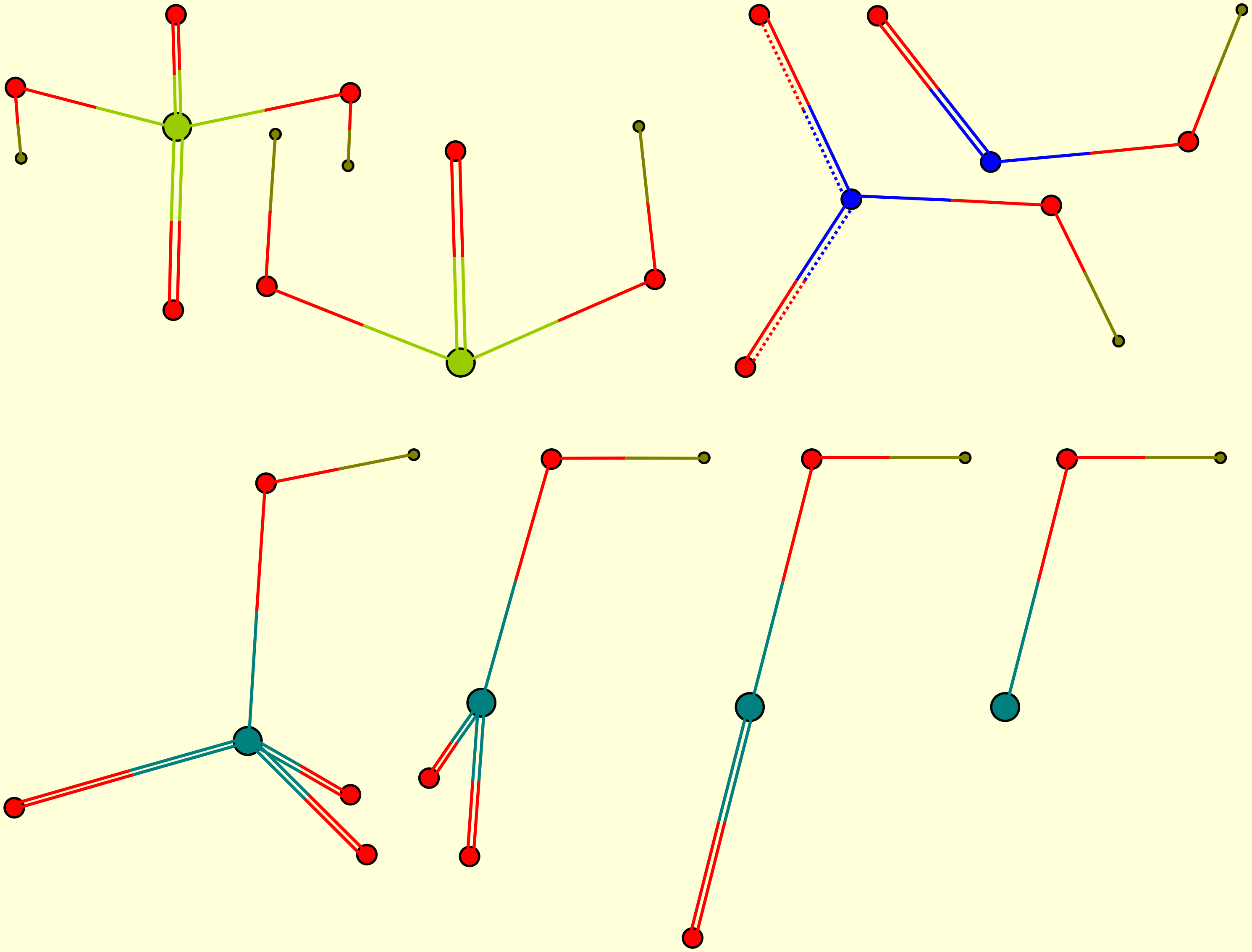


P_4O_{10}



$(P_4O_9)_3$

Oxyacids



H_2SO_4, H_2SO_3, HNO_3, HNO_2, $HClO_4$, $HClO_3$, $HClO_2$, $HClO$

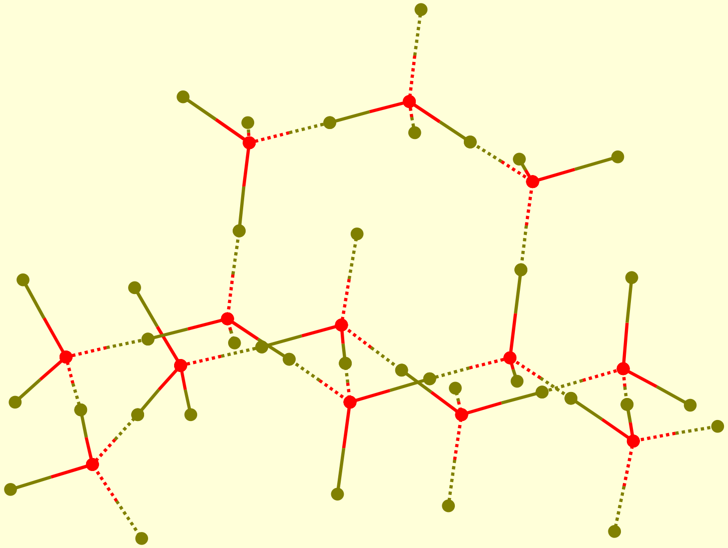
Q & R

In connection with the compounds containing oxygen:	
0	$HClF_3$ and $HClF_4$ are oxyacids
0	HCl and $HClF_2$ are oxyacids
0	HNO and HNO_4 are oxyacids
0	H_2SO and H_2SO_2 are oxyacids
1	$HClO_3$ and $HClO_4$ are oxyacids
1	HClO and $HClO_2$ are oxyacids
1	HNO_2 and HNO_3 are oxyacids
1	H_2SO_3 and H_2SO_4 are oxyacids
0	Some phosphorus oxides are: P_3O_2, P_5O_2, $P_{10}O_4$, $(P_9O_4)_3$
1	Some phosphorus oxides are: P_2O_3, P_2O_5, P_4O_{10}, $(P_4O_9)_3$
0	The angle between the bonds of the oxygen is increasing as given: -Si-O-Si- < H_3C-O-CH_3 < H-O-H
1	The angle between the bonds of the oxygen is increasing as given: H-O-H < H_3C-O-CH_3 < -Si-O-Si-
0	The dicoordinated oxygen oxids R-O-R have linear molecules
1	The dicoordinated oxygen oxids R-O-R have angular molecules

Water – physical properties

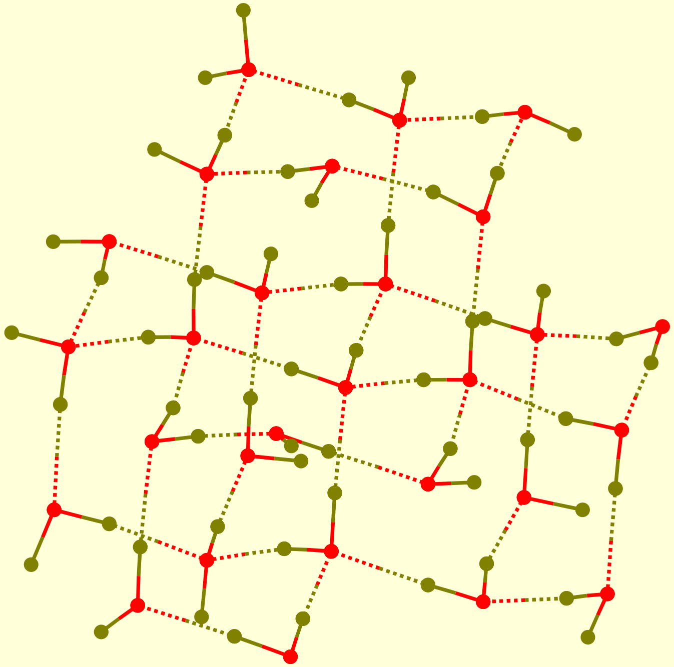
b.p.	100 °C
m.p.	0 °C
Vapor pressure (at 0°C)	4.68 atm.
Vaporization latent heat (L_V, at 100°C)	2219.85 J·mol^{-1}
Melting latent heat (L_M, at 0°C)	334.5 J·mol^{-1}
Dielectric constant (at 25°C)	78.54
Cryoscopic constant	1.86 °C
Ebullioscopic constant	0.52 °C
Superficial tension	72.7 dyn·cm^{-1}

Ice



Hexagonal

“not to scale”



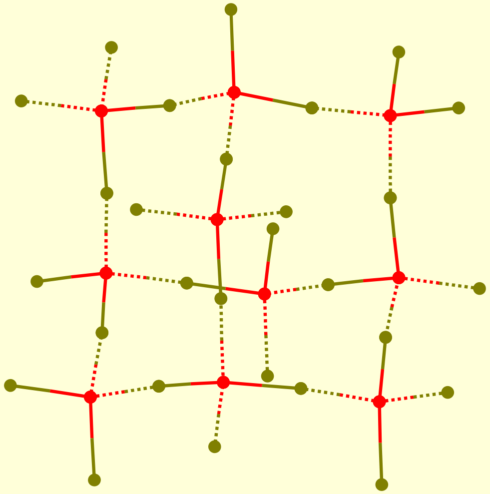
Hexagonal

“to scale”

d(O—H)=172pm

d(O…H)=285pm

Cubic



Were found no less than 15 phases of ice. At pressures till up about 1000 atm. and for temperatures till down about -200°C ice adopts two crystal structures, both “close-packed”: hexagonal (at upper temperatures) and cubic (at lower temperatures).

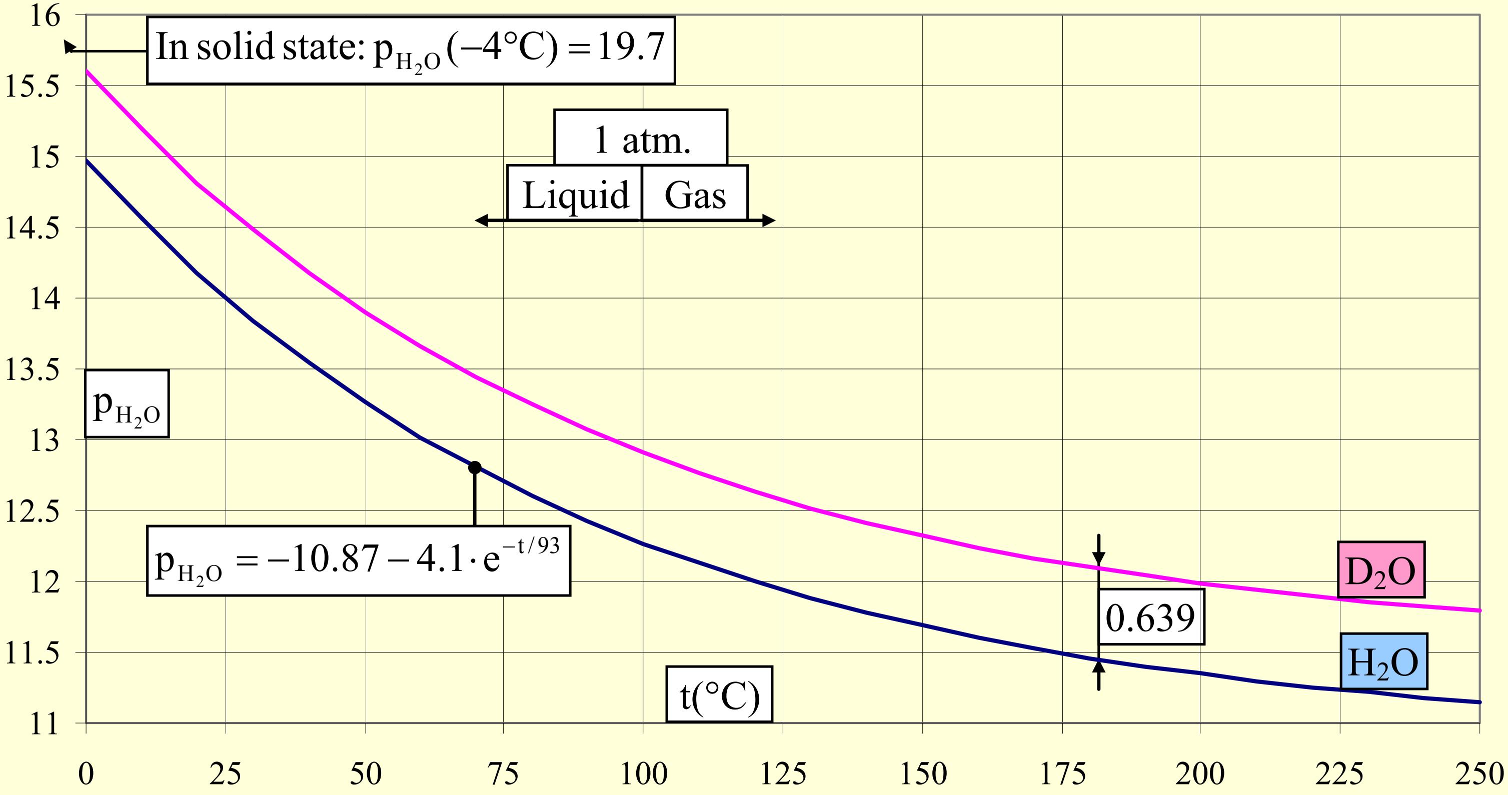
Q & R

In connection with H_2O:		
	1	At 25°C and 1 atm $pK_{H2O} = 14$ and $pH = 7$
	1	$pK_{H2O} = pH + pOH$, where $pH = -\log_{10}([H^+])$ and $pOH = -\log_{10}([OH^-])$
	0	$pK_{H2O} = \ln(K_{H2O})$, $K_{H2O} = [H_3O^+]\cdot[HO^-]/[H_2O]^2 \sim [H_3O^+]\cdot[HO^-]$, where $[\cdot]$ stands for molar concentration (or activity)
	0	$pK_{H2O} = \log_{10}(K_{H2O})$, $K_{H2O} = [H_3O^+]\cdot[HO^-]/[H_2O]^2 \sim [H_3O^+]\cdot[HO^-]$, where $[\cdot]$ stands for molar concentration (or activity)
	1	$pK_{H2O} = -\log_{10}(K_{H2O})$, $K_{H2O} = [H_3O^+]\cdot[HO^-]/[H_2O]^2 \sim [H_3O^+]\cdot[HO^-]$, where $[\cdot]$ stands for molar concentration (or activity)
	0	$pH = \ln([H^+])$, where $[\cdot]$ stands for molar concentration (or activity)
	0	$pH = \log_{10}([H^+])$, where $[\cdot]$ stands for molar concentration (or activity)
	1	$pH = -\log_{10}([H^+])$, where $[\cdot]$ stands for molar concentration (or activity)
	0	Ionic product of the water K_{H2O} decreases with temperature
	1	Ionic product of the water K_{H2O} increases with temperature
	0	Exists one phase of ice
	1	Were identified no less than 15 phases of ice

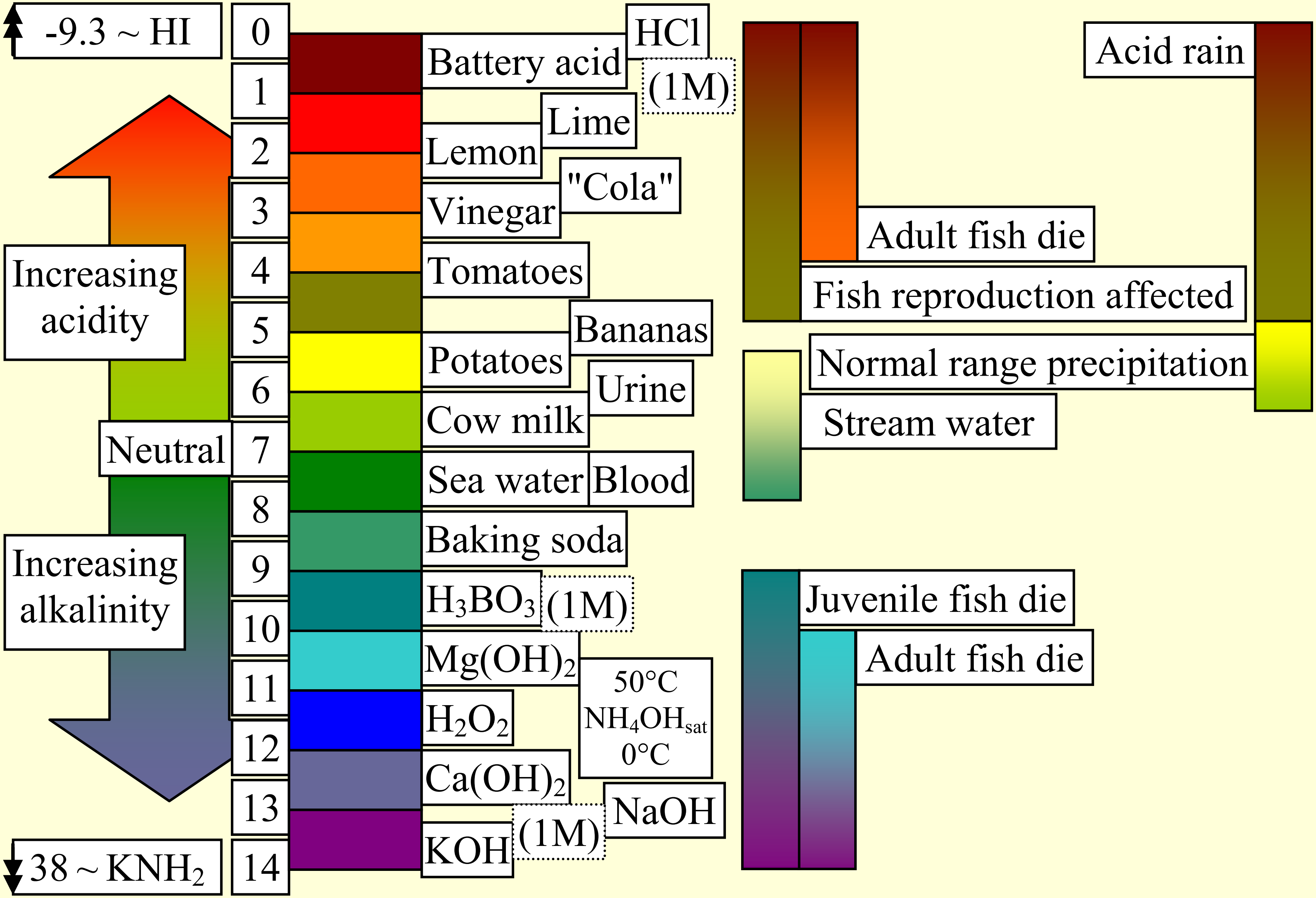
Water properties: pH

- As following diagram shows, pH ranges from 0 to 14, with 7 being neutral. pHs less than 7 are acidic while pHs greater than 7 are alkaline (basic). You can see that acid rain can be very acidic, and it can affect the environment in a negative way.

Other data: http://www.iapws.org/release.htm



pH scale



-9.3 ~ HI

0
HCl

1
Battery acid
(1M)

2
Lime
Lemon

3
"Cola"
Vinegar

4
Tomatoes

5
Bananas
Potatoes

6
Urine
Cow milk

7
Neutral
Sea water
Blood

8
Baking soda

9
H_3BO_3
(1M)

10
$Mg(OH)_2$

11
50°C
NH_4OH_{sat}
0°C
H_2O_2

12
$Ca(OH)_2$

13
NaOH
(1M)
KOH

14

38 ~ KNH_2

Increasing acidity

Increasing alkalinity

Acid rain

Adult fish die

Fish reproduction affected

Normal range precipitation

Stream water

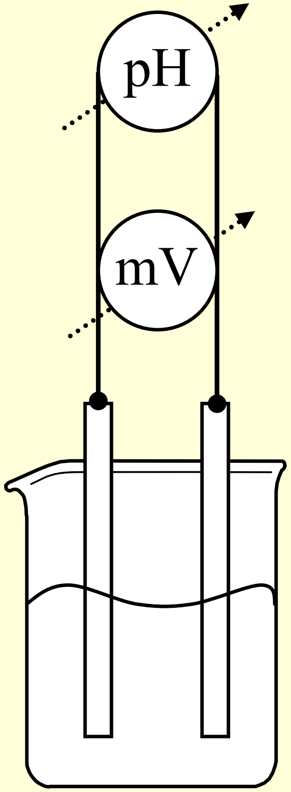
Juvenile fish die

Adult fish die

Q & R

In connection with the pH:		
	0	stream water pH is 7-8
	1	stream water pH is 6-7
	0	acid rain pH is 5-6
	0	normal rain pH is 1-5
	1	acid rain pH is 1-5
	1	normal rain pH is 5-6
	0	pH(milk of lime) < pH(Hydrogen peroxide) < pH(Baking soda) < pH(Seawater) < 7
	1	7 < pH(Seawater) < pH(Baking soda) < pH(Hydrogen peroxide) < pH(Milk of lime)
	0	7 < pH(Potatoes) < pH(Bananas) < pH(Tomatoes) < pH(Vinegar) < pH(Lemon) < pH(Battery acid) < pH(HCl)
	1	pH(HCl) < pH(Battery acid) < pH(Lemon) < pH(Vinegar) < pH(Tomatoes) < pH(Bananas) < pH(Potatoes) < 7

pH indicators



$$pH = -\frac{E(H^+/H_2) + E_{ref} - E^0{}_{ref}}{\ln(10)\cdot RT/F}$$

Indicator	Color low	Range	Color high
Picric acid	⬜	0.6-1.3	🟨
Thymol 'blue'	🟥	0.6-1.3	🟨
2,4-dinitrophenol	⬜	0.6-1.3	🟨
Methyl 'yellow'	🟥	2.9-4.0	🟨
Bromophenol 'blue'	🟨	3.0-4.6	🟪
Congo 'red'	🟪	3.0-5.0	🟥
Methyl 'orange'	🟥	3.1-4.4	🟨
Bromocresol 'green'	🟨	3.8-5.4	🟦
Methyl 'red'	🟥	4.3-6.2	🟨
Azolitmin	🟥	4.5-8.3	🟦
Bromocresol 'purple'	🟨	5.2-6.8	🟪
Bromothymol 'blue'	🟨	6.2-7.6	🟦
Phenol 'red'	🟨	6.4-8.0	🟥
Toluylene 'red'	🟥	6.8-8.0	🟨
Cresol 'red'	🟨	7.2-8.8	🟥
Naphtholphthalein 'blue'	🟪	7.3-8.7	🟦
Thymol 'blue'	🟨	8.0-9.6	🟦
Phenolphthalein	⬜	8.3-10.0	🟪
Thymolphthalein	⬜	8.3-10.0	🟦
Alizarine 'yellow'	🟨	10.1-12.0	🟥
Picrylnitromethylamine	⬜	10.8-13.0	🟥
Cyanidin	<3.0	7.0-8.0	>11

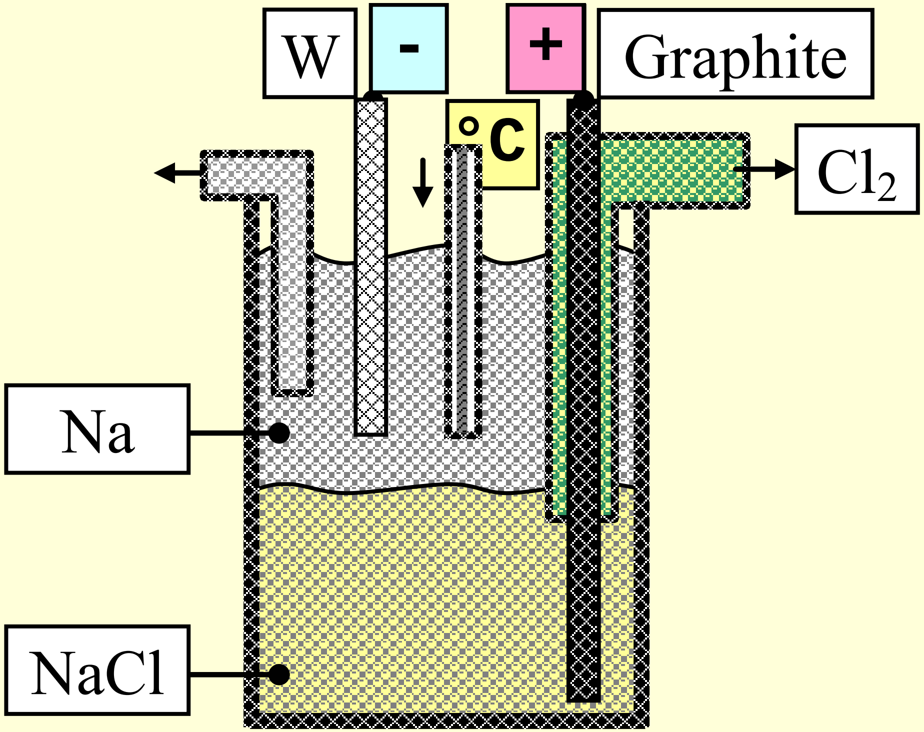
Course 5

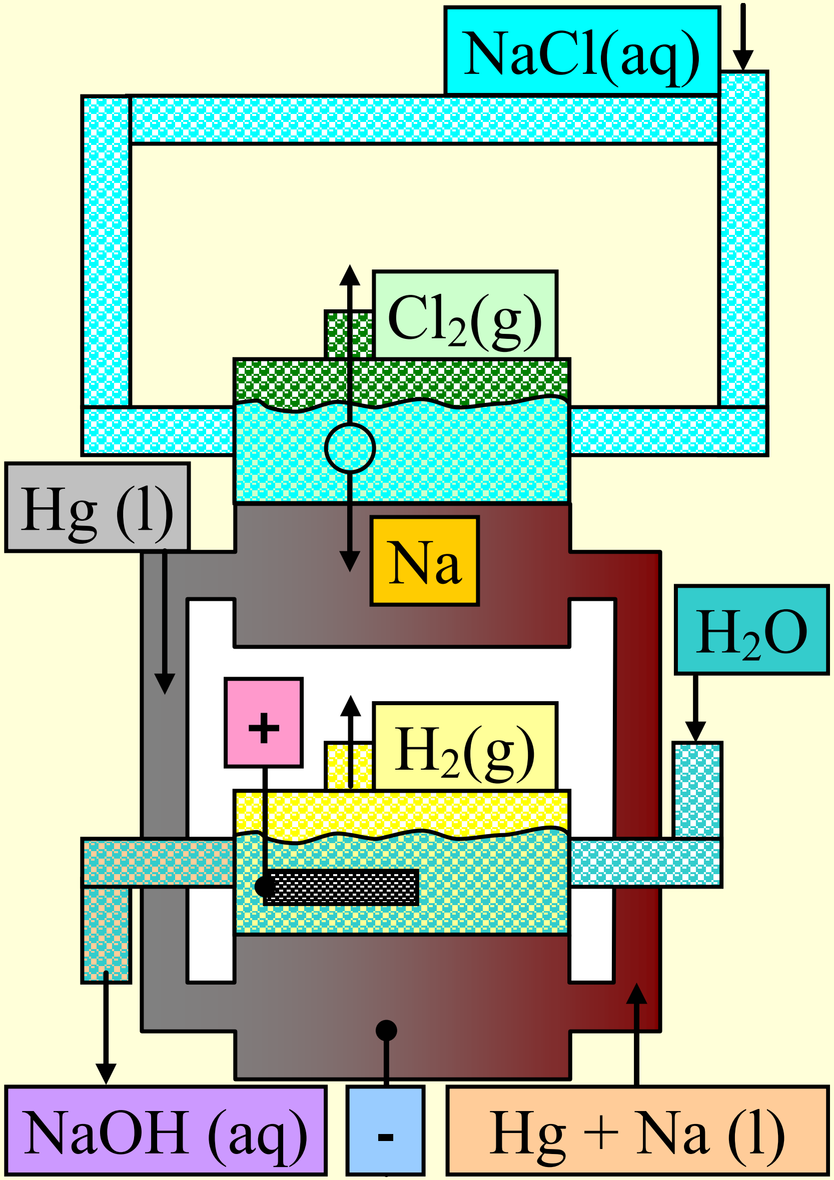
Alkali & alkaline earth metals

Li, Na, K, Rb, Cs, Fr

- Due to the shielding of the positive nuclear charge by the intermediary shells, the electron of valence interacts weakly with the nucleus (excepting Li): $M \rightarrow M^{+} + 1e^{-}$;
- ***Natural state***: All are too active to exist in free state. Combinations of them are spread, often together with Na. Na (clark: 2.64%) and K (clark: 2.35%) are from the 10 most present ones in the crust. See water contains important levels of them (1.14% Na, 0.04% K). Na and related compounds are obtained from NaCl, extracted from mineral ores or see water.

Electrolytic procedure to obtain metallic Na from melt and NaOH from aqueous solution





- Anode – central positioned – is from graphite and cathodes – half circular – surrounds the anode.

Anode reaction: $Cl^- \rightarrow Cl + e^-$ ($Cl + Cl \rightarrow Cl_2$)

Cathode reaction: $Na^+ + e^- \rightarrow Na$

- Melted sodium – less dense than the electrolyte – rises to the surface, being conducted to an exterior tank.
- Chlorine (gaseous) are separately collected.
- All alkali elements are separated through electrolysis of their melts – either from their chlorides or hydroxides. Before electrolysis the salts are purified by recrystallization from hot solutions.

Physical properties

Z	3	11	19	37	55	87
Symbol	Li	Na	K	Rb	Cs	Fr
Mass (g/mol)	6.94	23.0	39.1	85.5	133	223
m.p. (°C)	181	98	64	39	28	27
b.p. (°C)	1347	883	774	688	678	677
ρ ($g\cdot cm^{-3}$)	0.53	0.97	0.86	1.53	1.87	1.87
Electronegativity (Pauling)	0.98	0.93	0.82	0.82	0.79	0.70
Ionization (eV)	5.39	5.14	4.34	4.18	3.90	3.94
Reduction ε^0 (V)	-3.04	-2.71	-2.93	-2.92	-3.08	N/A

- Have typical for metals characters: metallic luster (in fresh cut), silvery white appearance (except cesium - golden), conductors for heat and electricity (better one has only Ag, Cu, Al, Au);
- Hardest is Li; Na are easily cut with the knife and K is plasticine-like;
- Vapors of alkali are intensely colored, easily recognizable: Li – dark pink, Na - yellow, K – bright red, Rb – violet, Cs – blue, Fr - green (qualitative recognition).
- Above and near to their boiling points about 1% of their vapors are diatomic molecules – which proofs the existence of the covalent character in their bonds

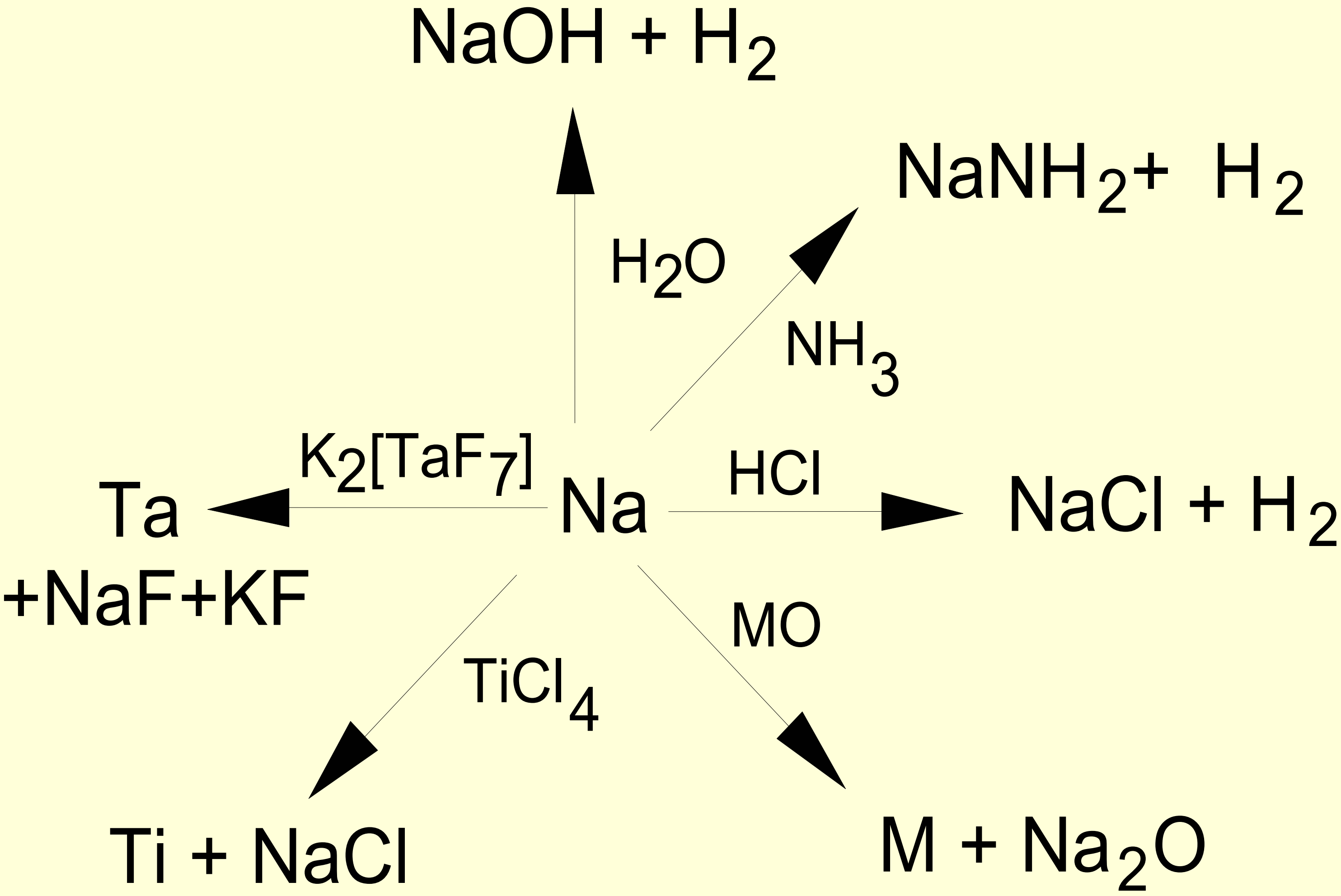
Chemical properties

- ***In air and oxygen:*** reactive; thus Na and K loose their sheen staying in the air fast; Rb and Cs burns in air; => Li, Na, K are kept covered with paraffin; Rb, Cs, Fr in evacuated glass ampoules; Combinations: $Na + O_2 \rightarrow Na_2O$; $Na_2O + H_2O \rightarrow 2NaOH$; $NaOH + CO_2 \rightarrow Na_2CO_3$; At hot occurs Na_2O_2 (NaOONa) – peroxide and superoxides - KO_2 (Rb, Fr)
- ***In water:*** releases the hydrogen upon contact with water; More energetically become the reaction from Li to Fr:

$$M_{(s)} + HOH_{(l)} \rightarrow M^{+}{}_{(aq)} + HO^{-}{}_{(aq)} + {}^{1}/_{2}H_{2(g)}$$

- ***With other metals:*** at worm conditions leads to alloys or intermetallic compounds. At cold, Hg with Na mixes in a blend sodium amalgam – denoted Na(Hg) – with solid state at room temperature for over 2% Na

Chemical reactions



$NaOH + H_2$

H_2O

$NaNH_2 + H_2$

NH_3

$K_2[TaF_7]$

Ta

$+NaF+KF$

Na

HCl

$NaCl + H_2$

MO

$TiCl_4$

$Ti + NaCl$

$M + Na_2O$

Uses

- NaCN, KCN (electrolytic processes);
- Na_2O_2 (oxidant) – indoor air renewal (Na – pigboats; Li – lighter - spacecrafts):

$$Na_2O_{2(s)} + CO_{2(g)} \rightarrow Na_2CO_{3(s)} + {}^{1}/_{2}O_{2(g)}$$

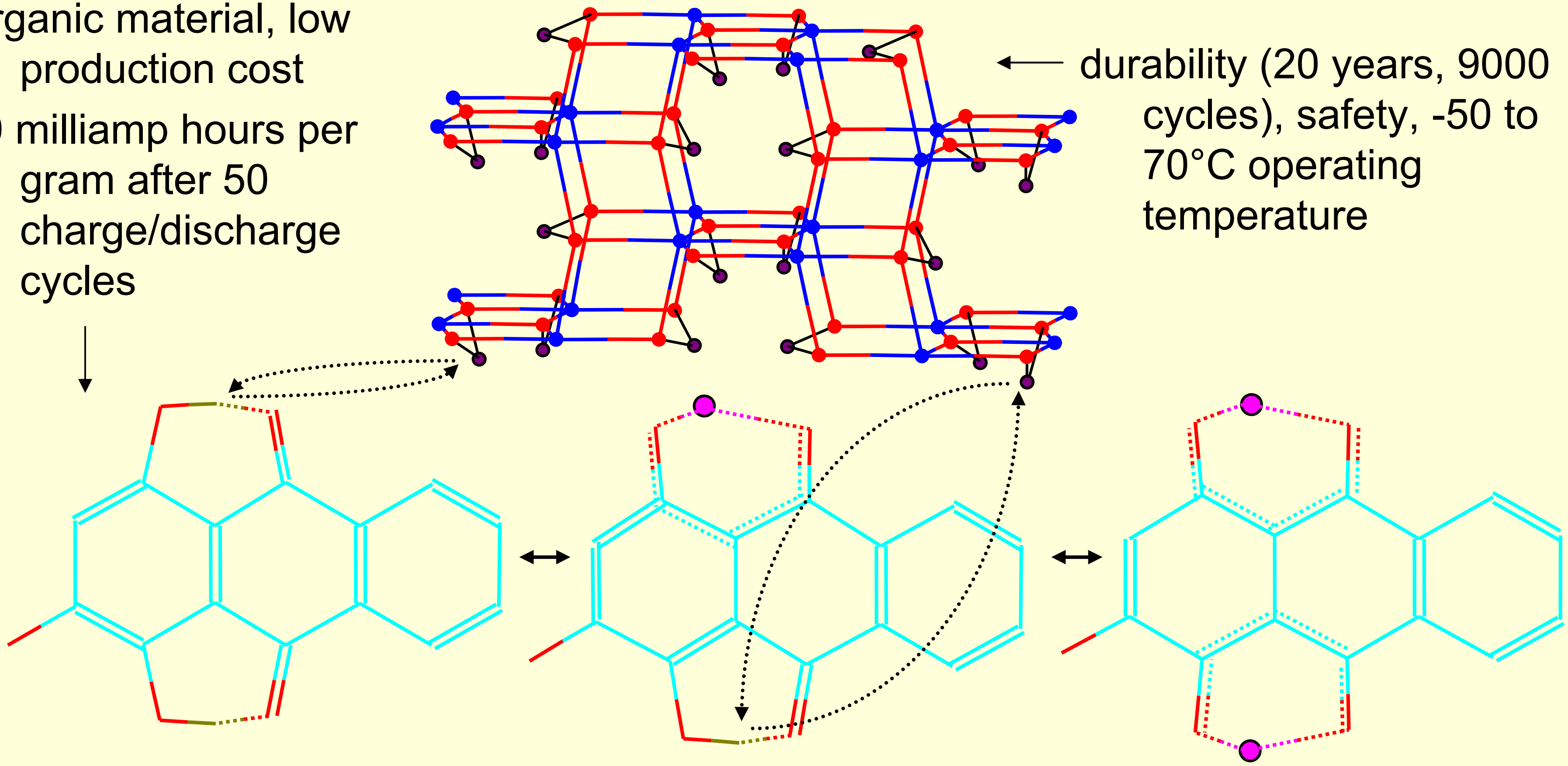
- **Na**: with Ti ($TiCl_4$ + Na) is thermal agent in nuclear reactors (high thermal conductivity, low melting point); monochromatic lamps (with vapors of Na); alloying element (in small quantities)
- **Na-K**: liquid thermometers for high temperatures (replacing Hg);
- **Rb, Cs**: has special use for cathodes in solar cells

Lithium ion polymer batteries

Organic material, low production cost

90 milliamp hours per gram after 50 charge/discharge cycles

durability (20 years, 9000 cycles), safety, -50 to 70°C operating temperature



Anode (Li$_2$TiO$_3$) -

Cathode (1,2,4-Trihydroxyanthraquinone) +

Complex coordinative combinations

Inorganic Components of Detergents Builders and Other Additives

- Complex (or condensed) Phosphates
- These have a lower alkalinity than trisodium phosphate. The commonly used complex phosphate are:

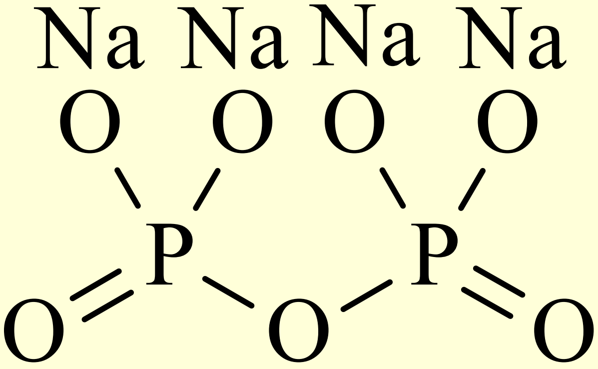
Tetrasodium pyrophosphate $Na_4P_2O_7$

Sodium tripolyphosphate $Na_5P_3O_{10}$

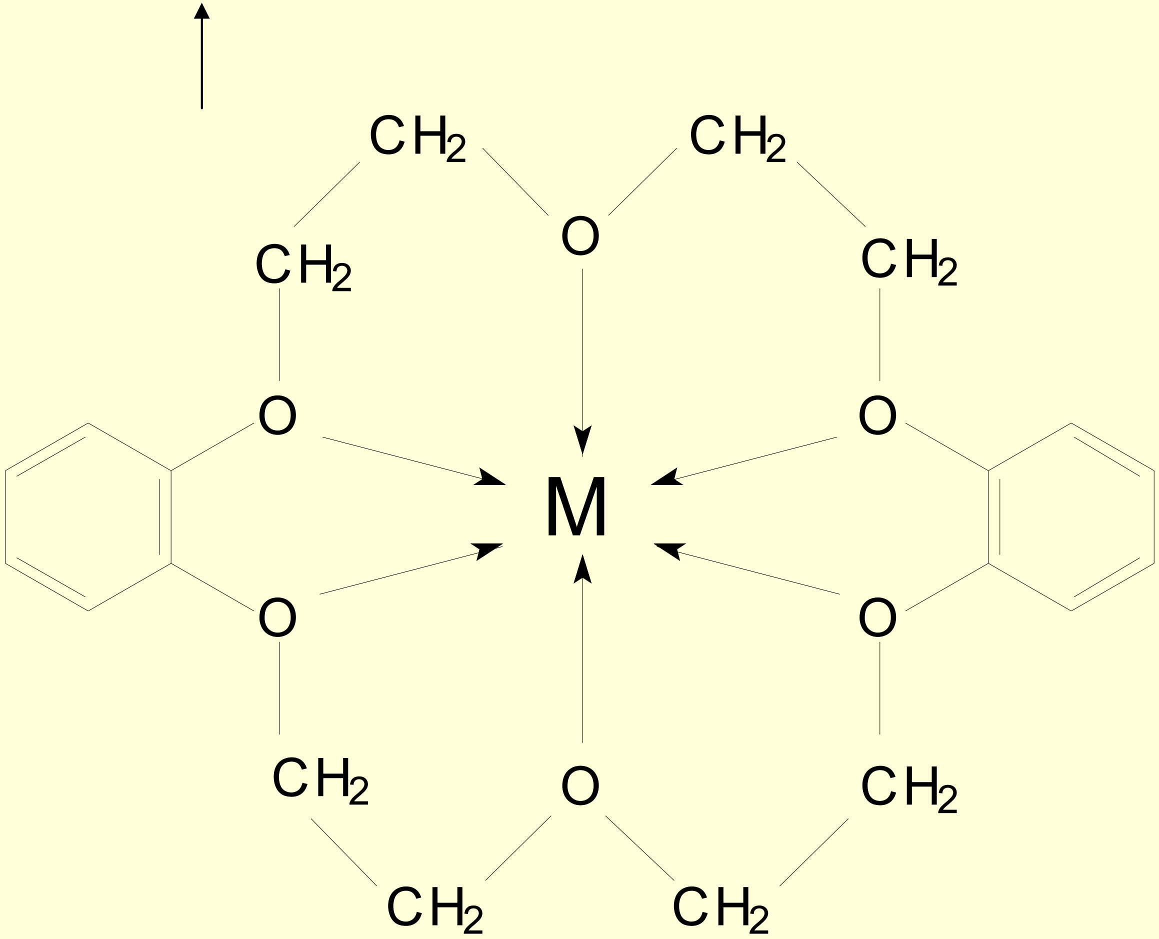
Sodium tetraphosphate $Na_6P_4O_{13}$ (hygroscopic)

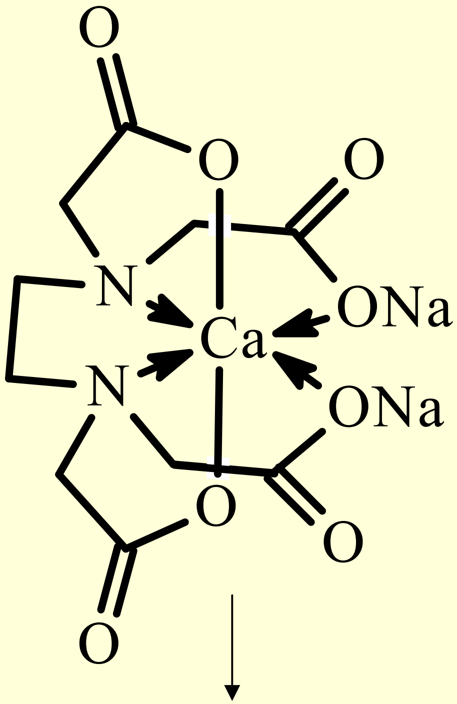
Sodium hexametaphosphate $(NaPO_3)_6$ (hygroscopic)

- **Carbonates**
- Soda ash (sodium carbonate) Na_2CO_3
- **Oxygen Releasing Compounds**
- Sodium Perborate $Na_2B_2O_4(OH)_4$



dibenzo-18-crown-6 – representative of a class of alkali complexes





Hexa-coordinated
Ca^{2+} in EDTA

Q & R

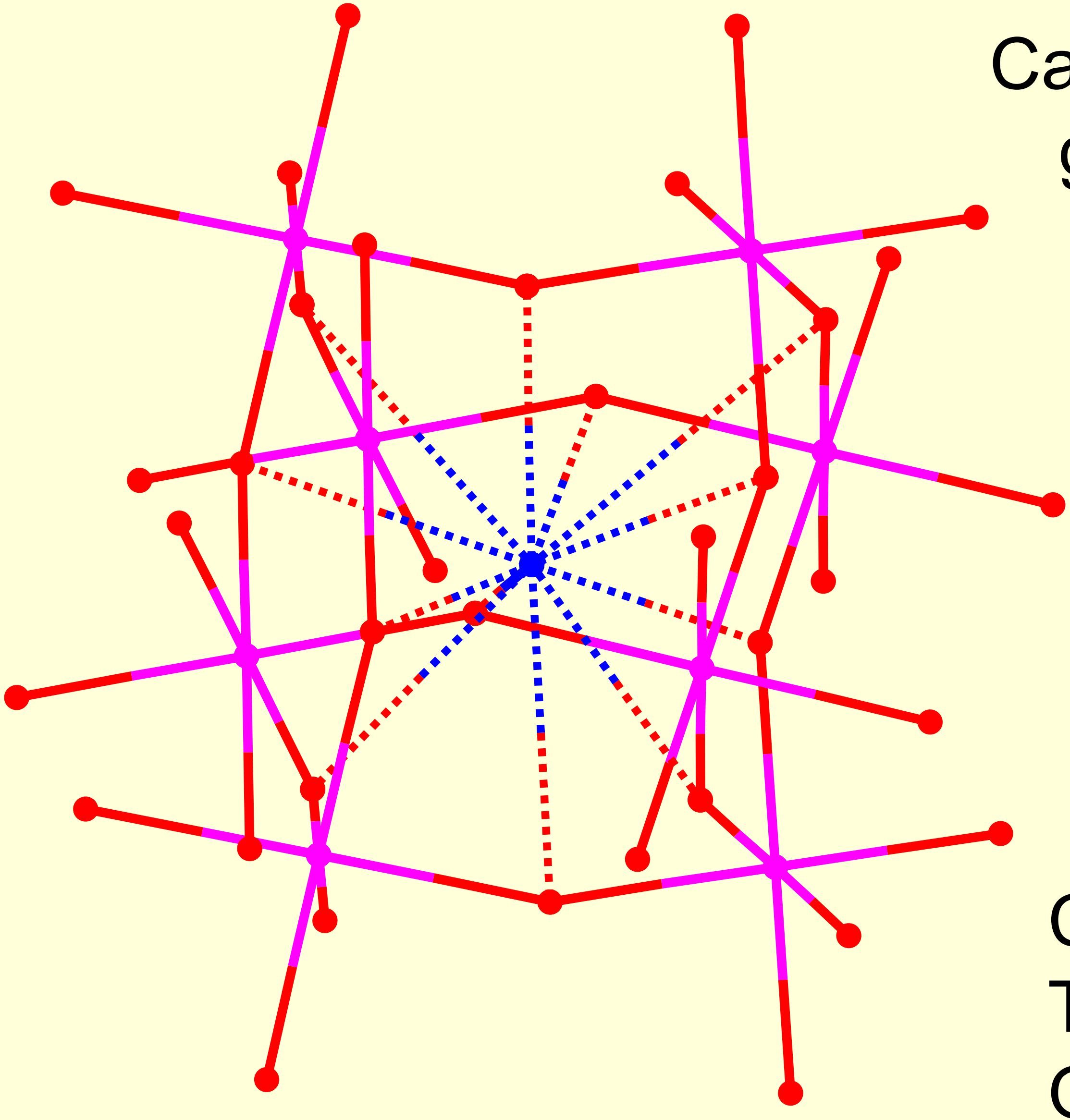
Alkali metals applications include:		
	0	Fe-Cu in liquid thermometers for high temperature (replacing Hg)
	1	Na-K in liquid thermometers for high temperature (replacing Hg)
	0	RbCN and CsCN in electrolytic processes
	0	Li in solar cells
	0	K in Lithium-ion-polymer batteries
	0	Li in detergents
	1	Na in detergents
	1	Li in Lithium-ion polymer batteries
	1	Rb and Cs in solar cells
	1	NaCN and KCN in electrolytic processes

Be, Mg, Ca, Sr, Ba, Ra

- Most spread elements of this group are the Calcium and the Magnesium. Beryllium is rare in the crust ($6 \cdot 10^{-4}$ %) being mainly found along with Aluminum – with which is chemically similar – in chrysoberyl ($BeAlO_4$) and in a silicate - *beryl* ($Be_3Al_2Si_6O_{18}$). Emeralds are a variety of beryl.

- Ionization reaction for the group: $M \rightarrow M^{2+} + 2e^-$

Perovskite



$CaTiO_3$ – perovskite group

$M^{II}M^{IV}O_3$, M^{IV}: Ti, Zr, Hf; M^{II}: Ca, Sr, Ba, Zn

$M^{I}M^{V}O_3$, M^{V}: Nb, Ta; M^{I}: Li, Na, K

$M^{II}M^{V}O_6$, M^{V}: Nb, Ta; M^{II}: Ca, Sr, Ba

Ca: blue

Ti: pink

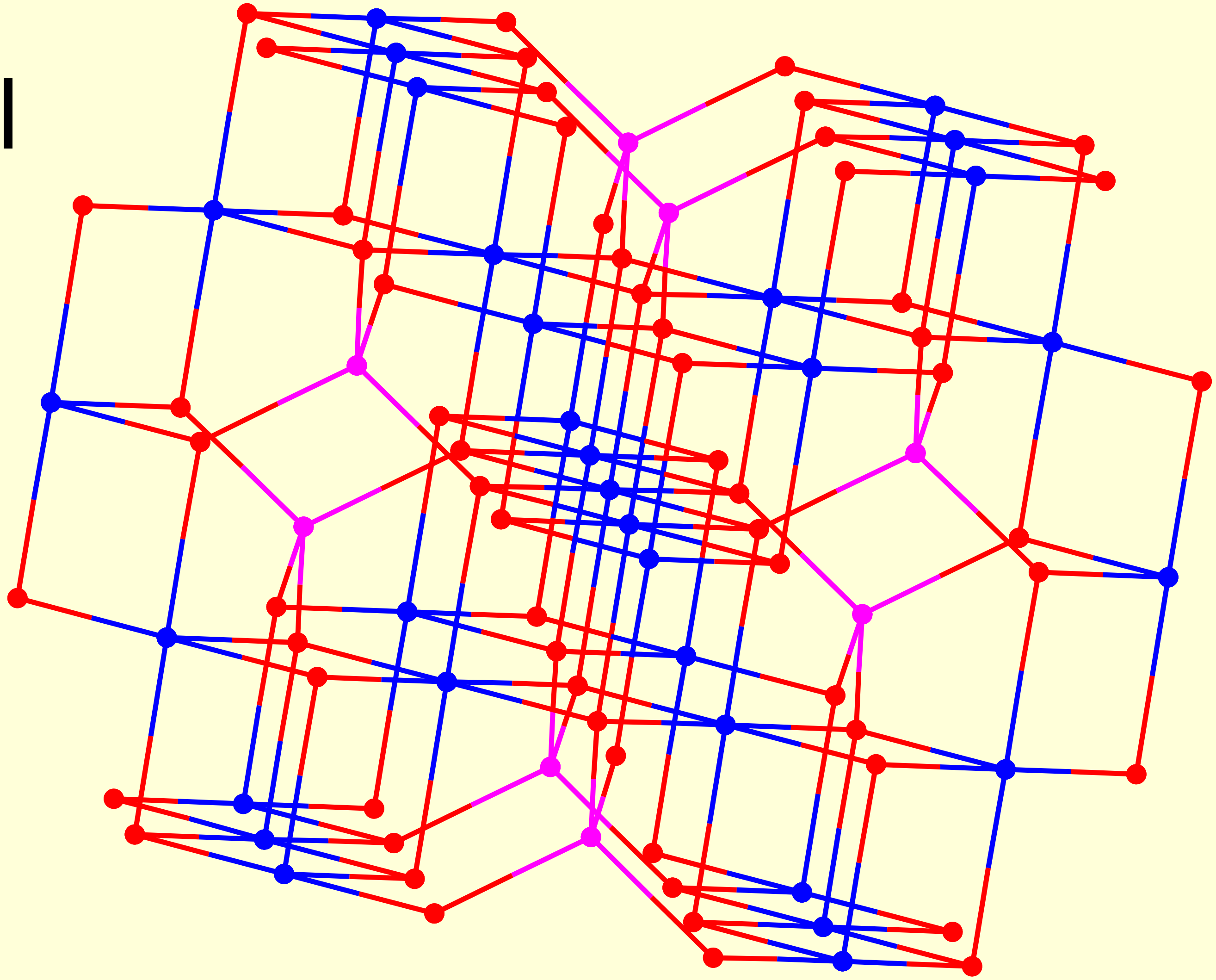
O: red

Spinel

Mg: pink

Al: blue

O: red



- $MgAl_2O_4$ – Spinel group - $M^{II}M^{III}{}_2O_4$

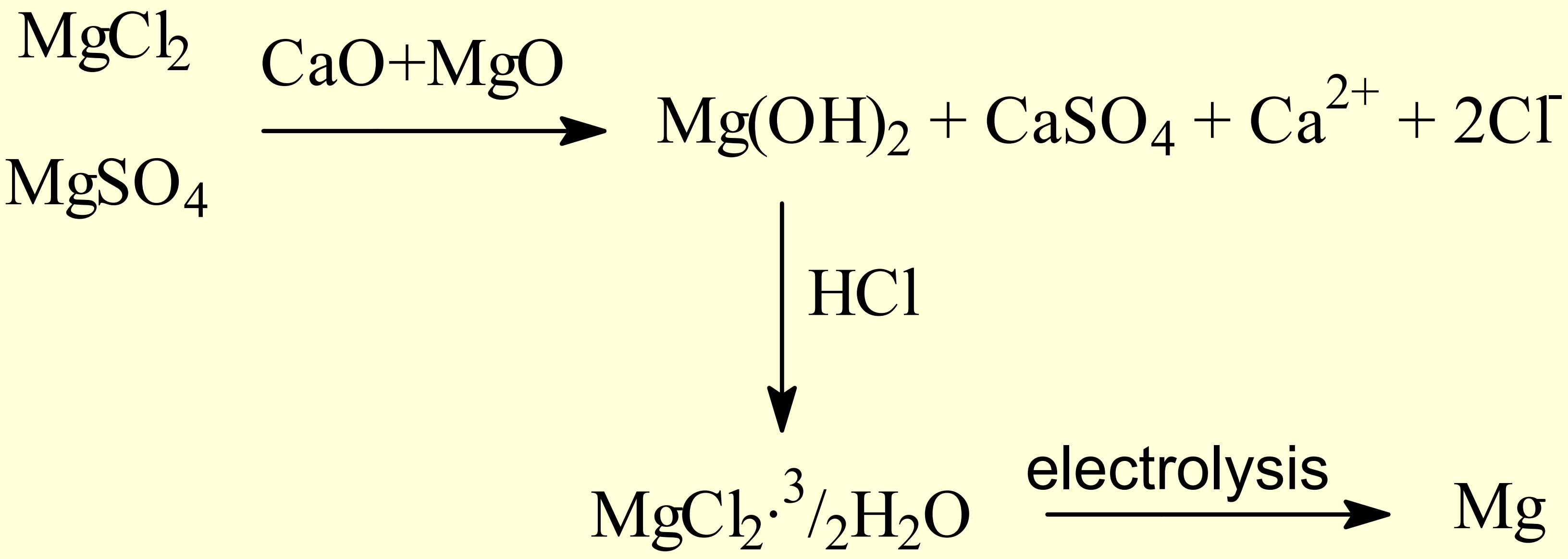
  M^{III} = Al, Fe^{III}, Co^{III}, Cr^{III}, Mn^{III}, Ga;

  M^{II} = Mg, Fe, Co, Ni, Zn, Cd, Cu

- Magnesium (2.3% in crust) are found as *magnesite* ($MgCO_3$), dolomite $CaMg(CO_3)_2$, brucite $Mg(OH)_2$, *carnallite* ($KCl \cdot MgCl_2 \cdot 6H_2O$), olivine $(Mg,Fe)_2SiO_4$ and other valuable minerals. Chlorophyll is a organic complex having as central ion the magnesium.
- Calcium (3.4%) is one of the crust most 10 spread elements too. The main mineral is CaCO3 – with different amorphous and crystalline varieties (including calcite, aragonite and vaterite as pure calcium carbonate minerals). $CaSO_4 \cdot 2H_2O$ known as gypsum is important variety too.
- Strontium (0.02%) are found as $SrCO_3$ and $SrSO_4$ and barium (0.04%) as $BaSO_4$ or mixed with $BaCO_3$.
- Radium is extracted from Uraninite (UO_2, with small amounts of Ra - 0.14 g Ra/ton – derived from the decay of Uranium – equilibrium ratio being Ra/U ~ $3.7 \cdot 10^{-7}$.

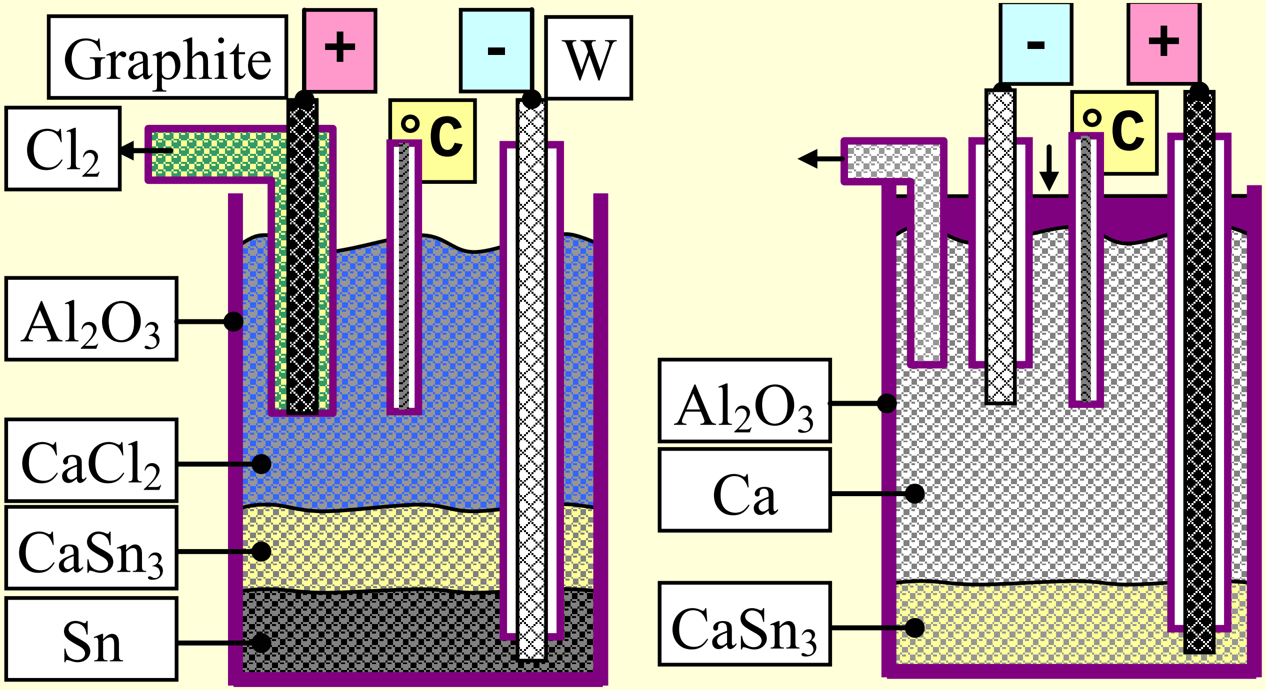
Obtaining – Be & Mg

- Beryllium are commonly separated from beryl after melting with fondants. After treatment with sulfuric acid a series of soluble sulfates (of Be, Al, Alkali) are treated (with $(NH_4)_2SO_3$ for precipitating Al) and then Be are recrystallized as $BeSO_4$, treated with NH_4OH to give $Be(OH)_2$ and finally BeO results after calcining.
- Magnesium are economically efficient extracted from sea water as depicted.



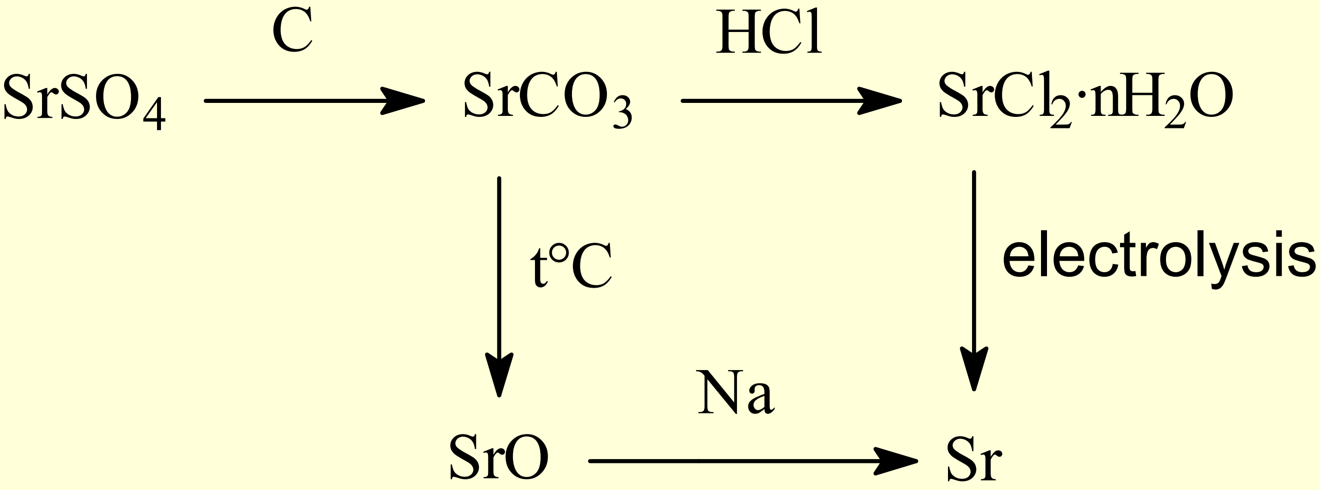
$$\begin{tikzcd} \begin{matrix} MgCl_2 \\ MgSO_4 \end{matrix} \arrow[r, "CaO+MgO"] & Mg(OH)_2 + CaSO_4 + Ca^{2+} + 2Cl^- \arrow[d, "HCl"] & \\ & MgCl_2\cdot{}^3/_2H_2O \arrow[r, "\text{electrolysis}"] & Mg \end{tikzcd}$$

Two step Ca electrolysis

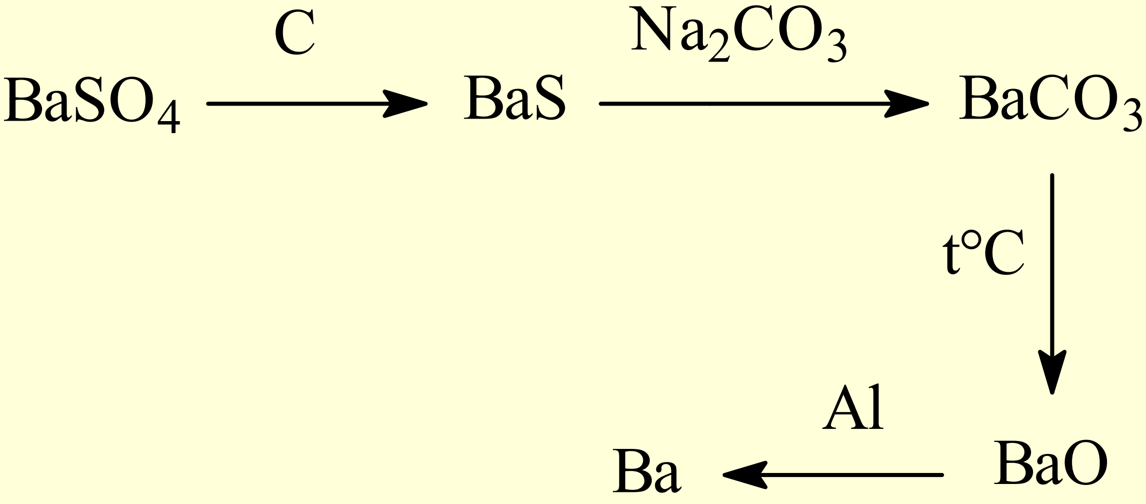


- Calcium is obtained from electrolysis of the $CaCl_2$ in a Al_2O_3 crucible.
- The other elements (Strontium and Barium) has more dedicated extraction techniques and uses (see next).

Obtaining of Sr and Ba



$$\begin{tikzcd}
SrSO_4 \arrow[r, "C"] & SrCO_3 \arrow[r, "HCl"] \arrow[d, "t°C"] & SrCl_2\cdot nH_2O \arrow[d, "\text{electrolysis}"] \\
 & SrO \arrow[r, "Na"] & Sr
\end{tikzcd}$$



$$\begin{tikzcd}
BaSO_4 \arrow[r, "C"] & BaS \arrow[r, "Na_2CO_3"] & BaCO_3 \arrow[d, "t°C"] \\
 & Ba & BaO \arrow[l, "Al"']
\end{tikzcd}$$

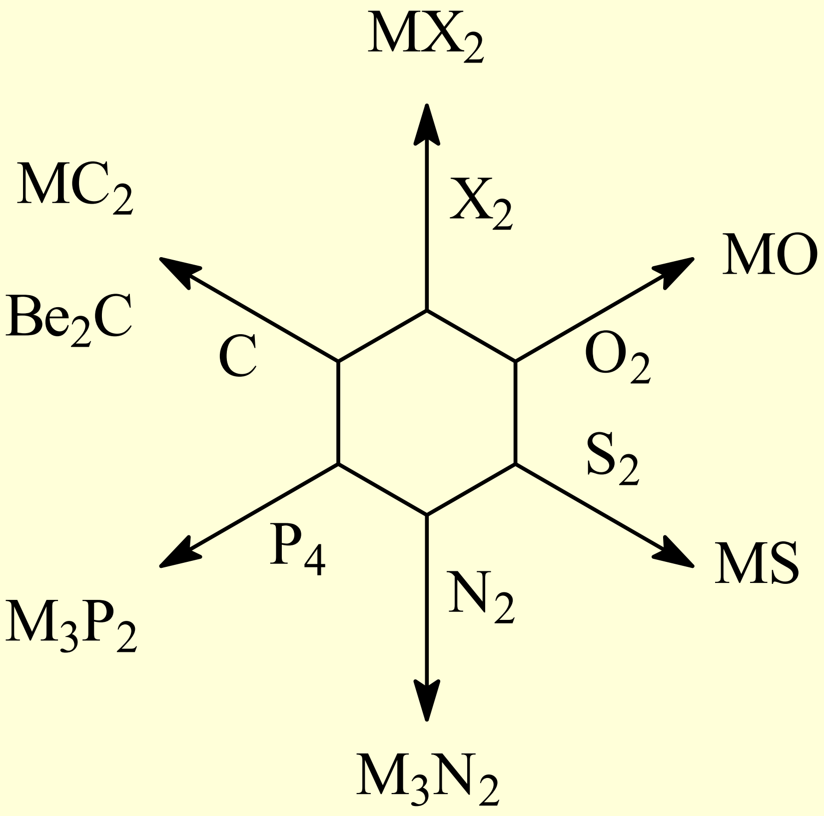
Physical properties

Z	4	12	20	38	56	88
Symbol	Be	Mg	Ca	Sr	Ba	Ra
Mass (g/mol)	9.0	24.3	40.1	87.6	137.4	226.1
M.p. (°C)	1280	657	850	757	710	700
B.p. (°C)	2967	1102	1439	1364	1638	1140
ρ (g/cm^3)	1.85	1.74	1.54	2.61	5.5	6
Ip (eV)	18.1	15.1	11.9	10.9	10.0	10.2
ε^0 (V)	-1.69	-2.35	-2.87	-2.89	-2.90	-2.92

- The general rule of monotony has almost always exceptions (see for instance m.p. for Mg).
- In non-oxidized state all solid states of the elements from 2nd group are white-silver colored (exception Be - white-gray).
- Ionization energies degreases in group (from top to bottom) being tree times higher than of the corresponding alkali.
- Redox potentials (ε^0), all negative, are few less negative than of the alkali and thus alkaline earth elements are less chemical active than the alkali.

Chemical properties & reactions

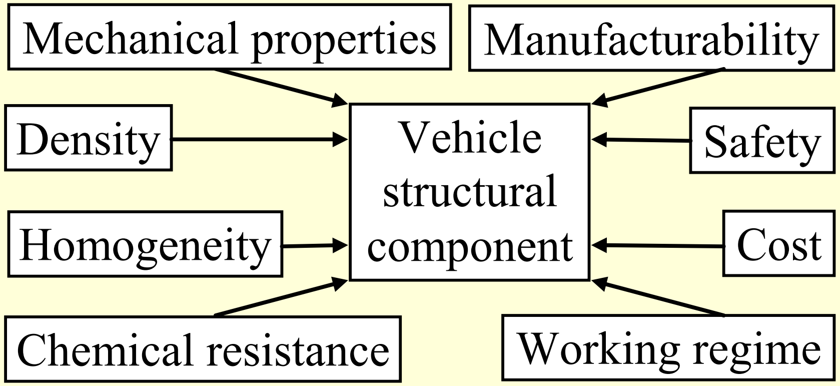
- Only berilium and magnesium may be kept in the air safely. Rising the temperature in air produces a bright crust on all – due to a mixture of oxide and nitride formed on the surface.
- At Be and Mg the oxide at the surface creates a protective shell which protects the metal to be oxidized in depth.



Uses

- *Magnesium* is far the most industrial used element as precursor for obtaining of other less active metals as well as alloying component. Beryllium follows it as importance and the third comes Calcium.
- Most important alloys are magnalium (Al – main component, 2%Mg, smaller amounts of Co, Ni, Pb), duralumin (Al – main component, 4.4%Cu, 1.4%Mg, 0.6%Mn) – both for the car wheel bag, elektron (94-95%Mg, small amounts of Al, Zn, Mn) – incendiary bombs, magnesium-zirconium alloys (Mg – main component, 3%Zn, 0-7%Zr) – for aircraft parts.
- Beryllium is a hard, mechanical resisting element, light, with high melting point and corrosion resistant. It passes these properties to their alloys. Bronzes of Be (Cu – main component, 2%Be, smaller amounts of Ni) are steel-like properties but with some better improvements – for instance no sparks at hits, important property in flammable environments.

Mg based alloys for structural components



Mechanical properties

Manufacturability

Density

Vehicle structural component

Safety

Homogeneity

Cost

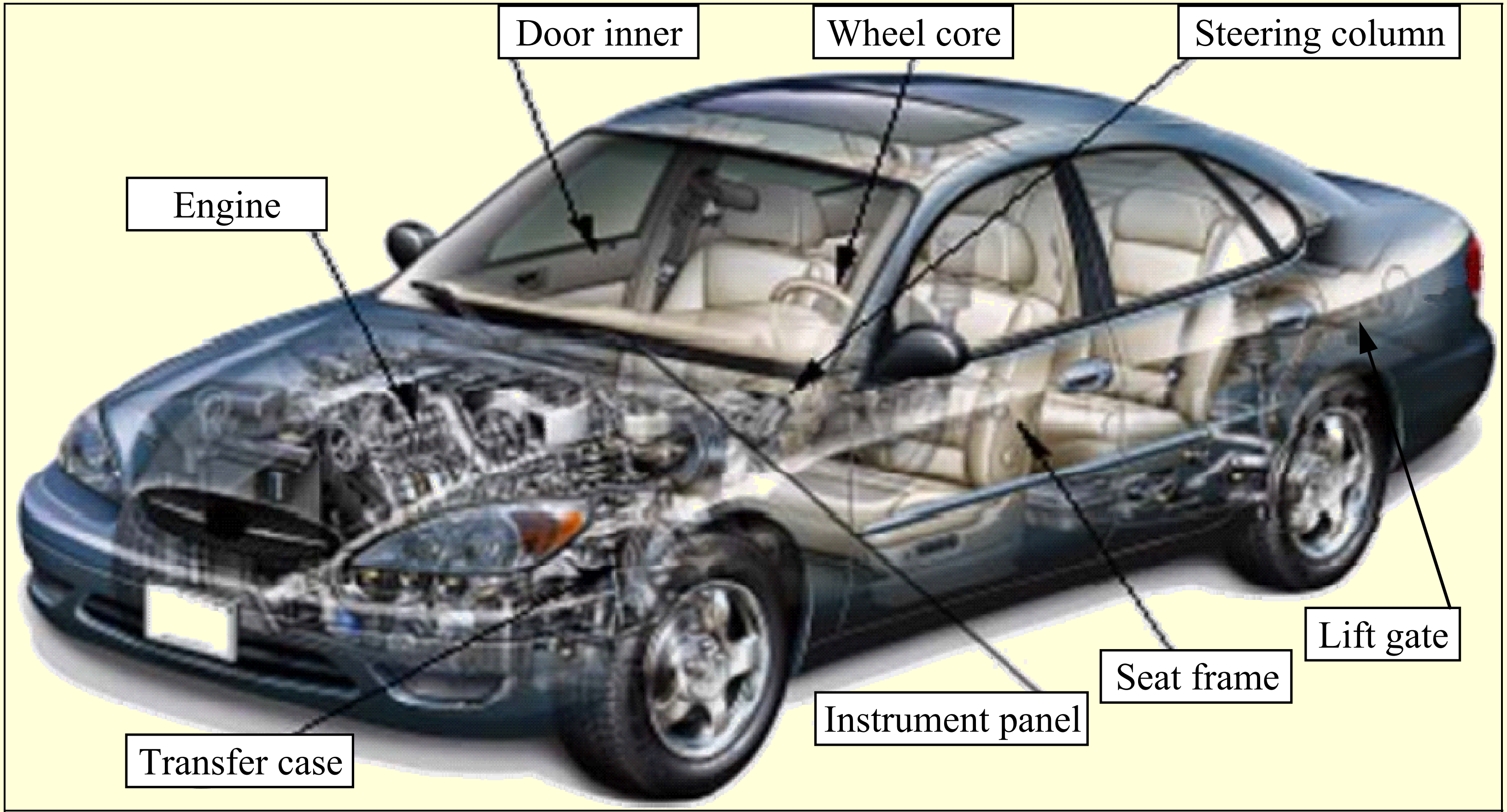
Chemical resistance

Working regime

Data	N.-Am. Die Cast. Ass. A-3-10-06 standard
RE	Rare earths (50% Ce, 25% La, 15% Nd)
IS	Impact strength (J)
HD	Hardness, Brinell hardness number
YS	Yield strength (MPa)
El	Elongation (%)
TE	Thermal expansion (μm/m·K)
TC	Thermal conductivity (W/m·K)

Alloy	of Mg	AZ81	AZ91	AM60	AM50	AM20	AS41	AE42	AE44
Additives (%)	Al	8	9	6	5	2	4	4	4
	Zn	0.7	0.7	6					
	Mn	0.2	0.2	0.3	0.4	0.6	0.4	0.3	0.4
	Si						1		
	RE							2.5	4
	ΣOth	<0.07	<0.15	<0.35	<0.35	<0.25	<0.20	<0.30	<0.03
Properties	IS	N/A	2.2	6.1	9.5	N/A	4.1	5.8	5.5
	HD	72	75	62	57	47	75	57	56
	YS	150	160	130	120	105	140	140	140
	El	3	3	7	8	10	6	9	9
	TE	25	25	25.6	26	26	26.1	26.1	26.2
	TC	51	72	62	62	60	68	68	68

Mg alloys advantage for vehicles parts



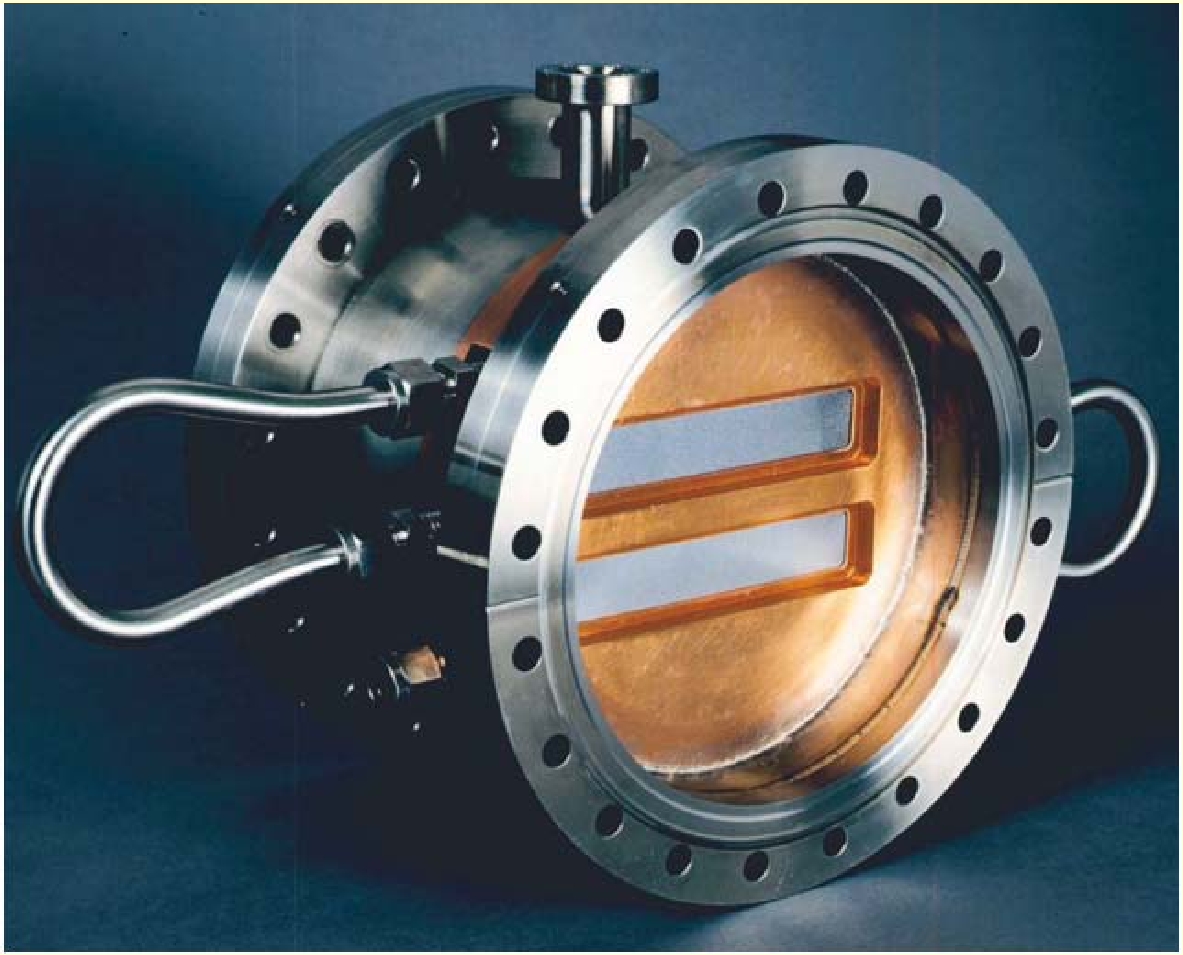
Mg alloys use reduces the weight with:
65% (replacing Fe alloy) for instrument panel & car seat frame;
40% (replacing Al alloy) for lift gate & steering column;
30% (replacing different other alloys) for wheel core, door inner & transfer case;
20-70% (replacing different other alloys) for engine.

Magnesium Oil and Sports Medicine

With magnesium oil, the concentrate can simply be applied to the skin or poured into bath water, and in an instant we have a powerful medical treatment.

http://magnesiumforlife.com/transdermal-magnesium/magnesium-oil/

Beryllium uses



X-ray apps: Beryllium window (FMB Oxford, 2009)

James Webb Space Telescope

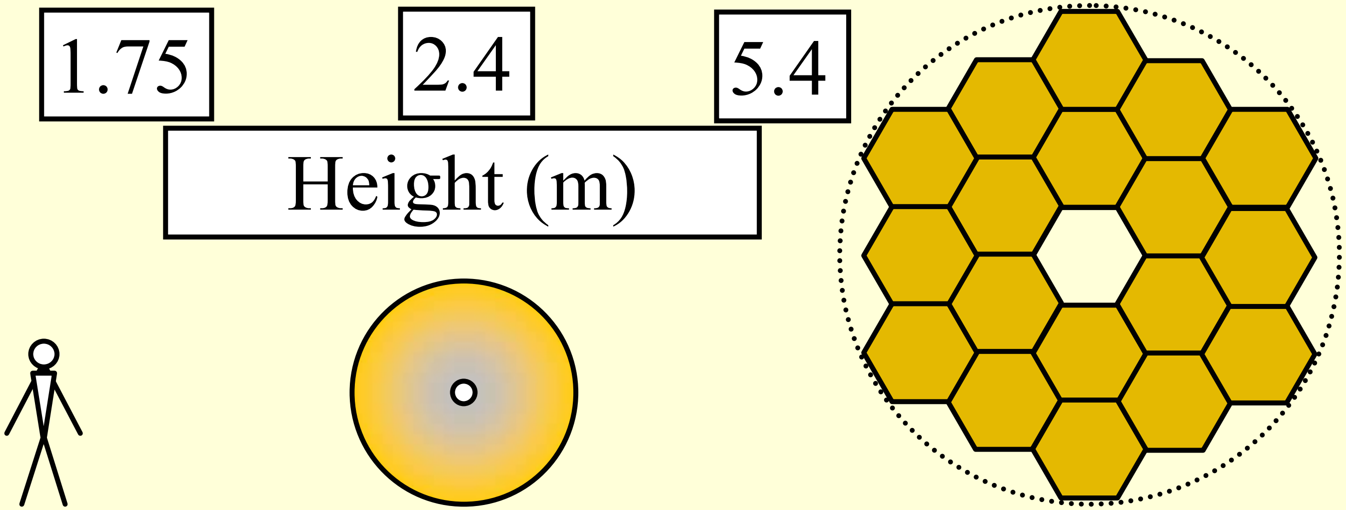
Gold coated beryllium reflector

Mass: 6 times less than Hubble

Mirror: 5 times larger than Hubble

January 25, 2022
https://www.mediafax.ro/life-inedit/james-webb-a-ajuns-la-destinatie-ce-distanta-a-parcurs-noua-masina-a-timpului-20480856

One panel



1.75

2.4

5.4

Height (m)

Human

Hubble mirror

James Webb mirror

2015 - the earliest possible launch date

- F-35B Aircraft (photo from www.jsf.mil) and many other aerospace vehicles rely on electrical and mechanical components made of beryllium alloys.

- Calcium is used in small quantities together with Pb in alloys for bearings, increasing their hardness. Extraction of other elements (Si, Ti, Cr, U, Pt) uses Mg and Ca. Be, Mg, Ca uses for ‘extraction’ – in slag - of S and O from the melt in metallurgy.
- Be, Mg and Ca chlorides are deliquescent – ‘eat’ (absorbs) water from environment till become from solid a saturated solution – use for humidity control.

Calcium uses

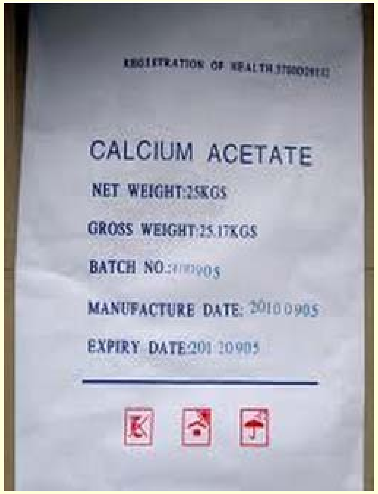
$CaCO_3$ - paints

$CaCl_2$ - dust control for unpaved roads

$CaSO_4\cdot\frac{1}{2}H_2O$ - medical apps

$Ca_3(PO4)_2$ - fertilizers

CaC_2 - carbide - welding



$Ca(CH_3COO)_2$ - foods additive

Ca, Mg, Vitamins - pharmaceutical

CaO - building industry

- In industry ***carbonates*** are a source of oxides (CaO or MgO) for obtaining of oxide materials. Lime is involved in the following reactions:

$$CaCO_3 \rightarrow CO_2 + CaO \text{ (from ore)}$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \text{ (for painting the wall)}$$

$$Ca(OH)_2 + CO_2 \rightarrow H_2O + CaCO_3 \text{ (on the wall, in time)}$$

- White marble is a allotropic form of $CaCO_3$.

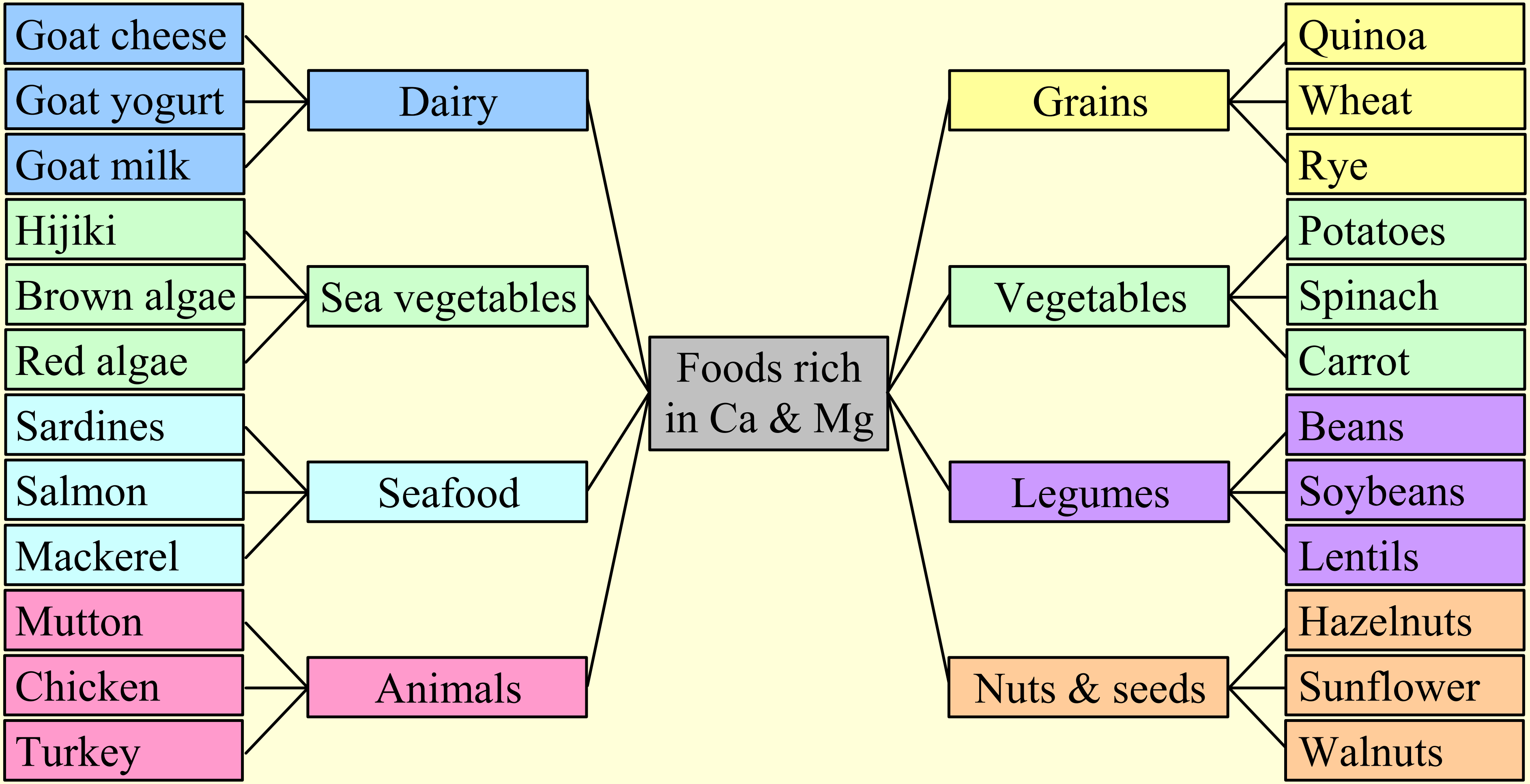
- ***Nitrites***, ***$M(NO_3)_2$*** are obtained from carbonates and are used in pyrotechnics.
- ***Sulfates***, ***MSO_4*** excepting of Be are found in nature. Some hydrates of them are important ones: $MgSO_4 \cdot 7H_2O$ (Epsom salt) and $CaSO_4 \cdot 2H_2O$ (gypsum).

Epsom salt – for bath

Q & R

Alkali earth metal applications include:		
	0	Medical: HgO
	0	Construction: BaO
	0	Welding: BeC_2
	0	Solvents: CaS_2
	1	Fertilizer: $Ca_3(PO_4)_2$
	1	Humidity control: $CaCl_2$
	1	X-ray windows: Be
	1	Sports Medicine: Mg
	1	Steel-like alloys: Be in alloys based on Cu
	1	Durable and lightweight alloys: Mg in alloys based on Al

Sources of Ca & Mg in foods



Foods rich in Ca & Mg

- Dairy
  - Goat cheese
  - Goat yogurt
  - Goat milk
- Sea vegetables
  - Hijiki
  - Brown algae
  - Red algae
- Seafood
  - Sardines
  - Salmon
  - Mackerel
- Animals
  - Mutton
  - Chicken
  - Turkey
- Grains
  - Quinoa
  - Wheat
  - Rye
- Vegetables
  - Potatoes
  - Spinach
  - Carrot
- Legumes
  - Beans
  - Soybeans
  - Lentils
- Nuts & seeds
  - Hazelnuts
  - Sunflower
  - Walnuts

Course 6

“p^3-p^6” block (groups 15 - 18)

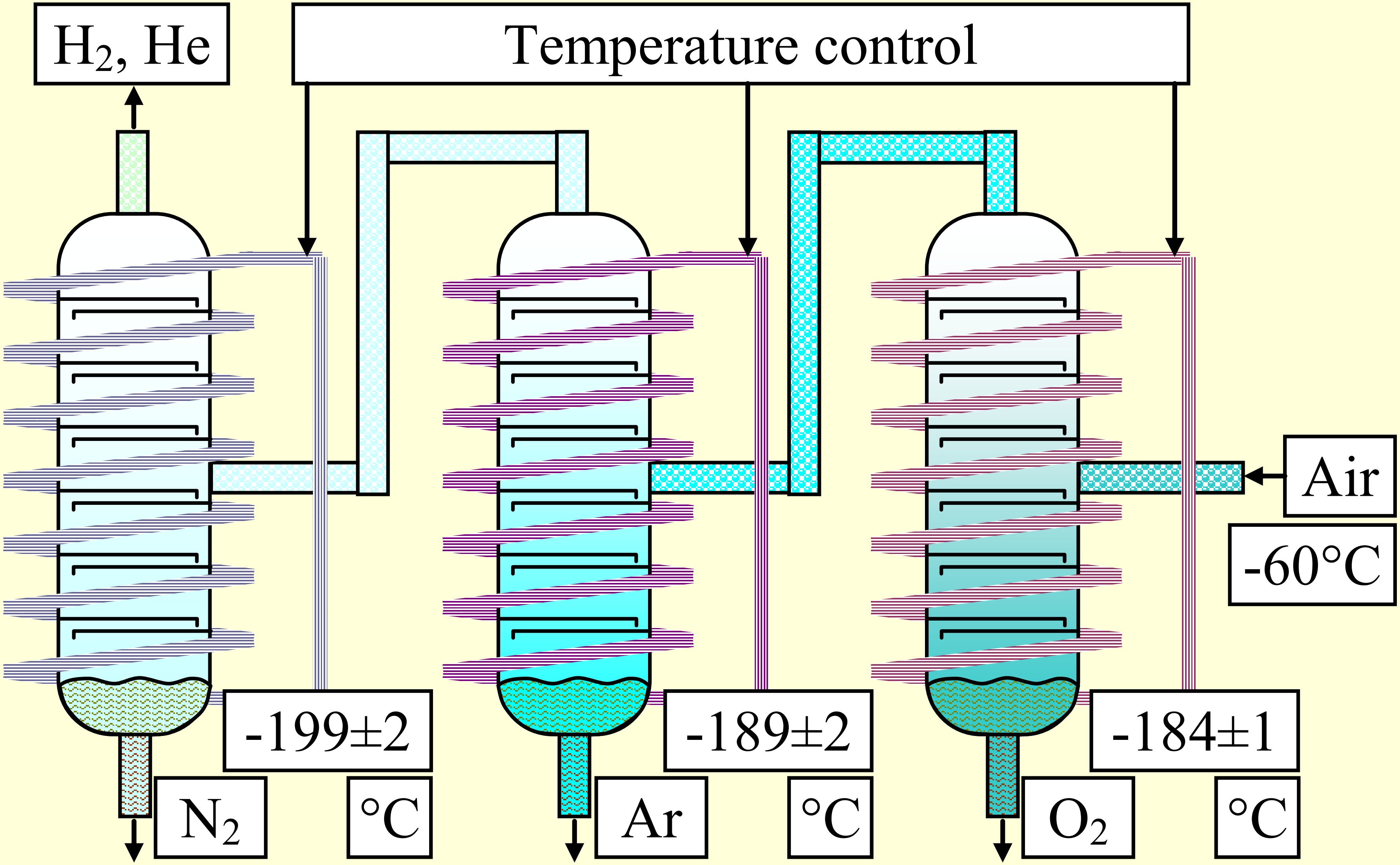
“p” block

	p1	p2	p3	p4	p5	p6
2	**B**	**C**	**N**	**O**	**F**	**Ne**
3	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
4	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
5	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
6	**Tl**	**Pb**	**Bi**	**Po**	**At**	**Rn**
e^-	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6

N, P, As, Sb, Bi

- The group 15 is important for the two life-supporting elements: nitrogen (N) and phosphorus (P), first being indispensable in the proteins and enzymes composition. Phosphorus is essential for nervous tissues, bones, and cell cytoplasm. Nitrogen has important applications as fertilizer (NH_4NO_3) and in surface treatment (nitriding, for hardening the surface). On the opposite, arsenic (As) and antimony (Sb) and its compounds are toxic, biological organisms having the tendency to confound As with P and S, and the presence of the As in place of P and S block the normal biological mechanisms. Sb has far less toxicity than As, but is still toxic.

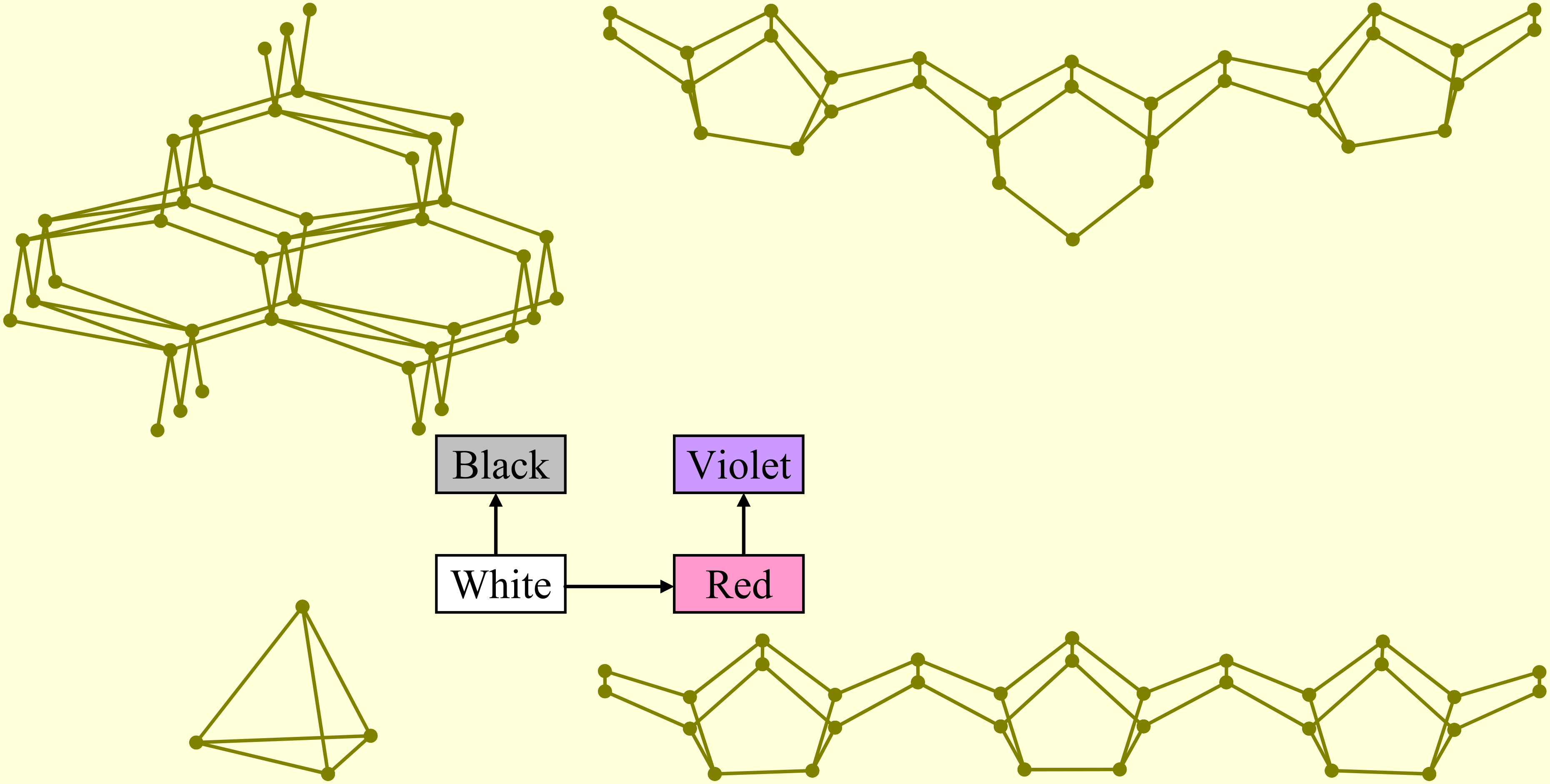
Separating air through distillation



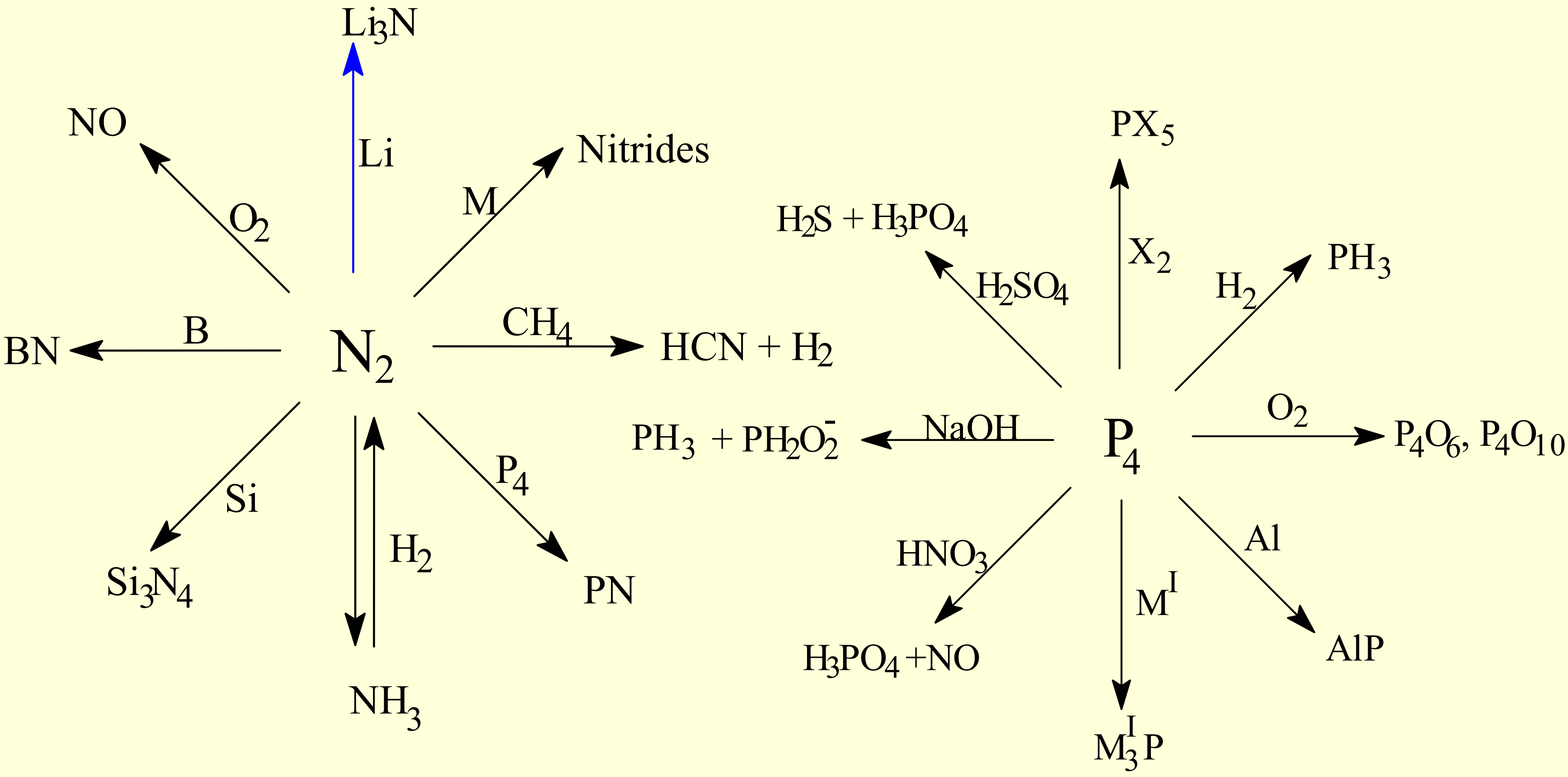
Separating of N through distillation

- Obtaining nitrogen by Claude procedure is based on successive condensations and air detention which results in a sufficient decrease its liquefaction temperature which is strictly necessary. Liquid air is then sent some rectification column which is inserted into the middle of them and at the top, some liquid nitrogen, obtained by condensation (bp = -195.8 °C), flows from top to bottom on some plates, while gas (evaporated air) rises bottom up. Such liquid separates top with lower boiling - nitrogen - and the base less volatile liquid oxygen (bp = -183 °C). Traces of oxygen that remains in nitrogen generally be removed by passing over copper glow when there is reaction: $2Cu + O_2 \rightarrow 2CuO$

Phosphorus allotropes



N, P – chemical properties



$N_2 \xrightarrow{Li} Li_3N$

$N_2 \xrightarrow{O_2} NO$

$N_2 \xrightarrow{M} \text{Nitrides}$

$N_2 \xrightarrow{B} BN$

$N_2 \xrightarrow{CH_4} HCN + H_2$

$N_2 \xrightarrow{Si} Si_3N_4$

$N_2 \underset{}{\overset{H_2}{\rightleftarrows}} NH_3$

$N_2 \xrightarrow{P_4} PN$

$P_4 \xrightarrow{X_2} PX_5$

$P_4 \xrightarrow{H_2SO_4} H_2S + H_3PO_4$

$P_4 \xrightarrow{H_2} PH_3$

$P_4 \xrightarrow{NaOH} PH_3 + PH_2O_2^-$

$P_4 \xrightarrow{O_2} P_4O_6, P_4O_{10}$

$P_4 \xrightarrow{HNO_3} H_3PO_4 + NO$

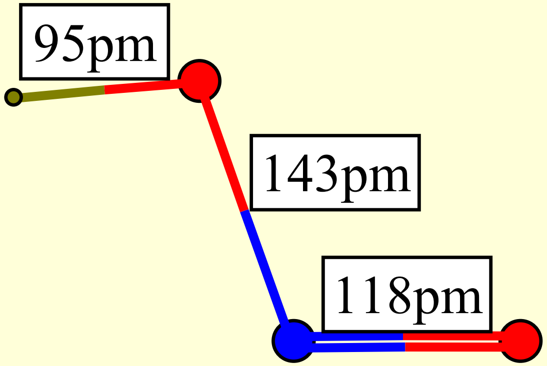
$P_4 \xrightarrow{M^I} M^I_3P$

$P_4 \xrightarrow{Al} AlP$

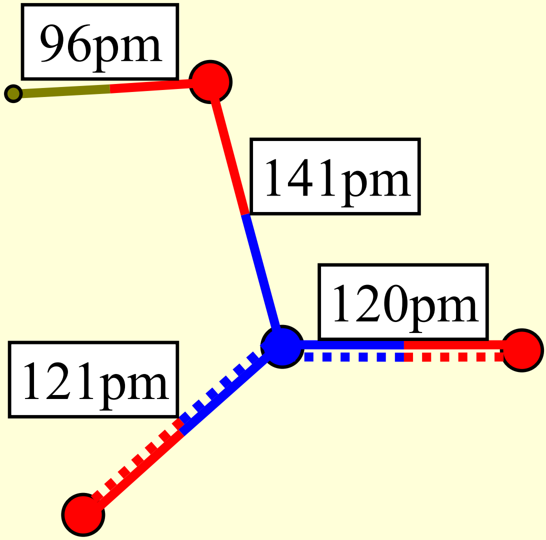
N, P - Uses

- ***Nitrogen*** is transported, is gas state, under pressure, in bottles at about 150 atm, or as liquid, at very low temperatures (77K). Its main use is for obtaining of ammonia – about ¾ of ammonia serves to obtain fertilizers. Other applications include organic compounds, explosives, and plastics. It uses also as inert gas or protection gas in modern electronics, chemistry, metallurgy, and even for inflating tires due to its small coefficient of dilatation with temperature. Surface treatment are often done with nitrogen from ammonia rather than from N_2.
- ***Phosphorus*** is used for matches, incendiary bombs, smoke grenades, and tracer rounds. Even if is an undesired element in steels, and in general in alloys, small quantities are present along with Fe, Cu and Sn. An example is phosphorus bronzes. In steels, a certain level of P concentration assures machinability for cutting and wear resistance.

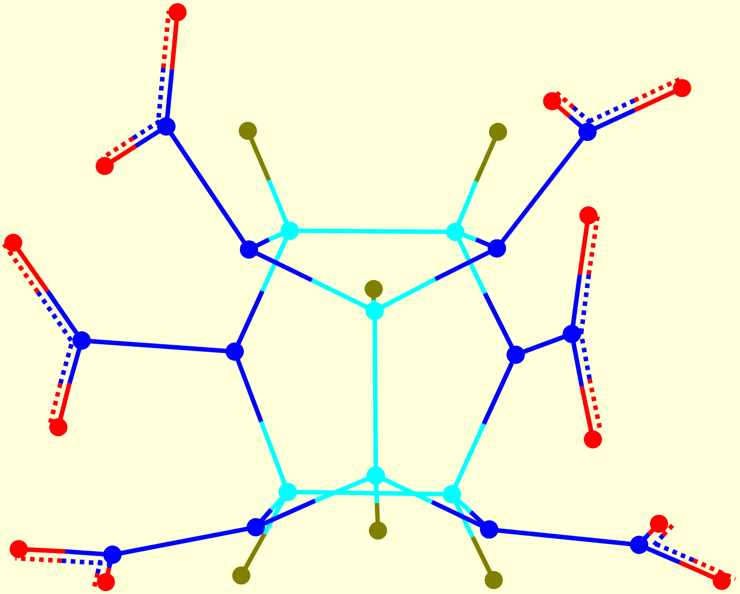
Nitrites and nitrates



HNO_2



HNO_3



CL-20: hexaazaisowutzitane

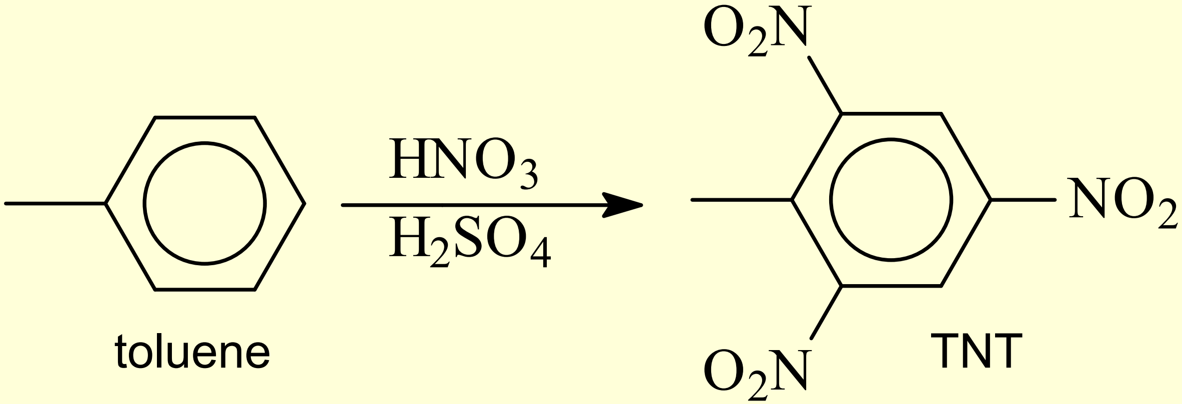
Explosions

CL-20: $C_6H_6N_{12}O_{12}(s) \rightarrow 6N_2(g) + 3CO(g) + 3CO_2(g) + 3H_2O(g)$

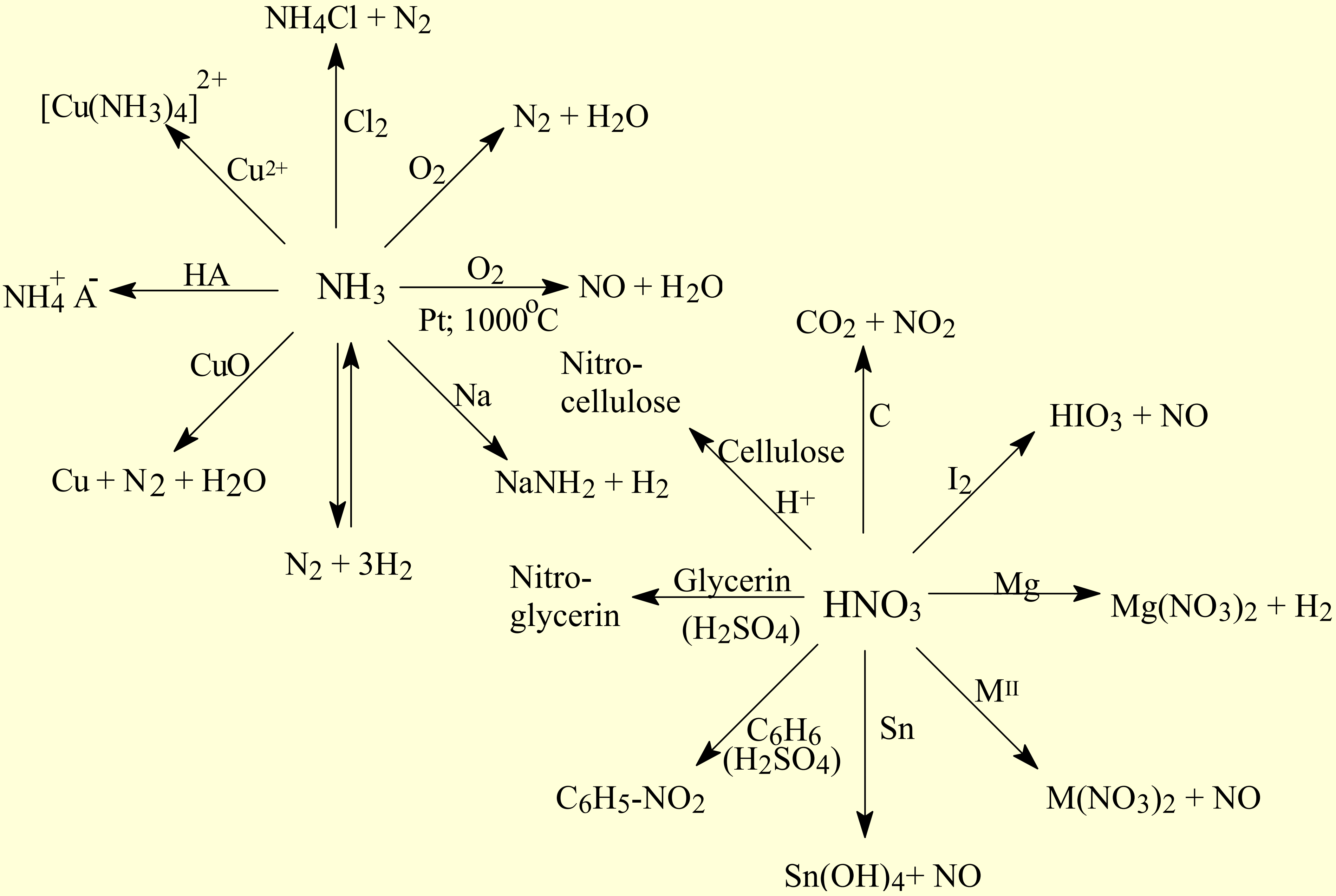
TNT: $2C_7H_5N_3O_6(s) \rightarrow 3N_2(g) + 7CO(g) + 5H_2O(g) + 7C(s)$

TriNitroToluene (TNT)

- TNT is explosive for two reasons. First, it contains the elements carbon, oxygen and nitrogen, which means that when the material burns it produces highly stable substances (CO, CO_2 and N_2) with strong bonds, so releasing a great deal of energy. This is a common feature of most explosives; they invariably consist of many nitrogen or oxygen containing groups (usually in the form of 2, 3 or more nitro-groups), attached to a small, constricted organic backbone.



Ammonia & nitric acid – chemical properties



$NH_3 \xrightarrow{Cl_2} NH_4Cl + N_2$

$NH_3 \xrightarrow{Cu^{2+}} [Cu(NH_3)_4]^{2+}$

$NH_3 \xrightarrow{O_2} N_2 + H_2O$

$NH_3 \xrightarrow{HA} NH_4^+ A^-$

$NH_3 \xrightarrow[Pt;\ 1000^oC]{O_2} NO + H_2O$

$NH_3 \xrightarrow{CuO} Cu + N_2 + H_2O$

$NH_3 \rightleftarrows N_2 + 3H_2$

$NH_3 \xrightarrow{Na} NaNH_2 + H_2$

$HNO_3 \xrightarrow{C} CO_2 + NO_2$

$HNO_3 \xrightarrow[H^+]{Cellulose}$ Nitrocellulose

$HNO_3 \xrightarrow{I_2} HIO_3 + NO$

$HNO_3 \xrightarrow[(H_2SO_4)]{Glycerin}$ Nitroglycerin

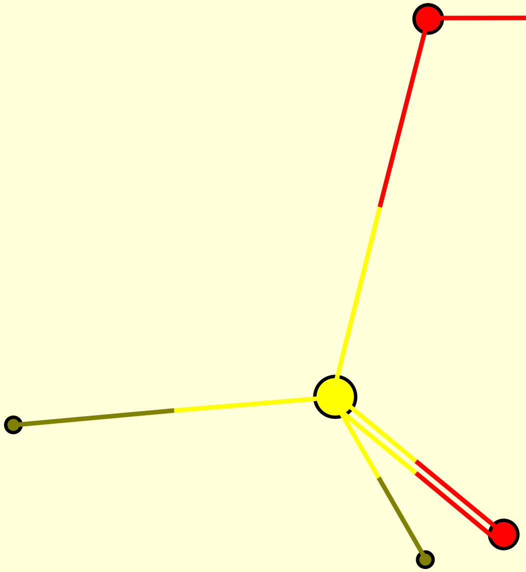
$HNO_3 \xrightarrow{Mg} Mg(NO_3)_2 + H_2$

$HNO_3 \xrightarrow[(H_2SO_4)]{C_6H_6} C_6H_5\text{-}NO_2$

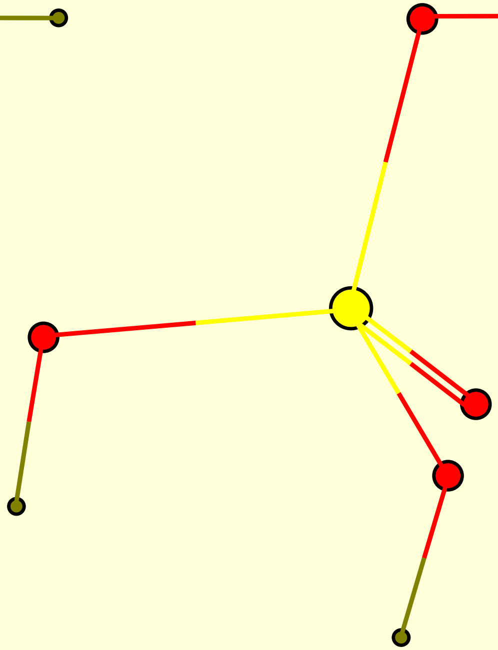
$HNO_3 \xrightarrow{Sn} Sn(OH)_4 + NO$

$HNO_3 \xrightarrow{M^{II}} M(NO_3)_2 + NO$

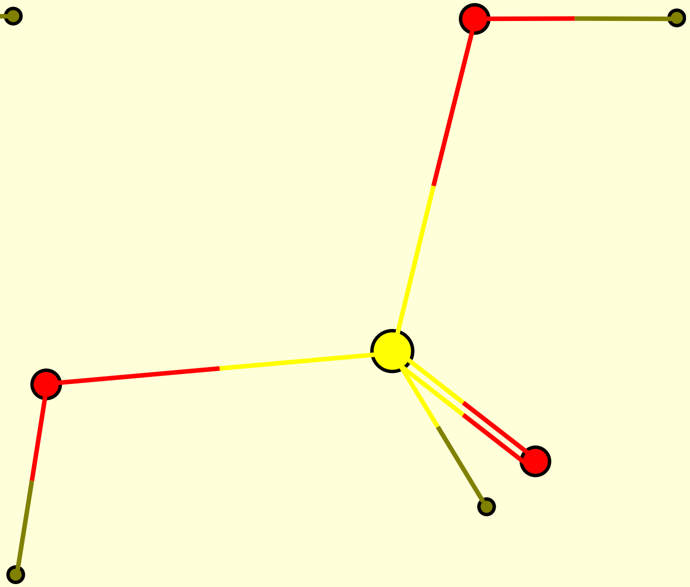
Phosphorus oxyacids



H_3PO_2

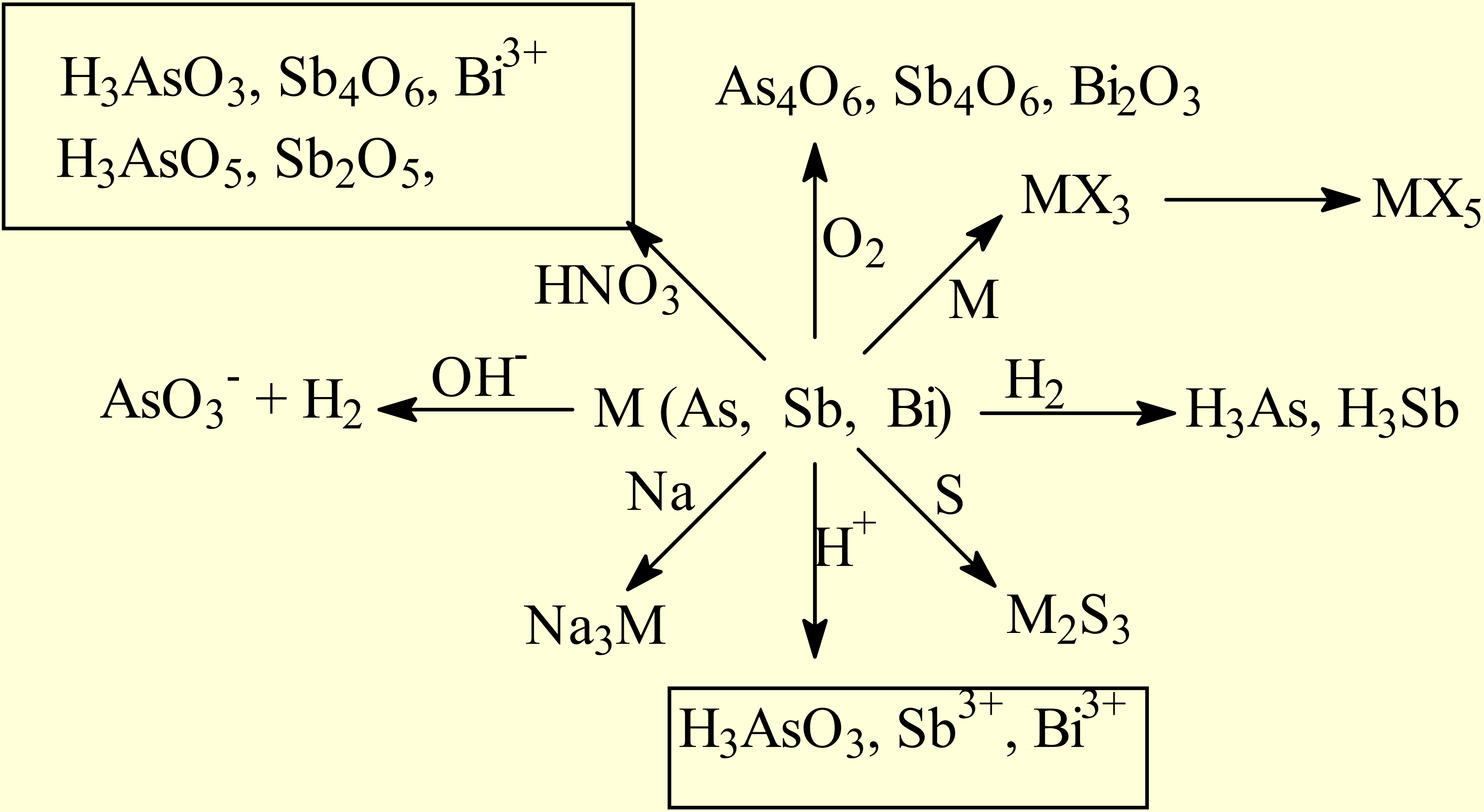


H_3PO_3



H_3PO_4

As, Sb, Bi – chemical properties



H_3AsO_3, Sb_4O_6, Bi^{3+}

H_3AsO_5, Sb_2O_5,

As_4O_6, Sb_4O_6, Bi_2O_3

MX_3 → MX_5

HNO_3

O_2

M

$AsO_3^- + H_2$ $\xleftarrow{OH^-}$ M (As, Sb, Bi) $\xrightarrow{H_2}$ H_3As, H_3Sb

Na

H^+

S

Na_3M

M_2S_3

H_3AsO_3, Sb^{3+}, Bi^{3+}

As, Sb, Bi - Toxicity

- As, Sb and all their combinations including oxides and salts are toxic. Bi is not toxic, but their compounds, with some exceptions, are. Volatility of As and its compounds coupled with the toxicity makes that As to be a very dangerous element. As and their compounds may occurs as pollutants of water and air. As in the case of Hg, As may be transformed by bacteria in methyl-derivatives, even more toxic and mobile:

Methyl-cobalt-amine = B_{12} vitamin

$$H_3AsO_4 + 2H^+ + 2e^- \rightarrow H_3AsO_3 + H_2O$$

$$H_3AsO_3 + B_{12} \rightarrow CH_3AsO(OH)_2$$ – methyl-arsenic acid

$$CH_3AsO(OH)_2 + B_{12} \rightarrow (CH_3)_2AsO(OH)$$ – di-methyl-arsenic acid

$$(CH_3)_2AsO(OH) + 4H^+ + 4e^- \rightarrow 2H_2O + (CH_3)_2AsH$$ - dimethylarsine

Q & R

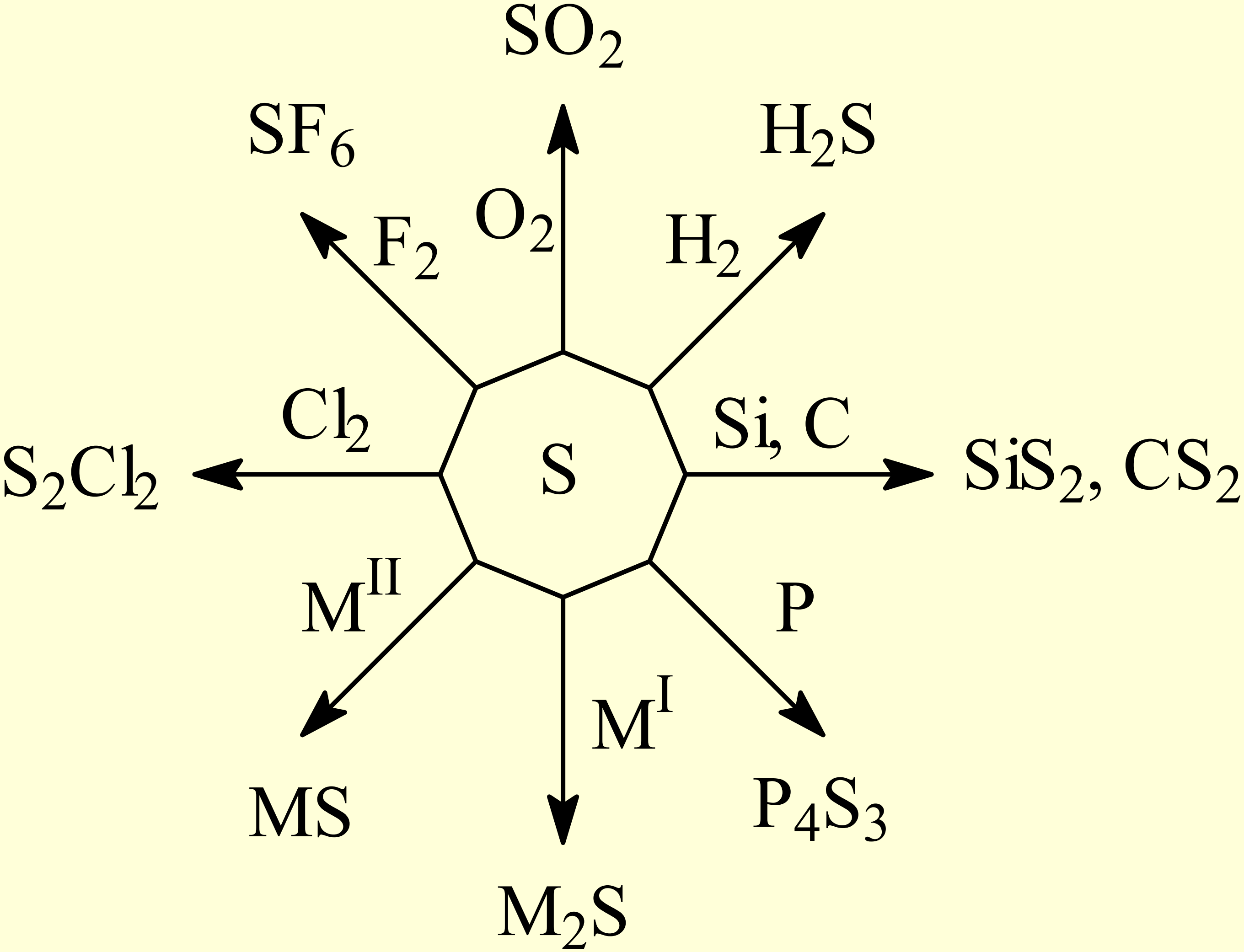
In connection with the group 15 elements (N, P, As, Sb, Bi):		
	0	N is used for matches
	1	P is used for matches
	0	P has applications in surface treatment - phosphing
	1	N has applications in surface treatment - nitring
	0	N and P and their compounds are toxic to biological organisms
	1	As and Sb and their compounds are toxic to biological organisms
	0	Bi is used in fertilizers: BiH_4BiO_3
	1	N is used in fertilizers: NH_4NO_3
	0	As and Sb sustain life (As: enzymes, proteins; Sb: nerve tissue, bone, cell cytoplasm)
	1	N and P sustain life (N: enzymes, proteins; P: nerve tissue, bone, cell cytoplasm)

Sulfur allotropes

Over 30 (more than any other element)

A mixture of allotropes mainly contains S_8 with small amounts of S_6 & S_7.

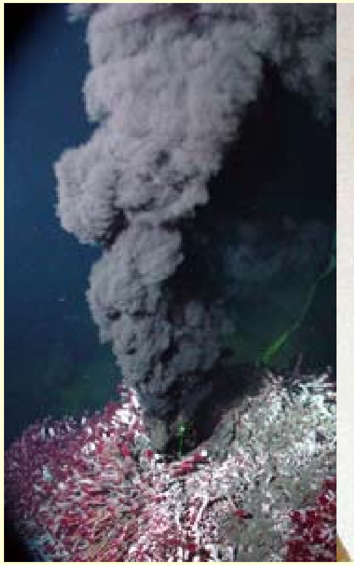
Sulfur: chemical properties

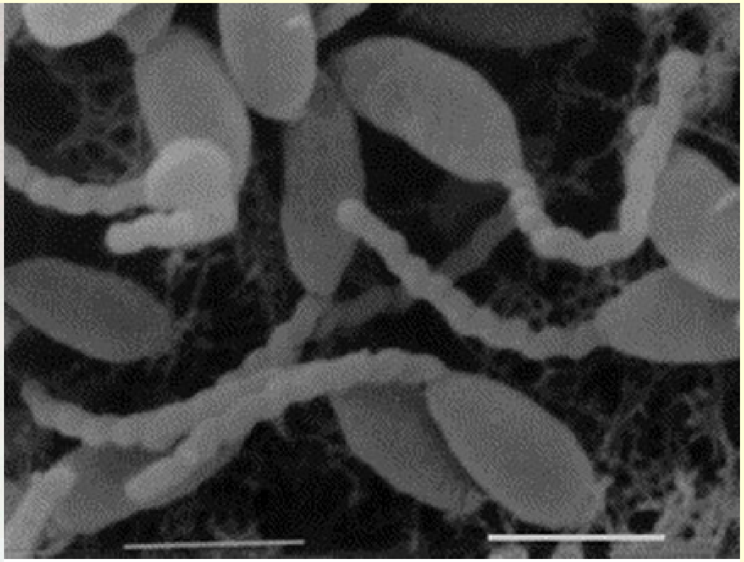


Sulfur biochemistry

- Sulfur is an essential constituent, even in minor quantities, to proteins, and amino-acids such as cysteine and methionine.
- In both proteins and enzymes sulfurs is found as –S–S– bridges. Vitamin B1, coenzyme A and many other organics contains S (for instance mustard and garlic). Sulfur based fermentations made by some anaerobic microorganisms – which in their oxidation processes reduces the sulfates to sulfides (SO_4^{2-} to S^{2-}) play an important role in formation of oil reserves.
- It exists bacteria which process sulfur as other process oxygen and it survives to temperatures till 150°C.

Sulfur-based living organisms





Riftia pachyptila worm (till 2m long) lives from 1Km to 10Km in ocean deep, near ***'black smokers'*** and is in symbiosis with ***Hyphomicrobium sulfonivorans***

dimethylsulfone $(CH_3)_2SO_2$

$$(CH_3)_2SO_2 \xrightarrow[NAD^+ + H_2O]{NADH + H^+} (CH_3)_2SO$$

dimethylsulfoxide $(CH_3)_2SO$

$$(CH_3)_2SO \xrightarrow[NAD^+ + H_2O]{NADH + H^+} (CH_3)_2S$$

dimethylsulfide $(CH_3)_2S$

$$(CH_3)_2S \xrightarrow[NAD^+ + H_2O]{NADH + H^+ + O_2} CH_3SH + HCHO$$

methanethiol $CH_3SH + HCHO$

Assimilation of formaldehyde

CH_3SH methanethiol

$$CH_3SH \xrightarrow[H_2O_2]{H_2O + O_2} HCHO + H_2S$$

$HCHO+ H_2S$

CH_3SO_3H methanesulfonate

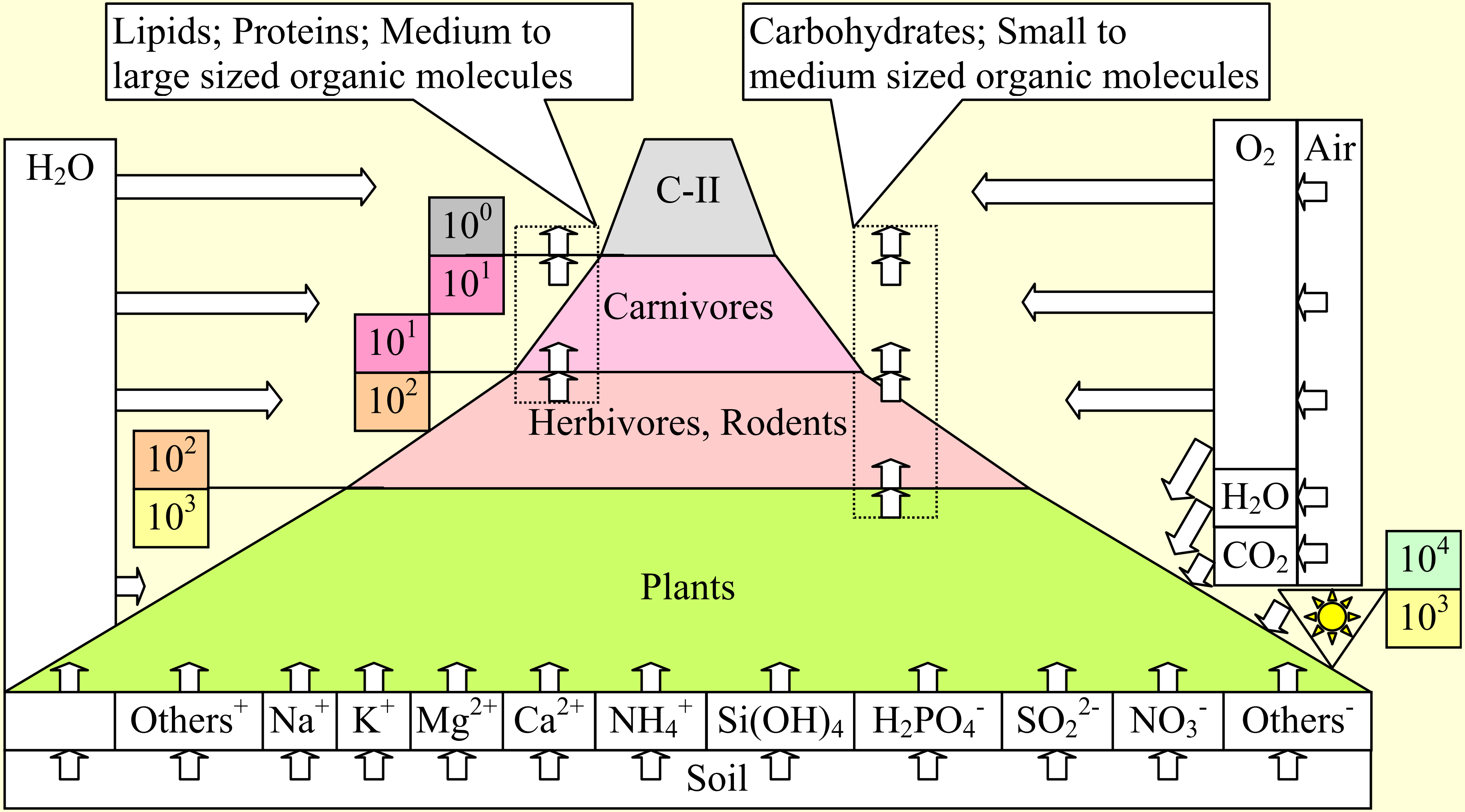
$$CH_3SO_3H \xrightarrow[NAD^+ + H_2O]{NADH + H^+ + O_2} HCHO + H_2SO_3$$

$HCHO+ H_2SO_3$

S, Se, Te - Uses

- **Sulfur** has uses mainly as combinations. On large scale are produced sulfuric acid (90% of sulfur involved in). About 60% from sulfuric acid is for production of fertilizers. Sulfites, bisulfites and SO_2 are used in large quantities as bleach. Elemental S are used to obtain CS_2 (precursor of CCl_4) and viscose fibers. An important application is on rubber vulcanization. Other applications includes obtaining of fungicides, pesticides and gunpowder (a mixture of KNO3 – 75%, C – 15%, S – 10%).
- **Selenium** is used for glass discoloration (and a mixture of Cu, S & Se for coloring the glass in red colors range). Applications include photocopy machines, image capturing (thin film of Se on Al support) and photovoltaic cells. Selenides are used for toning in photographies development. Adding of Se in steels and alloys generally increases the resistance to corrosion. In small quantities is a part of some enzymes. Large quantities are toxic.
- **Tellurium** is used as alloying element for steels and non-ferrous alloys (with Cu, Ag, Pb) to color in blue the glasses, in photography development as well as for rubber vulcanization.

Trophic chain, biomass & energy conversion



Lipids; Proteins; Medium to large sized organic molecules

Carbohydrates; Small to medium sized organic molecules

H_2O

O_2

Air

10^0

10^1

C-II

10^1

10^2

Carnivores

Herbivores, Rodents

10^2

10^3

Plants

H_2O

CO_2

10^4

10^3

Others$^+$ | Na^+ | K^+ | Mg^{2+} | Ca^{2+} | NH_4^+ | $Si(OH)_4$ | $H_2PO_4^-$ | SO_2^{2-} | NO_3^- | Others$^-$

Soil

Q & R

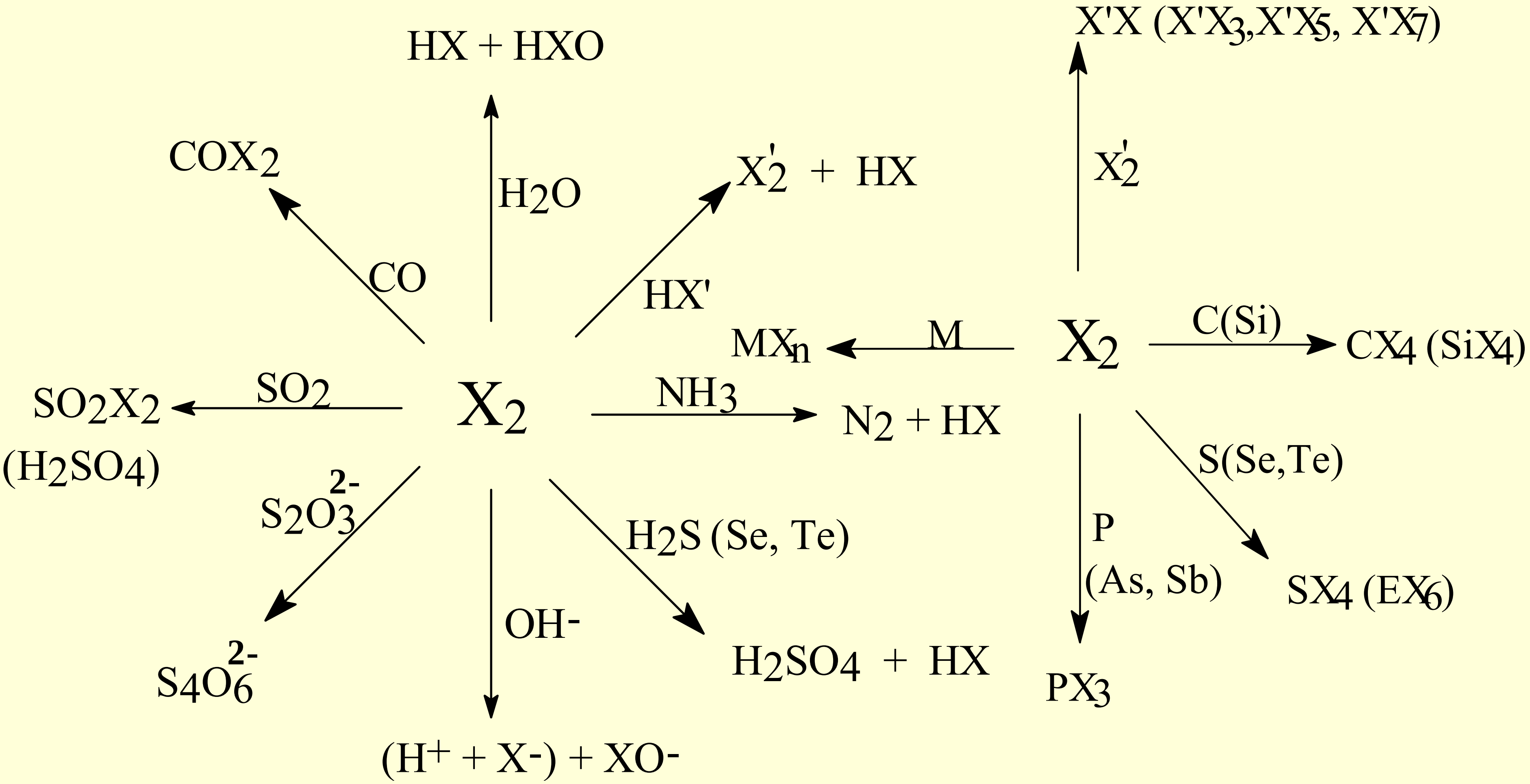
In connection with elements from group 16 (S, Se, Te, Po):		
	0	Are living organisms based on Te
	0	Are living organisms based on Se
	1	Are living organisms based on S
	0	$S + H_2 \rightarrow H_6S$
	1	$S + H_2 \rightarrow H_2S$
	0	$O_2 + F_2 \rightarrow OF_6$
	0	$S + F_2 \rightarrow SF_2$
	1	$O_2 + F_2 \rightarrow OF_2$
	1	$S + F_2 \rightarrow SF_6$
	0	Te has over 30 allotropes (Te_2, Te_3, Te_4, Te_5, Te_6, Te_7, Te_8, Te_9, ...)
	0	Se has over 30 allotropes (Se_2, Se_3, Se_4, Se_5, Se_6, Se_7, Se_8, Se_9, ...)
	1	S has over 30 allotropes (S_2, S_3, S_4, S_5, S_6, S_7, S_8, S_9, ...)

Halogens – physical properties

Property	F	Cl	Br	I	At
M.p., °C	-220	-101	-7	114	
B.p., °C	-188	-35	59	183	
Solubility, in water, at 20°C	-	0.09	0.21	0.002	
Electronegativity (Pauling)	4	3	2.8	2.5	2.2
ε^0 – reduction potential, V	2.87	1.36	1.07	0.54	0.3
Dissociation energy, $kJ\cdot mol^{-1}$	157	244	193	15.1	116
Atomic radius, nm	6.4	9.9	11.1	21.8	-
Ionic radius, nm	13.3	18.1	19.6		-

All halogens have an characteristic unpleasant, toxic smell. All solves in organic solvents.

Halogens – chemical properties



$X_2 \xrightarrow{H_2O} HX + HXO$

$X_2 \xrightarrow{CO} COX_2$

$X_2 \xrightarrow{HX'} X'_2 + HX$

$X_2 \xrightarrow{SO_2} SO_2X_2$ (H_2SO_4)

$X_2 \xrightarrow{NH_3} N_2 + HX$

$X_2 \xrightarrow{S_2O_3^{2-}} S_4O_6^{2-}$

$X_2 \xrightarrow{OH^-} (H^+ + X^-) + XO^-$

$X_2 \xrightarrow{H_2S\ (Se,\ Te)} H_2SO_4 + HX$

$X_2 \xrightarrow{X'_2} X'X\ (X'X_3, X'X_5, X'X_7)$

$X_2 \xrightarrow{M} MX_n$

$X_2 \xrightarrow{C(Si)} CX_4\ (SiX_4)$

$X_2 \xrightarrow{S(Se,Te)} SX_4\ (EX_6)$

$X_2 \xrightarrow{P\ (As,\ Sb)} PX_3$

Q & R

Identify which oxidation states are correctly given for Chlorine:		
	0	Cl_2 => Cl: +1
	1	Cl_2 => Cl: 0
	0	Cl_2 => Cl: -1
	1	HClO => Cl: +1
	0	HClO => Cl: -1
	0	HCl => Cl: +1
	1	$HClO_4$ => Cl: +7
	1	HCl => Cl: -1

Halogens – uses

- Fluorine is used to obtain industrial CFC (chloro-fluorocarbons - abbreviated CFC) substances important for generating aerosols and as refrigerants and foaming agents (to obtain porous polymers). A certain range of CFC has found applications as artificial blood (colorless). May also be used in industrial synthesis of polytetrafluoroethylene (PTFE short, a polymer known under the trade name Teflon ®), which according to the number of units in the chain can be a lubricant (oil) or mechanically and thermally resistant plastic, gaskets used (even at high pressures) or as an agent that prevents adhesion (for example PTFE coated dishes). All elemental fluorine is synthesized UF_6 - an intermediary necessary to separate the isotope ^{235}U used in nuclear plants.

Halogens - uses

- Chlorine is used for organic synthesis: trichlorophenol is a disinfectant; vinyl chloride – for producing polyvinyl chloride (PVC) - one of the most used polymers. Also serves to obtain sodium hypochlorite, household disinfectant and bleaching agent; $CaCl_2$ - brine for refrigeration plants, ice and dust control on roads, and desiccation. Chlorine gas was first used warfare; chlorine derivatives serve the same purpose today, eg mustard gas ($Cl\text{-}(CH_2)_2\text{-}S\text{-}(CH_2)_2\text{-}Cl$). It is used less and less for drinking water treatment and disinfect. All of chlorine summarizes some important industrial solvents: chloroform - $CHCl_3$, carbon tetrachloride - CCl_4. It can be taken into account that 111-trichloroethane and perchloroethylene (Tetrachloroethylene) are industrial solvents used in degreasing or dry cleaners. Chloroform - $CHCl_3$, was the first general anesthetic used in surgery. Today other halogen derivatives (eg $CF_3\text{-}CHBrCl$) took his place as anesthetics. In addition, ethyl chloride, C_2H_5Cl, is a local anesthetic.

Halogens - uses

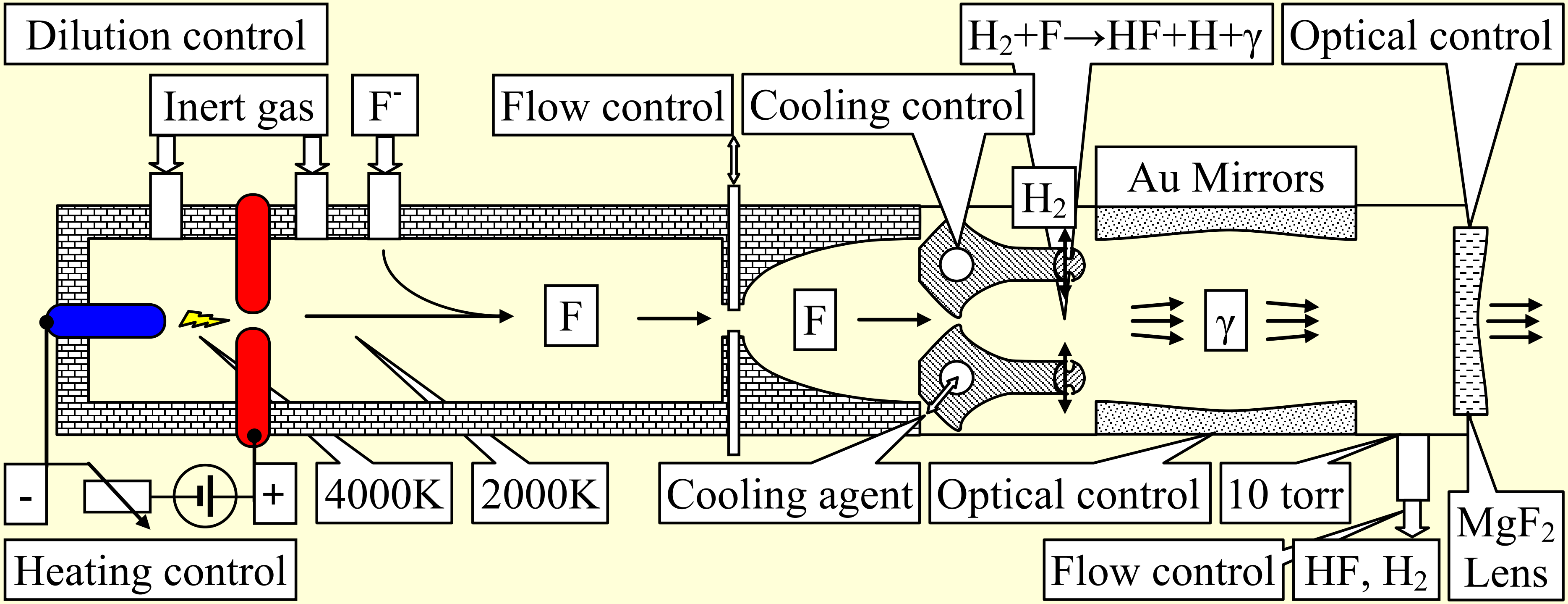
- **Bromine**: many organic synthesis, for example getting 1,2-dibromoethane, a gasoline additive that prevents sudden burning gasoline, octane rating boosting, bromo-chloro-methane (CH_2BrCl) synthesis - liquid used to fight fire - in the presence of heat forms a curtain of heavy gas (high density), covering the flame preventing combustion.
- **Iodine** in the form of alcoholic solution with potassium iodide serves as a disinfectant and fungicide in the treatment of superficial lesions and certain skin diseases. Also the presence of iodine in bulbs (known as halogen bulbs) causes an increase in the brightness & extension of service life. For instance the decomposition of gaseous tungsten chloride on incandescent tungsten filament is on exactly where it should be (thinner places) because there due to the thermal effect of electric current, filament temperature is higher. Iodoform (CHI_3) on the other hand, is a much used disinfectant - whose synthesis is also used iodine.

Q & R (see & Course1)

In connection with halogens (X: F, Cl, Br, I, At):		
	0	F is the most electropositive element
	1	F is the most electronegative element
	0	$S + Cl_2 \longrightarrow SCl_6$
	1	$S + F_2 \longrightarrow SF_6$
	0	$X_2 + X'_2 \longrightarrow XX'_6$ (X=I, X'=F)
	1	$X_2 + X'_2 \longrightarrow XX'_7$ (X=I, X'=F)
	0	$X_2 + X'_2 \longrightarrow XX'_4$ (X=Br, X'=F)
	1	$X_2 + X'_2 \longrightarrow XX'_5$ (X=Br, X'=F)
	0	$X_2 + X'_2 \longrightarrow XX'_2$ (X=Cl, X'=F)
	1	$X_2 + X'_2 \longrightarrow XX'_3$ (X=Cl, X'=F)

Chemical lasers

Continuous wave chemical laser (USPTO 3688215, 29 Aug 1972)



Dilution control

$H_2+F \rightarrow HF+H+\gamma$

Optical control

Inert gas

F^-

Flow control

Cooling control

H_2

Au Mirrors

F

F

γ

-

+

4000K

2000K

Cooling agent

Optical control

10 torr

Heating control

Flow control

HF, H_2

MgF_2 Lens

Inert gas: N_2, He (.54 moles/s)

F^-: SF_6, NF_3 (SF_6: .037 moles/s)

H_2: H_2, D_2 (1 moles/s)

Input energy: 30 kW

Chemical energy: 4 kW

Laser energy: 0.5 kW

The entity that has the property right to the patent: United States of America

(He), Ne, Ar, Kr, Xe, Rn

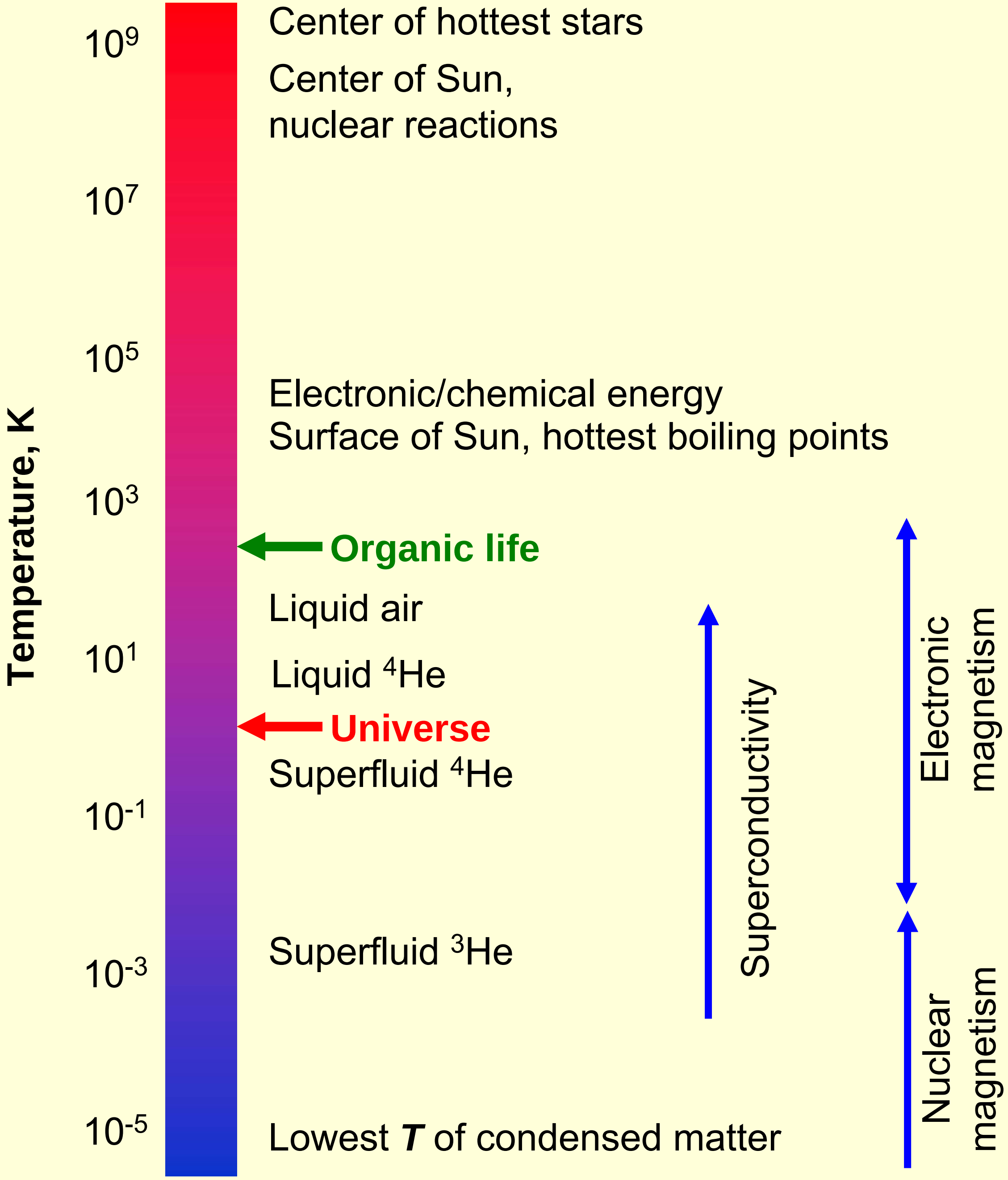
- **Inert?**
  - In 1962 the British Bartlett and Lohman were synthesized through reaction the xenon hexacloroplatinate:

$$Xe(g) + PtF_6(g) \rightarrow Xe[PtF_6](s)$$

  - The discovery was suggested by an oxidation reaction of oxygen (in a series of attempts to get more energetic oxidizers) ie:

$$O_2(g) + PtF_6(g) \rightarrow O_2[PtF_6](s)$$

  - The author of the discovery noted that the ionization energy of molecular oxygen (O_2) is very close to the of Xe. Experimental attempt was a success - xenon behave similar with molecular oxygen.



Center of hottest stars

Center of Sun,
nuclear reactions

Electronic/chemical energy
Surface of Sun, hottest boiling points

Organic life

Liquid air

Liquid ^{4}He

Universe

Superfluid ^{4}He

Superfluid ^{3}He

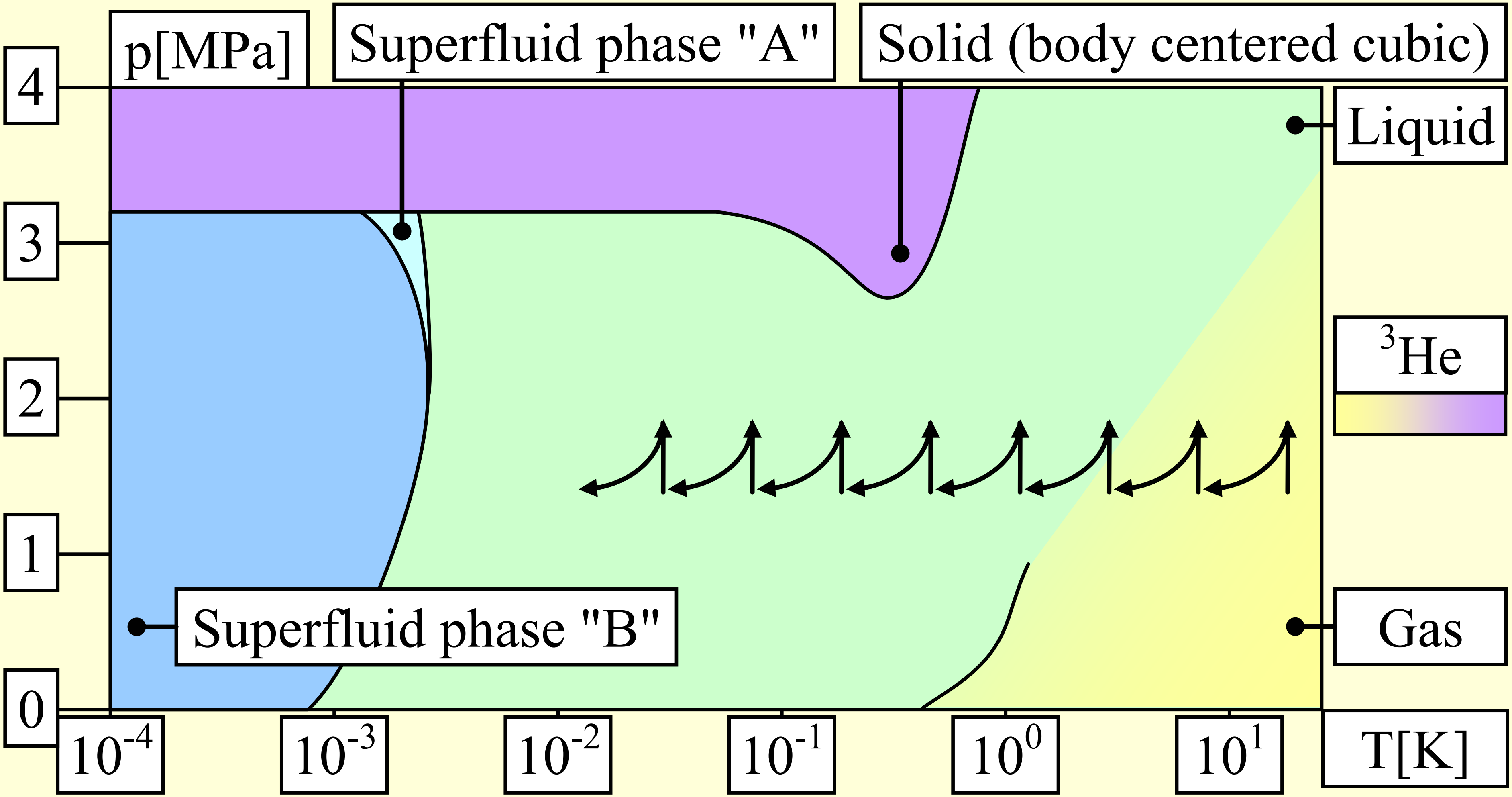
Lowest ***T*** of condensed matter

Superconductivity

Electronic
magnetism

Nuclear
magnetism

^{3}He – phases diagram



Noble gases – physical properties

- http://www.lps.ens.fr/~caupin/fichiersPDF/PhysicaB_2003_329-333_380-381.pdf, Very fast growth and melting of ^{4}He crystals He (at 2.5 MPa ~10 atm.): -272.2 °C (0.95 K)

Gas	I.P. (eV)	H.v. (kJ·mol^{-1})	M.P. (°C)	B.P. (°C)	Radius (nm)	Solubility (mg·l^{-1})
He	24.58	0.08	-	-269.0	12.0	13.8
Ne	22.56	1.7	-248.6	-246.0	16.0	14.7
Ar	15.75	6.5	-189.4	-186.0	19.1	37.9
Kr	14.00	9.1	-157.2	-153.6	20.0	73
Xe	12.13	12.7	-111.8	-108.1	22.0	110.9
Rn	10.75	18.1	-71	-62	-	-

Noble gases - uses

- **Helium** has the lowest boiling point of all liquids used in freezing known for obtaining extremely low temperatures (superconducting necessary studies or lasers) and the gas thermometers such temperatures. It was also used as cooling gas in some nuclear reactors or gas chromatographic analyzers bearer. Also used to replace nitrogen pressure cylinders containing "air" divers necessary because helium is less soluble in blood than nitrogen. Such a sudden pressure release dissolved nitrogen bubbles would block blood flow, causing death by "gas embolism". Because solubility lower risk of these accidents is reduced when using helium instead of nitrogen. He-Ne lasers are already widely used for red light (633 nm). Helium has been used, easily and nonflammable, to give aircraft lifts.

Noble gases - uses

- Large quantities of **argon** is used for making protective atmosphere especially in researching new materials industry and chemical compounds. Thus welding stainless steel, titanium, magnesium or aluminum and titanium production by Kroll and IMI processes are the main consumers of argon. Somewhat smaller quantities consumed and growth processes of silicon and germanium crystals. Also used for incandescent bulbs with argon, the argon or argon-nitrogen mixtures, is used to protect the incandescent tungsten - thus extending filament life. Argon for the same purpose but is used for fluorescent tubes and Geiger-Müller counters needed for radioactivity measurements. Also, the "torches" based on argon plasma used in spectral analysis is consuming argon.

Noble gases - uses

- **Neon** is used in small amounts for advertising lighting (fluorescent lamps) which presents in rarefied gas conditions, a red-orange color. To obtain other colors various mixtures with other inert gases are used.
- **Krypton** gives the tubes in which they occur lightning, a white light-intensive applications finding and warning lights at airports. An element that appears and fission reactions (nuclear bombs) presence is an indication of nuclear activity on a planetary scale.
- **Xenon** lamps are used in such automotive halogen lamps or flash (flashes) used in photography, giving a white light, very intense, even small size, allowing photography in artificial light.

Q & R

In connection with rare gases (He, Ne, Ar, Kr, Xe, Rn):		
	0	Xe is used in weather balloons
	1	He is used in weather balloons
	0	^{132}Xe is used in cryogenics
	1	^{3}He is used in cryogenics
	0	Xe behave similar to H_2
	1	Xe behave similar to O_2
	0	$O_2(g) + PtH_6(g) \longrightarrow Xe[PtH_6](s)$
	0	$Xe(g) + PtH_6(g) \longrightarrow Xe[PtH_6](s)$
	1	$O_2(g) + PtF_6(g) \longrightarrow Xe[PtF_6](s)$
	1	$Xe(g) + PtF_6(g) \longrightarrow Xe[PtF_6](s)$

Course 7

“d^1-d^5” block

Elements groups

	3 (d^1)	**4 (d^2)**	**5 (d^3)**	**6 (d^4)**	**7 (d^5)**	**8 (d^6)**	**9 (d^7)**	**10 (d^8)**	**11 (d^9)**	**12 (d^{10})**
4	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
5	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
6	57-71 La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
7	89-103 Ac-Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn

57 La	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
89 Ac	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

Transition elements, period 4, oxidation state - rule?

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electronic Structure	d^1s^2	d^2s^2	d^3s^2	**d^5s^1**	d^5s^2	d^6s^2	d^7s^2	d^8s^2	**$d^{10}s^1$**	$d^{10}s^2$
Oxidation Numbers	II III	II III IV	II III IV V	I II III IV V VI	II III IV V VI VII	II III IV V VI	II III IV V	II III IV	I II III	II

Mn – the element with highest number of oxidation states between the elements of first period of transition metals.

Q

&

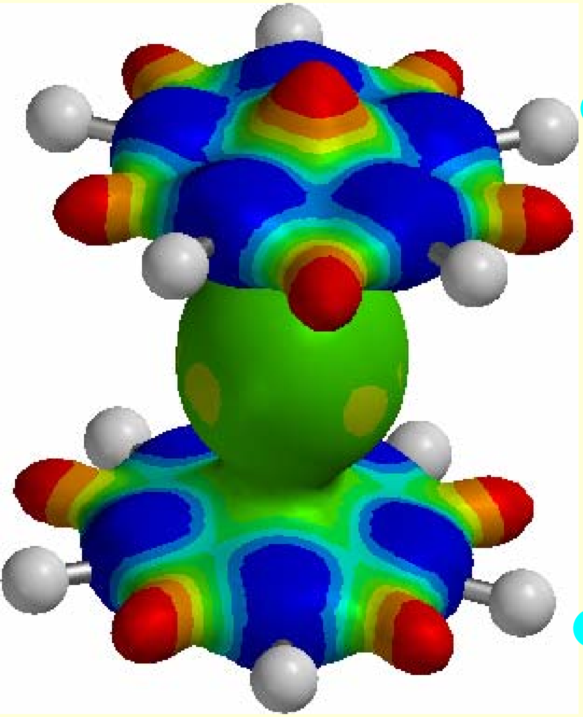
R

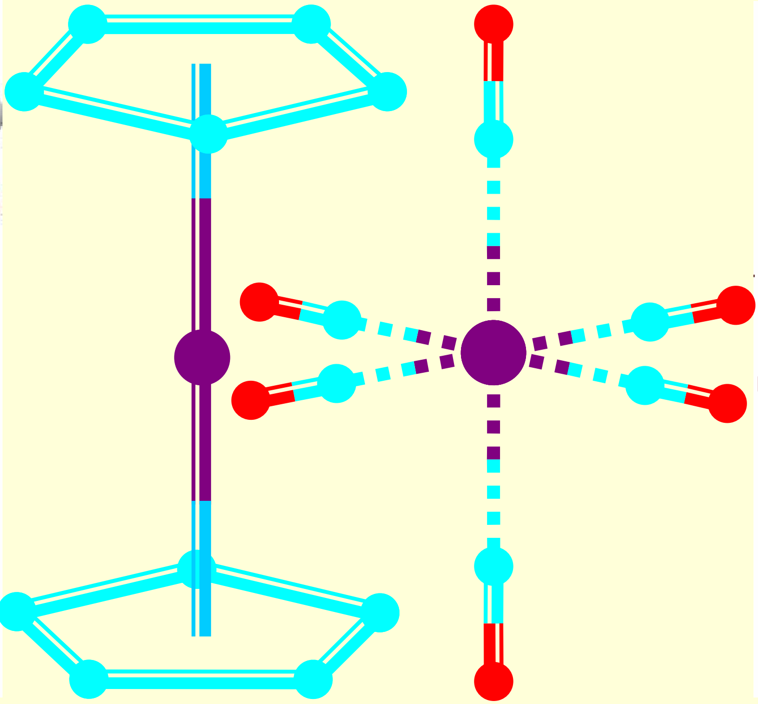
	In connection with the transitional elements of the 4th period (Sc: $3d^1 4s^2$, Ti: $3d^2 4s^2$, V: $3d^3 4s^2$, Cr: $3d^5 4s^1$, Mn: $3d^5 4s^2$, Fe: $3d^6 4s^2$, Co: $3d^7 4s^2$, Ni: $3d^8 4s^2$, Cu: $3d^{10} 4s^1$, Zn: $3d^{10} 4s^2$):
1	Can form complexes with unusual oxidation states (zero or negative) such as ($Fe(C_5H_5)_2$, $Cr(CO)_6$, $Mo(CO)_6$ si $V(CO)_6^-$
0	Zn may have 6 positive oxidation numbers: Zn^{2+}, Zn^{3+}, Zn^{4+}, Zn^{5+}, Zn^{6+}, Zn^{7+} ($Zn(NO_2)_2$, $ZnPO_4$, ($Zn(NO_3)_4$, K_3ZnO_4, K_2ZnO_4, $KZnO_4$)
1	Mn may have 6 positive oxidation numbers: Mn^{2+}, Mn^{3+}, Mn^{4+}, Mn^{5+}, Mn^{6+}, Mn^{7+} ($Mn(NO_2)_2$, $MnPO_4$, ($Mn(NO_3)_4$, K_3MnO_4, K_2MnO_4, $KMnO_4$)
0	Ti may have 6 positive oxidation numbers: Ti^{1+}, Ti^{2+}, Ti^{3+}, Ti^{4+}, Ti^{5+}, Ti^{6+} (TiH, $TiSO_4$, TiB, $TiCl_4$, TiF_5, TiO_2F_2)
1	Cr may have 6 positive oxidation numbers: Cr^{1+}, Cr^{2+}, Cr^{3+}, Cr^{4+}, Cr^{5+}, Cr^{6+} (CrH, $CrSO_4$, CrB, $CrCl_4$, CrF_5, CrO_2F_2)
0	One element - V - can have oxidation number +7 (V^{+7})
0	One element - Cr - can have oxidation number +7 ($Cr_2O_7^{2-}$)
1	One element - Mn - can have oxidation number +7 (MnO_4^-)
0	With one exception (Cu) these can have oxidation number +3 (ions Sc^{3+}, Ti^{3+}, V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Ni^{3+}, Zn^{3+})
1	With one exception (Zn) these can have oxidation number +3 (ions Sc^{3+}, Ti^{3+}, V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Ni^{3+}, Cu^{3+})
0	All off these can have oxidation number +3 (ions Sc^{3+}, Ti^{3+}, V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Ni^{3+}, Cu^{3+}, Zn^{3+})
1	All off these can have oxidation number +2 (ions Sc^{2+}, Ti^{2+}, V^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+})
0	Of these Sc can have oxidation number +1 (Sc^{1+} ion)
1	Of these Cr and Cu can have oxidation number +1 (ions Cr^{1+} and Cu^{1+})

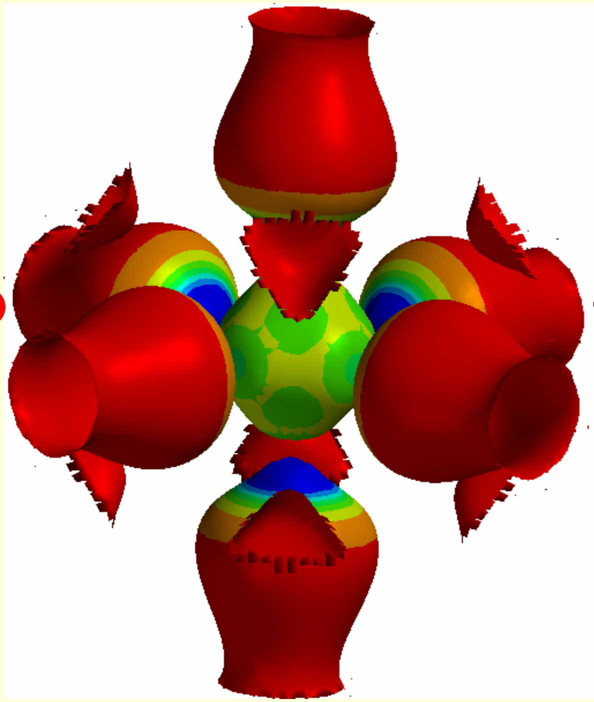
Transition elements – complex combinations

- Transition elements have a propensity to form complex combinations with molecules or ions able to donate electron pairs (e.g. NH_3, H_2O, CN^-, X^-, etc.). Usually in oxidation state III complexes are more stable than those in oxidation state II. At higher oxidation state elements occurs only in complex combinations - Fe (VI), Co (VI), Ni (IV). In complex combinations achieved a higher number of links than the corresponding to formal valence. Also form complexes in unusual oxidation states (zero or negative), for example metal carbonyls ($Mo(CO)_6$) or ferrocene ($Fe(C_5H_5)_2$) - all containing metal in 0 oxidation state).

Coordinative bonds with no oxidation state







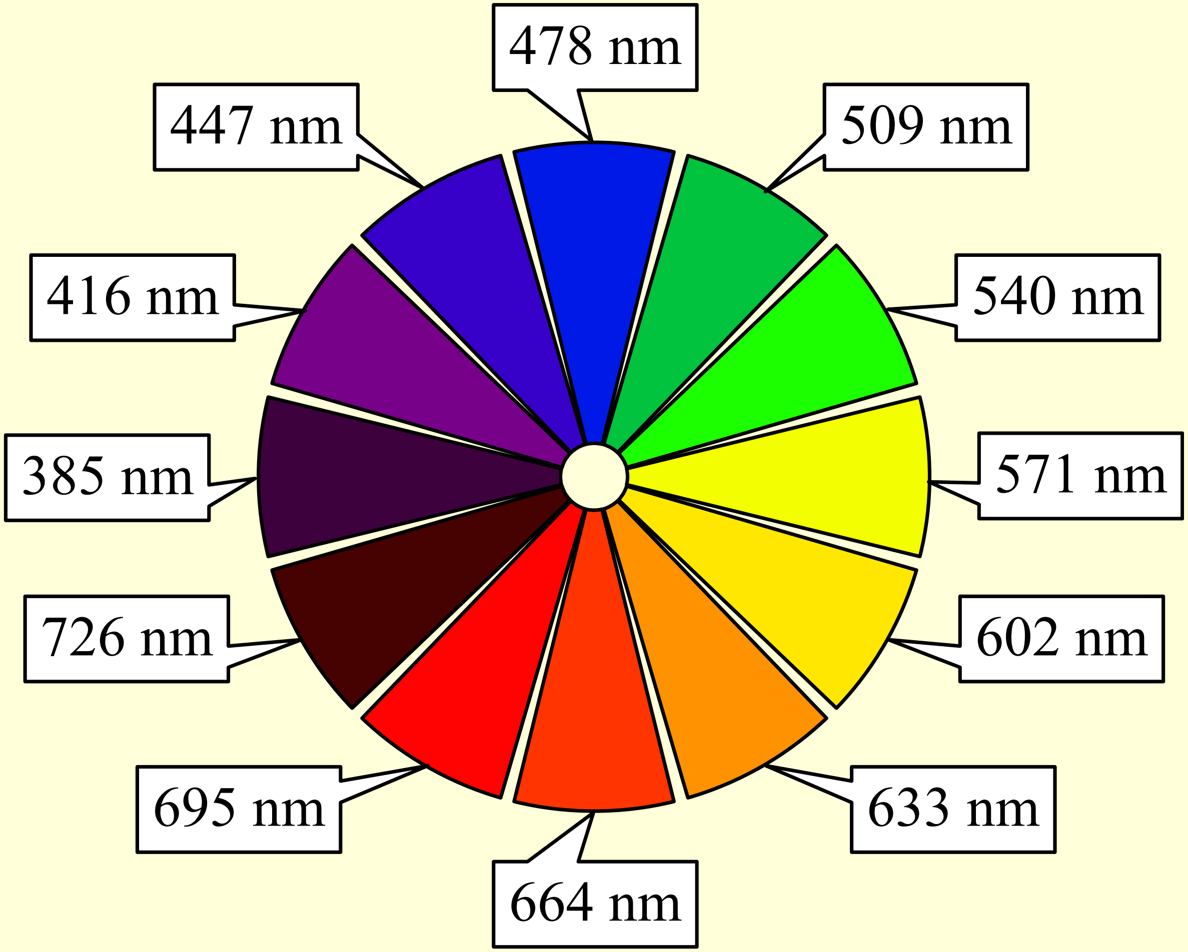
$Fe(C_5H_5)_2$

$Mo(CO)_6$

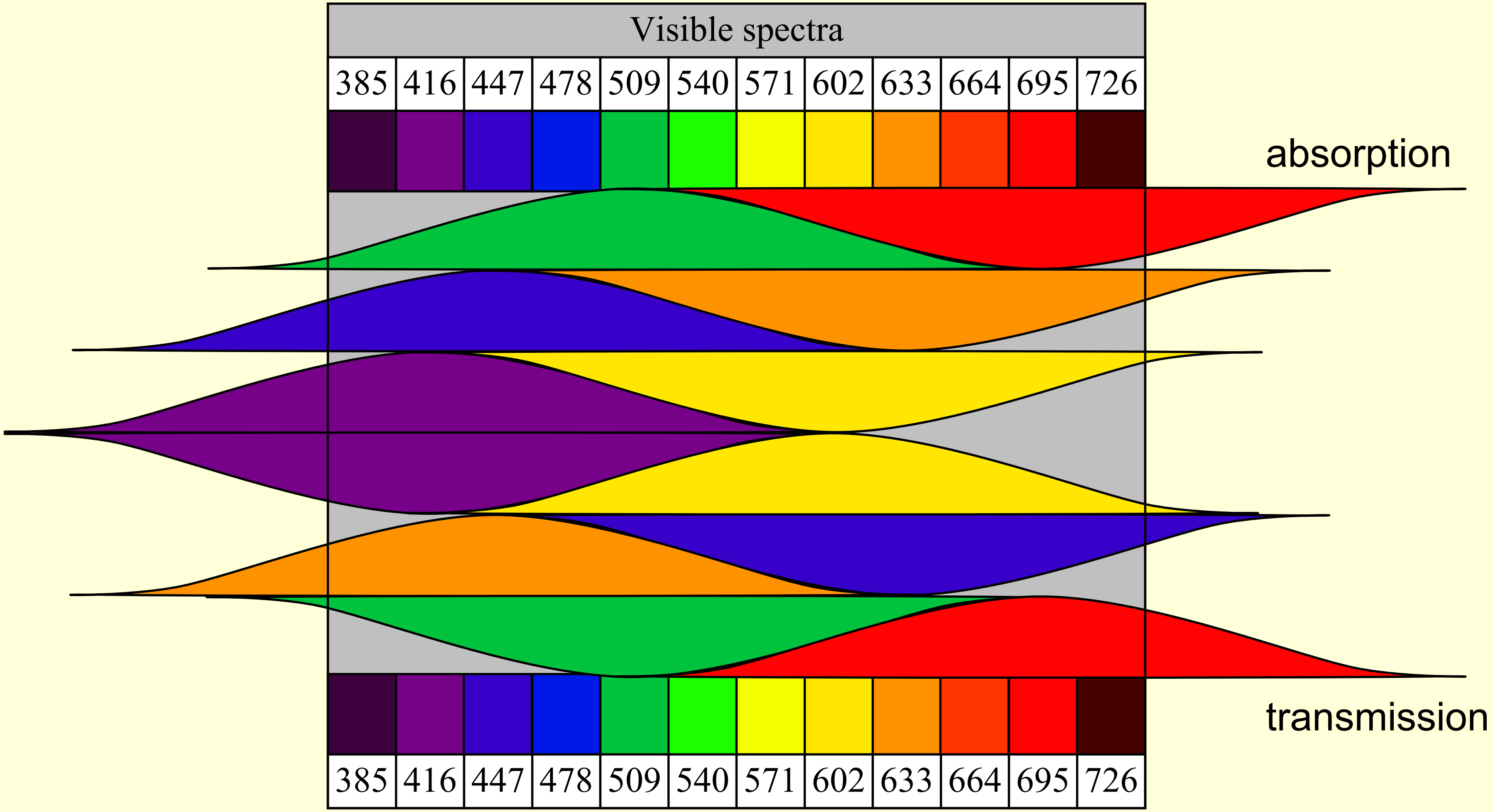
Charge distribution with Spartan 10

Transition elements – a source of color

If photons of a particular wavelength are absorbed by matter, then when we observe light reflected from or transmitted through that matter, what we see is the **complementary color**, made up of the other visible wavelengths remaining. For example beta-carotene has maximum absorption at 454 nm (blue light), consequently what visible light remains appears orange.



Complementary colors



Absorption vs. Transmission

Colors of transition ions

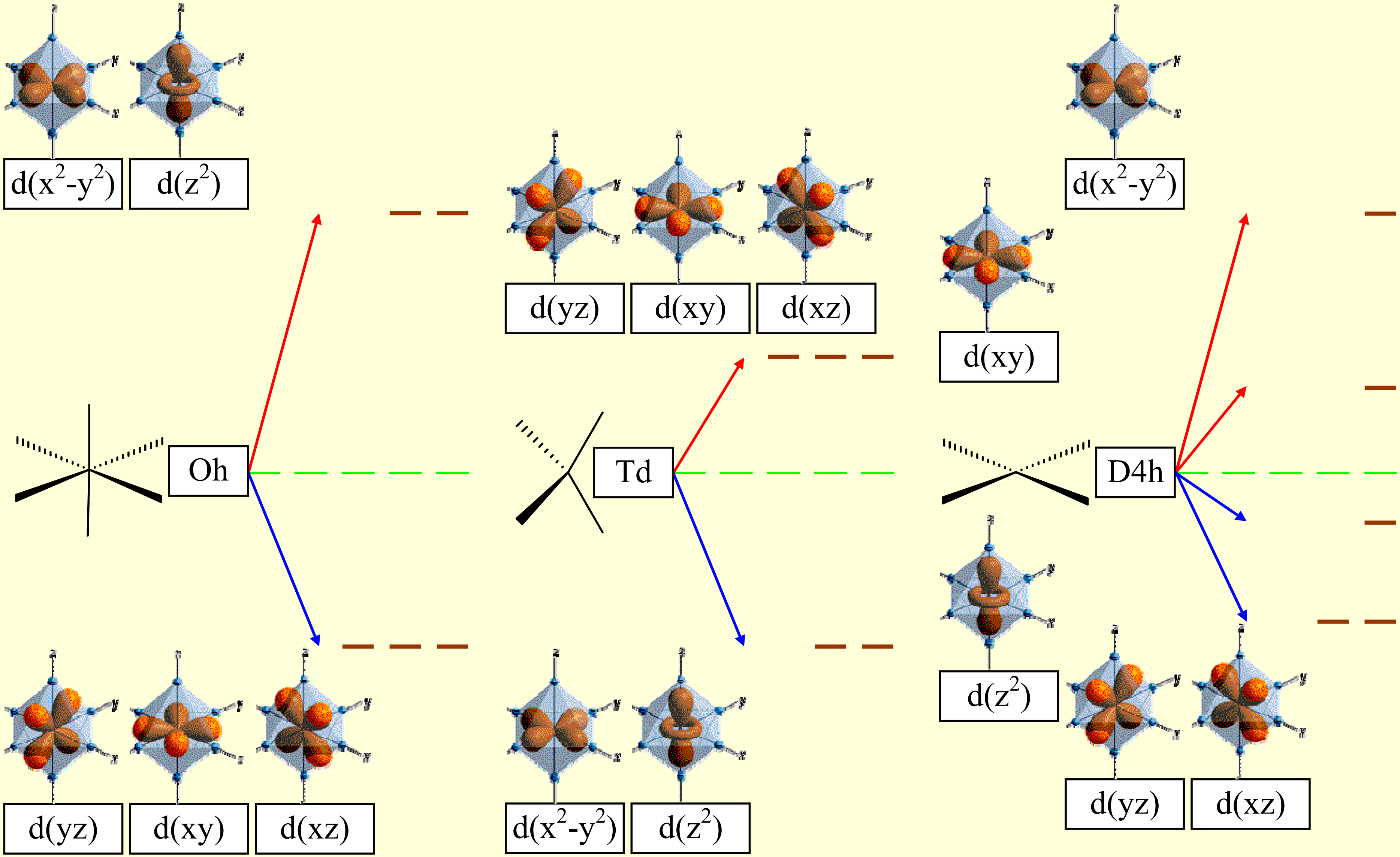
The most important source of color at transition elements is the existence of incomplete levels d and f. The ions of these elements can promote electrons from one level to d, another level d with higher energy, leading to absorption in visible.

Compound/Ion	Color	Name	#R-G-B
$(MnO_4)^{3-}_{(aq)}$	🟦	DarkBlue	#00008B
$Cu2+_{(aq)}$	🟦	MediumBlue	#0000CD
$(VO)^{2+}_{(aq)}$	🟦	Blue	#0000FF
$(MnO_4)^{2-}_{(aq)}$	🟩	DarkGreen	#006400
$Cr^{3+}_{(aq)}$	🟦	Teal	#008080
$CuCl_2 \cdot 2H_2O$	🟦	DarkTurquoise	#00CED1
$Fe^{2+}_{(aq)}$	🟦	DodgerBlue	#1E90FF
$(Cu(NH_3)_4)^{2+}_{(aq)}$	🟦	RoyalBlue	#4169E1
$(Ni(NH_3)_6)^{2+}_{(aq)}$	🟪	MediumSlateBlue	#7B68EE
$V^{3+}_{(aq)}$	🟩	DarkSeaGreen	#8FBC8F
$Ni^{2+}_{(aq)}$	🟩	LightGreen	#90EE90
$(MnO_4)^{-}_{(aq)}$	🟪	DarkViolet	#9400D3
$NiCl_2 \cdot 6H_2O$	🟩	PaleGreen	#98FB98
$(CuCl_4)^{2-}_{(aq)}$	🟩	YellowGreen	#9ACD32
$Fe^{3+}_{(aq)}$	🟫	Chocolate	#D2691E
$V^{2+}_{(aq)}$	⬜	Lavender	#E6E6FA
$Ti^{3+}_{(aq)}$	🟪	Violet	#EE82EE
$Zn^{2+}_{(aq)}$	⬜	AliceBlue	#F0F8FF
$CoCl_2 \cdot 6H_2O$	🟪	Magenta	#FF00FF
$(Cr_2O_7)^{2-}_{(aq)}$	🟧	Orange	#FFA500
$MnCl_2 \cdot 4H_2O$	🟥	LightPink	#FFB6C1
$Co^{2+}_{(aq)}$	🟥	Pink	#FFC0CB
$(Co(NH_3)_6)^{3+}_{(aq)}$	🟨	Gold	#FFD700
$(VO_2)^{+}_{(aq)}$	🟨	Yellow	#FFFF00

Co complexes

Ligands	Co^{3+} complex	Absorbed	Seen
$6(I^-)$	$[Co(I)_6]^{3-}$	800 nm	pale yellow
$6(Br^-)$	$[Co(Br)_6]^{3-}$	770 nm	yellow
$6(Cl^-)$	$[Co(Cl)_6]^{3-}$	740 nm	lime
$6(F^-)$	$[Co(F)_6]^{3-}$	700 nm	green
$6(HO^-)$	$[Co(OH)_6]^{3-}$	650 nm	sky blue
$4(OH_2); 2(HO^-)$	$[Co(OH_2)_4(OH)_2]^{1+}$	620 nm	blue
$6(H_2O)$	$[Co(OH_2)_6]^{3+}$	600 nm	violet
$5(NH_3); 1(Br)$	$[Co(NH_3)_5(Br)]^{2+}$	540 nm	brown
$5(NH_3); 1(Cl)$	$[Co(NH_3)_5(Cl)]^{2+}$	522 nm	red
$5(NH_3); 1(OH)$	$[Co(NH_3)_5(OH)]^{2+}$	502 nm	carmine
$5(NH_3); 1(OH_2)$	$[Co(NH_3)_5(OH_2)]^{3+}$	487 nm	orange
$6(NH_3)$	$[Co(NH_3)_6]^{3+}$	472 nm	gold
$5(NH_3); 1(NO_2^-)$	$[Co(NH_3)_5(NO_2)]^{2+}$	456 nm	yellow
$6(NO_2^-)$	$[Co(NO_2)_6]^{3-}$	365 nm	light yellow
$6(NC^-)$	$[Co(CN)_6]^{3-}$	310 nm	pale yellow

Octahedral, tetrahedral & square planar complexes



$d(x^2-y^2)$ $d(z^2)$

Oh

$d(yz)$ $d(xy)$ $d(xz)$

$d(yz)$ $d(xy)$ $d(xz)$

Td

$d(x^2-y^2)$ $d(z^2)$

$d(x^2-y^2)$

$d(xy)$

D4h

$d(z^2)$

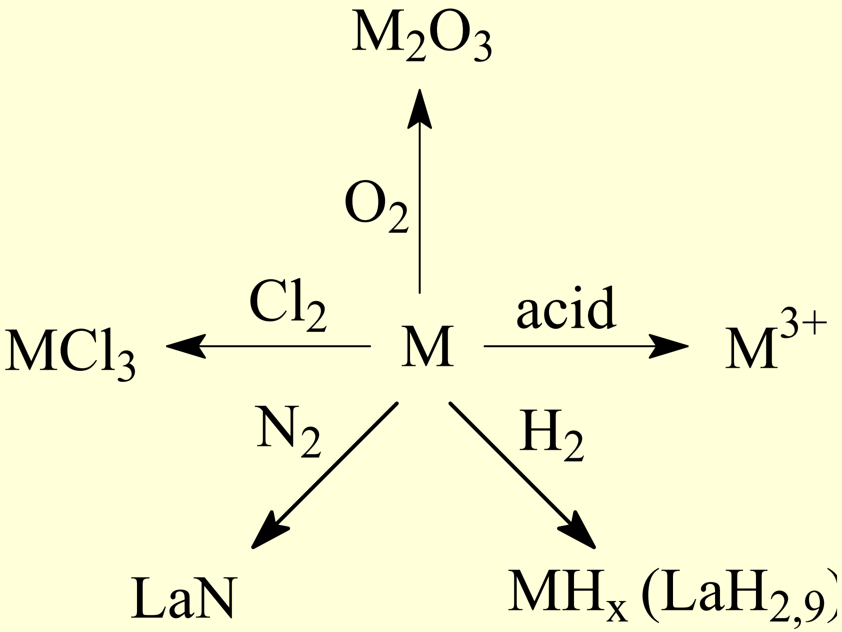
$d(yz)$ $d(xz)$

Interstitial compounds

- Crystalline networks of transition elements are generally compact and contain tetrahedral or octahedral gaps, where can enter small volume nonmetallic atoms (H, B, C, N) forming interstitial compounds, which are usually non-stoechiometric (with variable composition). These combinations - carbides, nitrides, borides - melts at very high temperatures (TiC - 3140ºC, ZrC - 3430ºC, HfC - 3890ºC), have very good hardness (8 to 10 on the Mohs scale) and some are extremely inert to chemical attack. Because of these properties have special technical applications (see discussed refractory ceramics).

Scandium, Yttrium, Lutetium, Lawrencium

Chemical properties



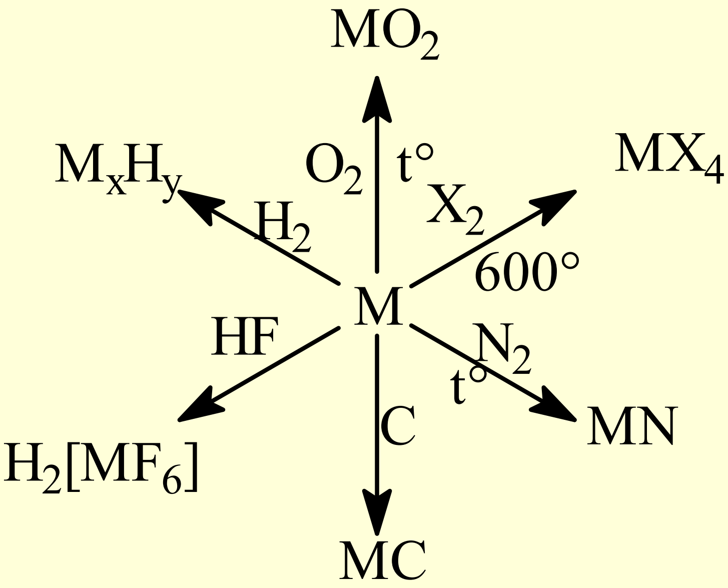
Lawrencium synthesis

$${}_{98}Cf + {}_{5}B \rightarrow {}_{103}Lr$$

- Scandium is apparently a much more abundant element in the sun and certain stars than on earth. Scandium iodide, along with sodium iodide, when added to a modified form of mercury-vapor lamp, produces a form of metal halide lamp. This lamp is a white light source with high color rendering index that sufficiently resembles sunlight to allow good color-reproduction with TV cameras.
- About 31 ppm of the Earth's crust is yttrium (28th) - 400 times more common than silver. Lunar rock samples collected during the American Apollo Project have a relatively high content of yttrium. Even if Yttrium has no known biological role, tends to concentrate in the liver, kidney, spleen, lungs, and bones of humans. With up to 700 ppm, the seeds of woody plants have the highest known concentrations.
- Lutetium aluminium garnet ($Al_5Lu_3O_{12}$) has been proposed for use as a lens material in high refractive index immersion lithography. Lutetium tantalate ($LuTaO_4$) is the densest known stable white material (9.81 g/cm^3). The only denser white material is thorium dioxide, (10 g/cm^3), but the thorium radioactive.

Titanium, Zirconium, Hafnium, Rutherfordium

Chemical properties



MO_2

M_xH_y O_2 t° MX_4

H_2 X_2

600°

M

HF N_2

t°

C MN

$H_2[MF_6]$

MC

Rutherfordium synthesis

$${}_{98}Cf + {}_{6}C \rightarrow {}_{104}Rf$$

Metals are very resistant to chemical agents at moderate temperatures due to the formation of a protective oxide layer on the surface. At room temperature are not attacked by acids or bases. Have the property of absorbing gases (H_2, O_2, N_2) are therefore used to produce advanced vacuum.

Titanium has many uses: has the advantage that it is stronger than steel, more light and with greater corrosion resistance, keeping its mechanical properties at high temperatures.

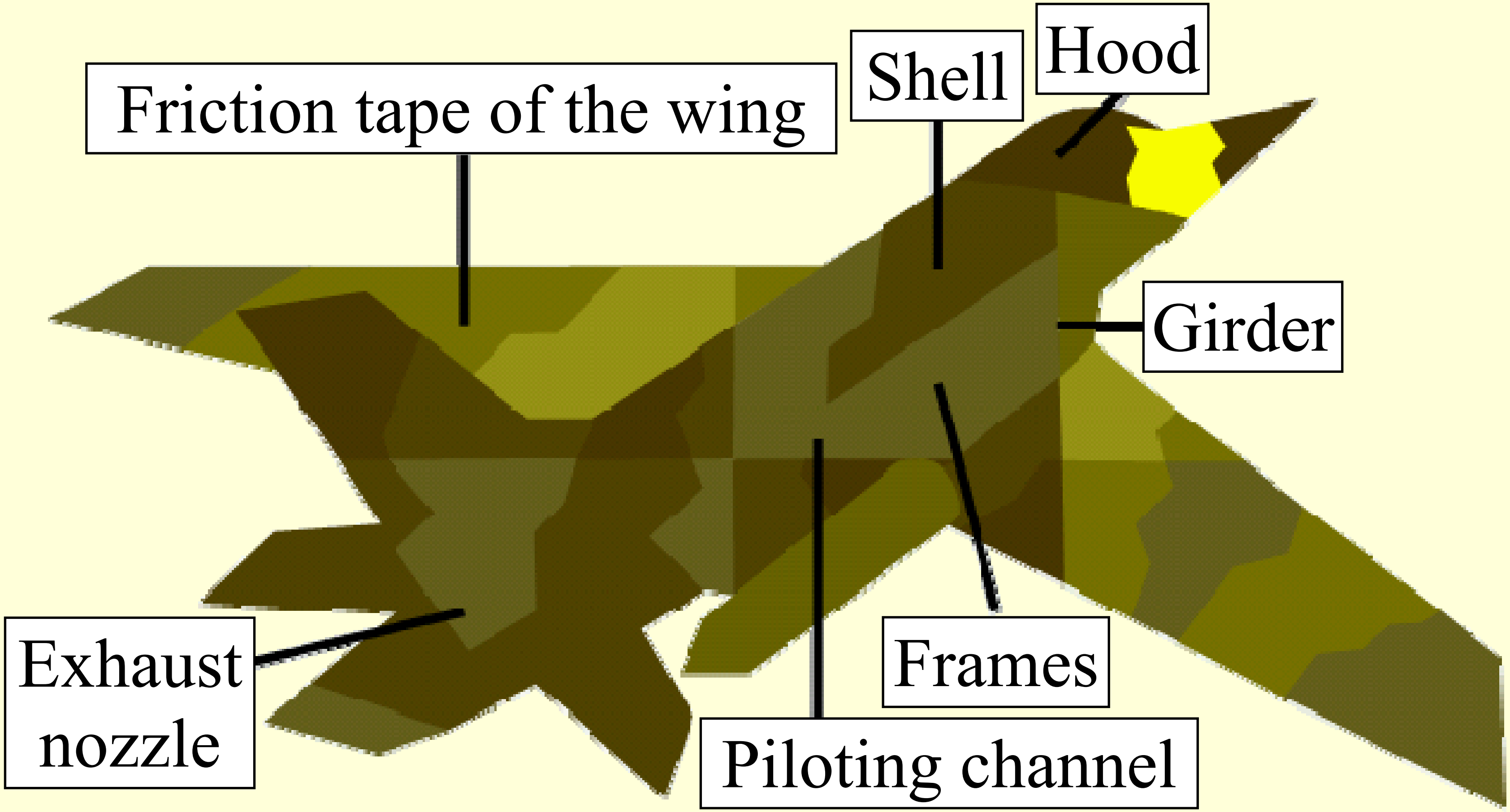
Zirconium is used in the manufacture of chemical equipment, and nuclear technology because it absorbs neutrons.

Hafnium is used in the construction of nuclear reactors and nuclear submarines.

80% TiC and 20% HFC mixture is highly refractory (m.p. 4215 °C). ZrO_2+15%Y_2O_3 gives an intense white light and is used in specialty lamps (Nernst lamps).

- Titanium alloy with 6% Al and 4% V has good mechanical properties and is used for gas tanks (H_2, O_2, F_2) and missiles. The fortunate combination of the basic characteristics of titanium finds in the aerospace industry its applicability. 90% of current production of titanium is used in the construction of supersonic aircrafts and spaceships.

F2 fighter - titanium and its alloys uses

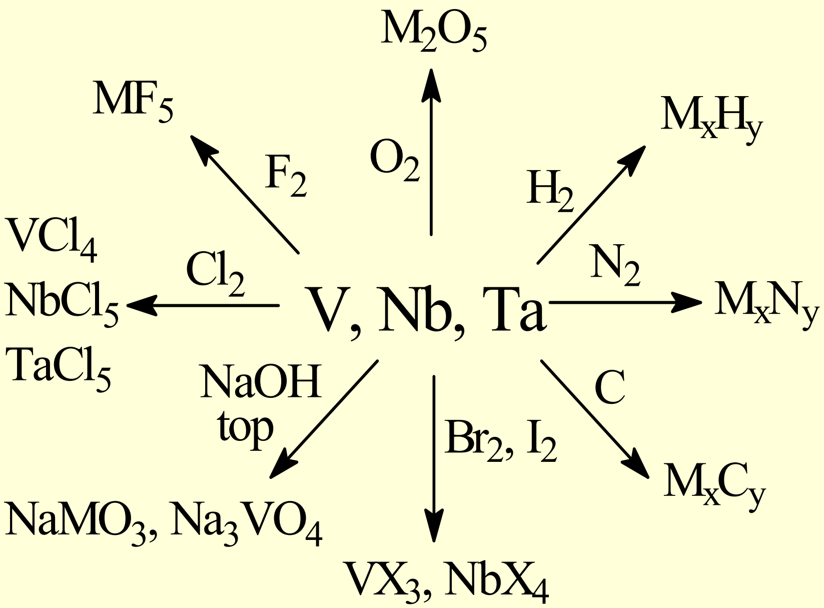


“Mother Russia” gigantic statue

- Memorial Park, Kiev, Ukraine
- Is a gigantic titanium female figure -108 meters (40 m - pedestal & 68 m - figure), to compare - Statue of Liberty in New York has the size of 100 meters (65m + 35 m).
- Sword was shortened after independence in 1991.
- Historians say this statue was initially proposed to be built atop Mount Poklonnaya in Moscow.
- The construction of the statue made of titanium in Kyiv turned out to be a complicated task. Employees of the Kyiv-based ProektStalKonstruktsiya R&D Institute were interested in the experience regarding the reconstruction of the Statue of Liberty in New York.
- Was completed on May 9, 1981. Soviet leader Leonid Brezhnev paid a special visit to Kyiv for the unveiling of the great monument.

Vanadium, Niobium, Tantalum, Dubnium

Chemical properties



$\mathrm{V, Nb, Ta} \xrightarrow{O_2} \mathrm{M_2O_5}$

$\mathrm{V, Nb, Ta} \xrightarrow{F_2} \mathrm{MF_5}$

$\mathrm{V, Nb, Ta} \xrightarrow{H_2} \mathrm{M_xH_y}$

$\mathrm{V, Nb, Ta} \xrightarrow{Cl_2} \mathrm{VCl_4,\ NbCl_5,\ TaCl_5}$

$\mathrm{V, Nb, Ta} \xrightarrow{N_2} \mathrm{M_xN_y}$

$\mathrm{V, Nb, Ta} \xrightarrow{\text{NaOH top}} \mathrm{NaMO_3,\ Na_3VO_4}$

$\mathrm{V, Nb, Ta} \xrightarrow{Br_2,\ I_2} \mathrm{VX_3,\ NbX_4}$

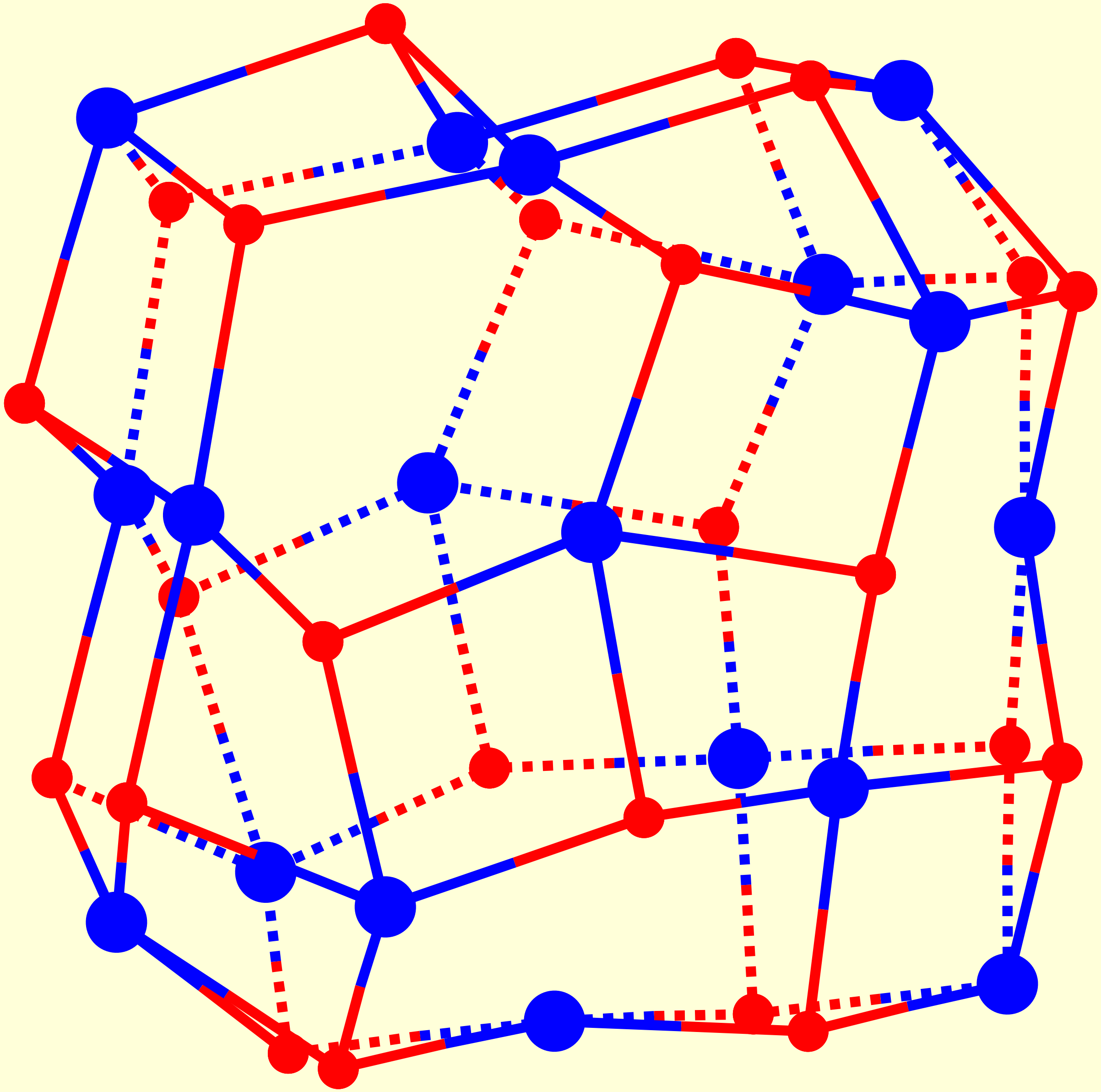
$\mathrm{V, Nb, Ta} \xrightarrow{C} \mathrm{M_xC_y}$

Dubnium synthesis

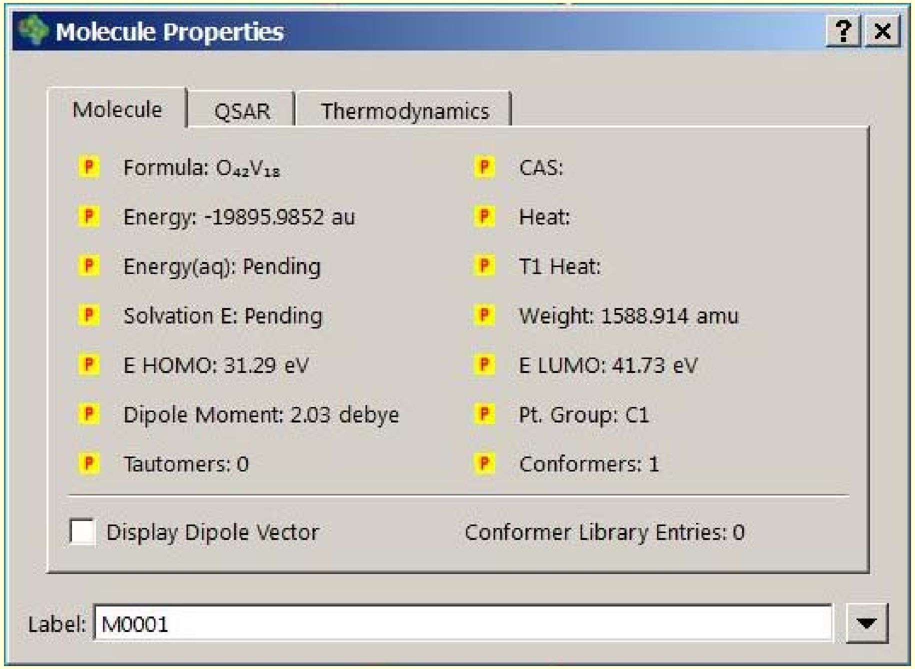
$${}_{98}\mathrm{Cf} + {}_{7}\mathrm{N} \rightarrow {}_{105}\mathrm{Db}$$

Vanadium is used especially for Ferrovanadium (Fe-V alloy) - for improved mechanical properties, increased hardness, corrosion and shock resistance. Vanadium pentaoxide, V_2O_5, is a good catalyst for oxidation reactions (such as for obtaining of H_2SO_4 - catalyst for oxidation of SO_2 to SO_3).
Nb and Ta have high capacity for electron emission, and are able to absorb gases at hot. Alloys with Nb, Ta, and NbC are thermoresistant, thermostable, hardly attacked by acids, and mechanically superhard.
Ta replaces Pt, Au, Ag and their alloys in the construction of chemical apparatus resistant to concentrated acids or bases such as heat exchangers, pumps, valves. Ta catalyses making synthetic diamonds from graphite (pressure ~ 1 GPa and temperatures of about 2200 °C. Ta wires are used in surgery.

$[V_{18}O_{30}]^{12+}$ cage, part of $[V_{18}O_{42}]^{12-}$ cage



$[V_{18}O_{42}]^{12-}$ properties (Spartan '10)

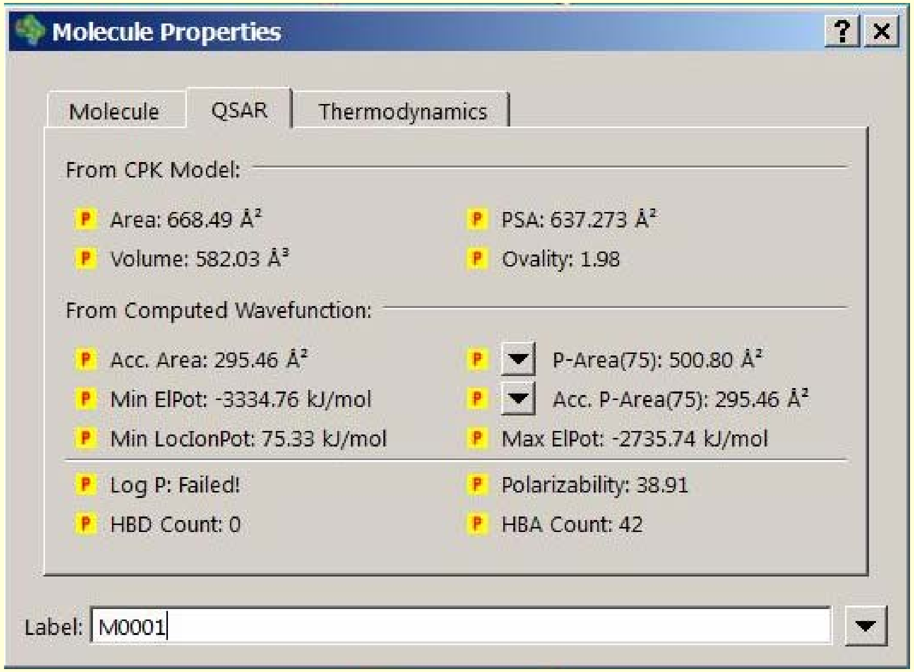


Formula: $O_{42}V_{18}$
Energy: -19895.9852 au
Energy(aq): Pending
Solvation E: Pending
E HOMO: 31.29 eV
Dipole Moment: 2.03 debye
Tautomers: 0

CAS:
Heat:
T1 Heat:
Weight: 1588.914 amu
E LUMO: 41.73 eV
Pt. Group: C1
Conformers: 1

☐ Display Dipole Vector
Conformer Library Entries: 0

Label: M0001



From CPK Model:

Area: 668.49 Å^2
Volume: 582.03 Å^3

PSA: 637.273 Å^2
Ovality: 1.98

From Computed Wavefunction:

Acc. Area: 295.46 Å^2
Min ElPot: -3334.76 kJ/mol
Min LocIonPot: 75.33 kJ/mol

P-Area(75): 500.80 Å^2
Acc. P-Area(75): 295.46 Å^2
Max ElPot: -2735.74 kJ/mol

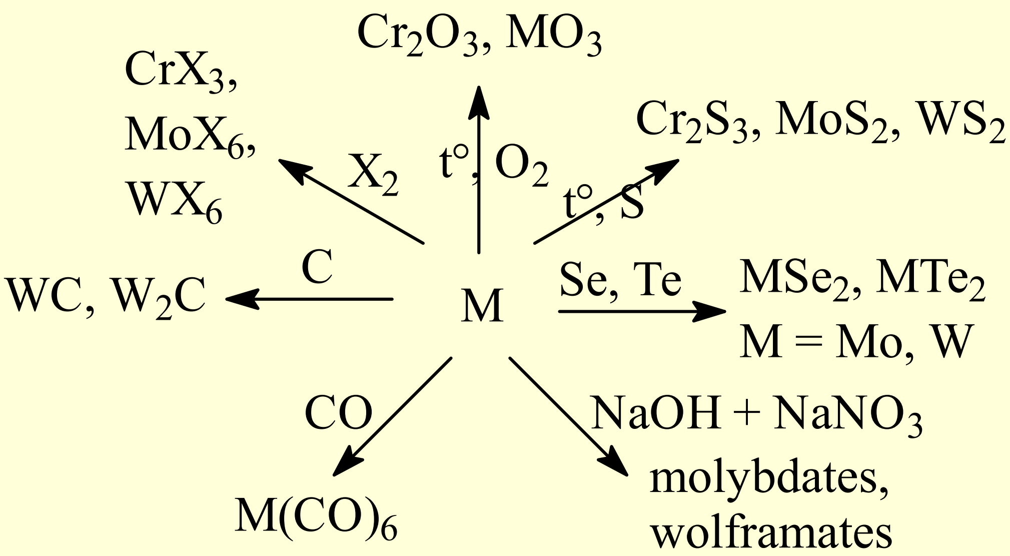
Log P: Failed!
HBD Count: 0

Polarizability: 38.91
HBA Count: 42

Label: M0001

Chromium, Molybdenum, Tungsten, Seaborgium

Chemical properties



CrX_3, MoX_6, WX_6

Cr_2O_3, MO_3

Cr_2S_3, MoS_2, WS_2

X_2

t°, O_2

t°, S

C

WC, W_2C

M

Se, Te

MSe_2, MTe_2

M = Mo, W

CO

$M(CO)_6$

$NaOH + NaNO_3$

molybdates, wolframates

Seaborgium synthesis

$$_{98}Cf + {}_{8}O \rightarrow {}_{106}Sg$$

W possess highest elemental m.p. (3380 °C).

Cr dissolve in diluted acids (HCl, H_2SO_4), while W is dissolved only in $HF+HNO_3$ mixture (eliminating NO in place of H_2).

In HNO_3 Cr are covered with a protective layer of oxide.

At normal temperature, Cr, Mo and W are resistant to air and moisture.

Cr reacts only at high temperatures with non-metals: O_2, X_2, N_2, S, B, C. Mo and W reacts bit harder.

W is highly resistant to acids.

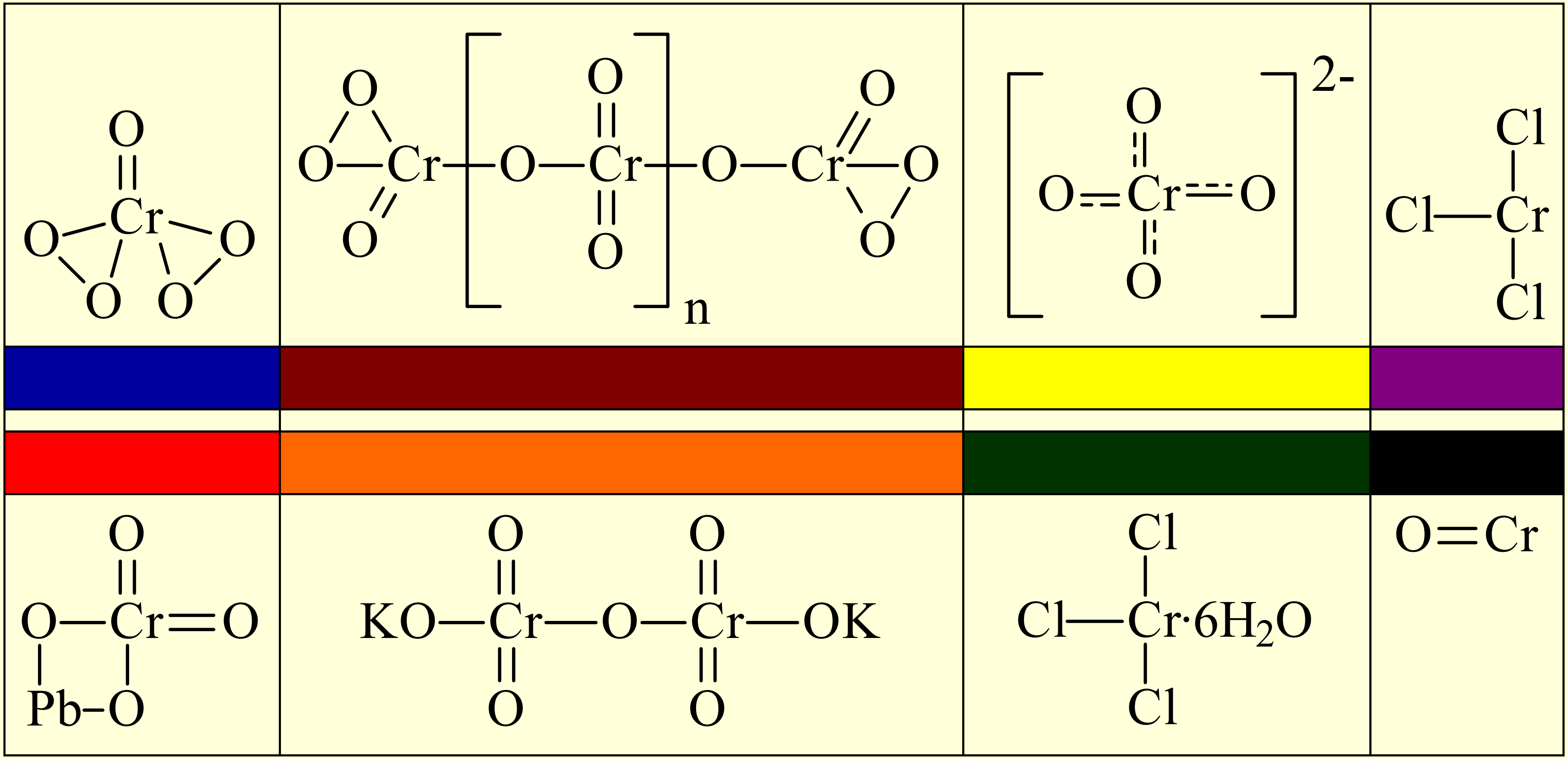
Cr-W-Co-C super hard high-speed tool steel

C	Cr	W	Mo	V	Co	Si	Mn	Fe
1.7-4.1%	3-10%	1-20%	1-15%	1-15%	≤15%	≤2%	≤1%	remaining
Carbon	0.1≤C-Ceq≤0.6; Ceq=0.06Cr+0.033W+0.063Mo+0.2V							
Molybdenum	18%≤W+2Mo≤40%							
Steel	(88%-98%) above mixture and (2-12%) G1, G2, or G3							
G1	nitrides of M, M= Ti, V, Zr, Nb, Hf, Ta							
G2	carbides of M, M= Ti, V, Zr, Nb, Hf, Ta							
G3	carbonitrides of M, M= Ti, V, Zr, Nb, Hf, Ta							
Hardness	≥ HRC71 (ASTM E18 & EN ISO 6508)							
USPTO	US4880461 (Norimasa UCHIDA, November 14, 1989)							

Chromium - uses

- Chromium is alloying element for special steels, giving better mechanical properties and high corrosion resistance.
- Alloys of Cr with Ni and Cu have uses in the manufacture of thermocouples.
- Electrolytic chromating is one of the most effective methods of protecting metals against corrosion.
- Dichromates (especially of sodium, cheaper) and chrome alum is used in tanning (process of treating skins of animals) and as a mordant (to fix the dyes) in dyeing.
- Dichromates are used as oxidants in organic chemistry. Some combinations of Cr have important uses as pigments, producing beautiful and very stable colors.

Chromium pigments

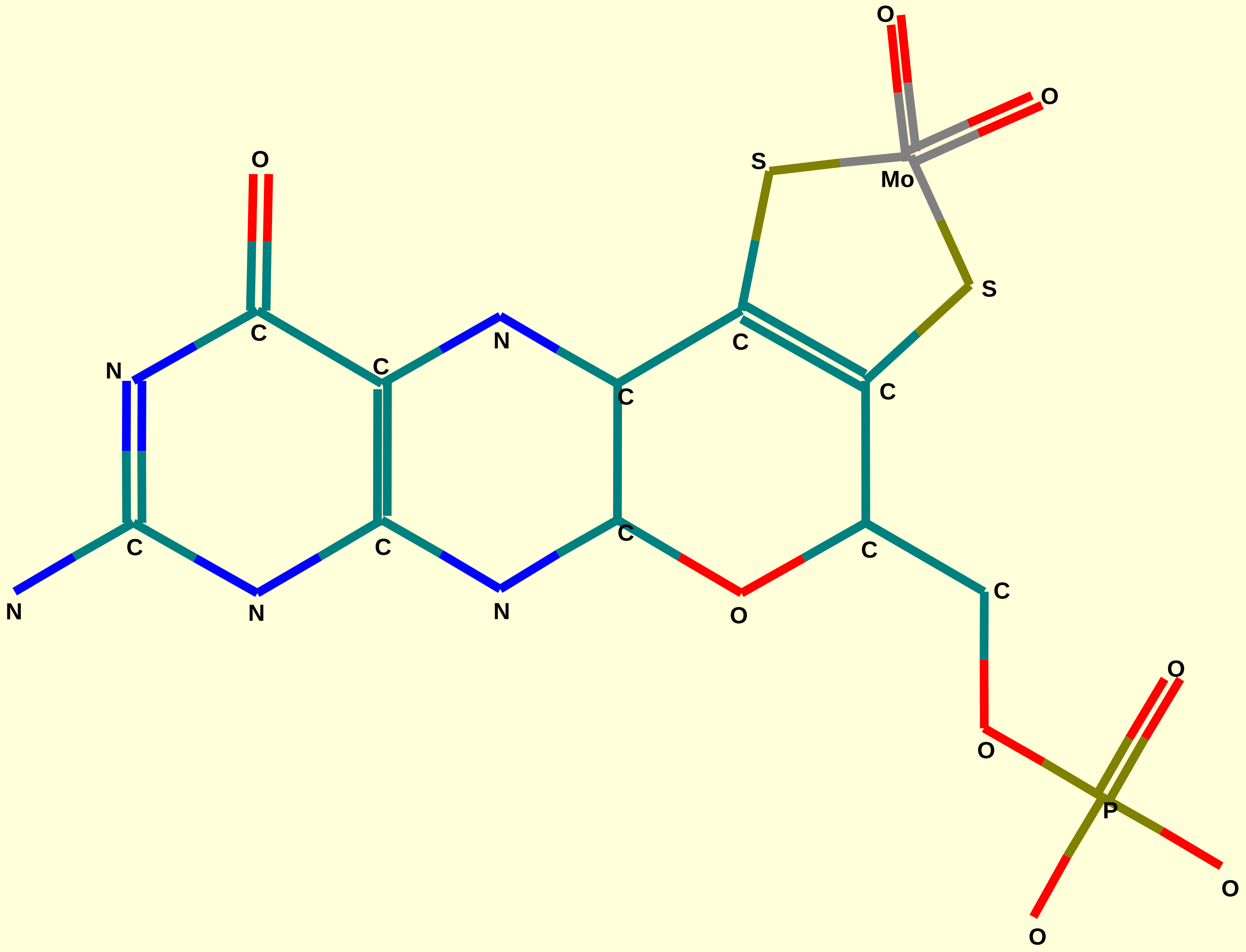


$MoCl_2$	$MoCl_3$	$MoCl_4$	$MoCl_5$	$MoCl_6$
🟨	🟥	⬛	🟩	🟫

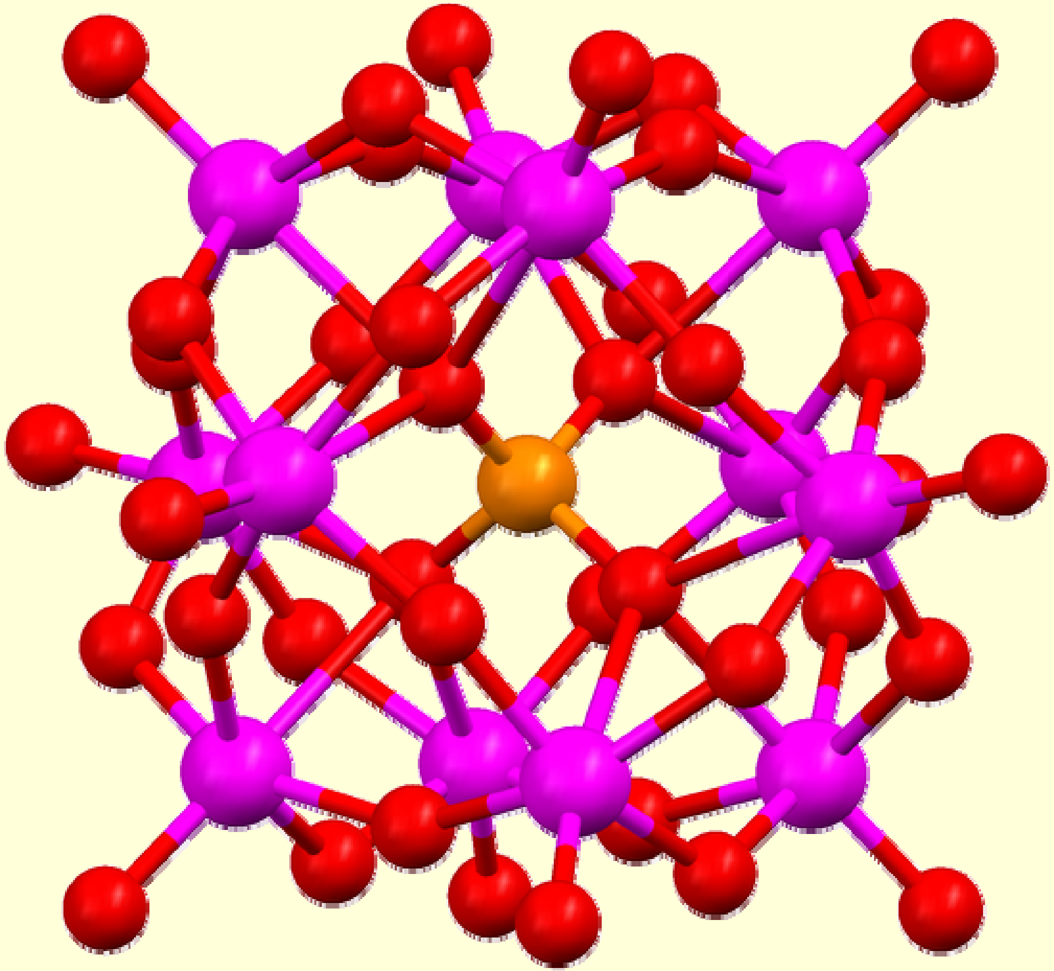
Molybdenum - uses

- MoS_2 is used as a solid lubricant and a high-pressure high-temperature antiwear agent. It is a semiconductor - electronics applications.
- $MoSi_2$ is electrical conductor (ceramic with use for heating elements operating at temperatures above 1500 °C in air).
- MoO_3 is used as an adhesive between ceramics and metals.
- $PbMoO_4 + PbCrO_4 + PbSO_4$ is an **orange** pigment used for ceramics and plastics.
- $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (**yellow-green**) is fertilizer.
- Molybdenum enzymes in plants and animals catalyze the oxidation and sometimes reduction of certain small molecules, as part of the regulation of nitrogen, sulfur and carbon cycles. All molybdenum-using enzymes so far identified in nature use the molybdenum cofactor.

Molybdenum cofactor



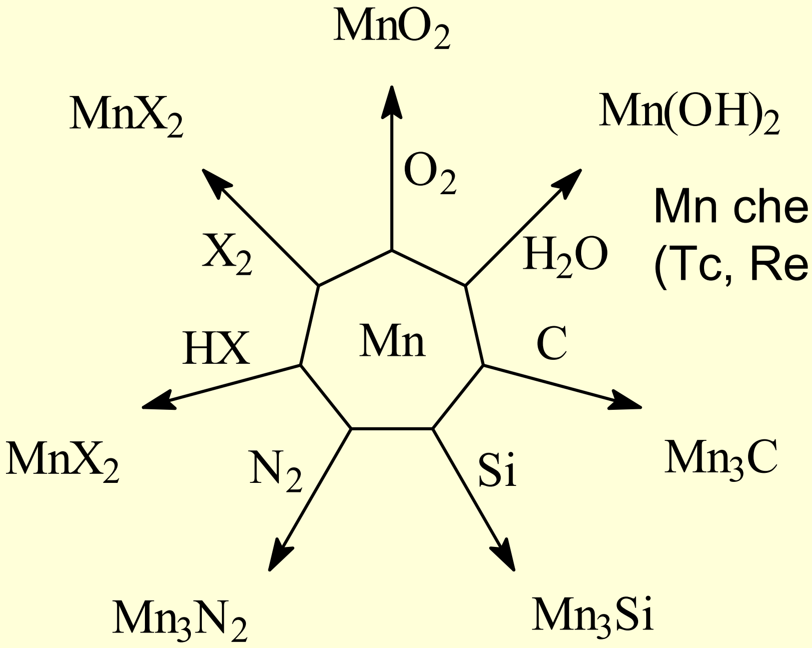
Keggin structures



$[AM_{12}O_{40}]^{n-}$,
A = P^{5+}, Si^{4+}, B^{3+}
M = Mo, W

The first Keggin anion, $(NH_4)_3[PMo_{12}O_{40}]$ (ammonium phosphomolybdate), was first reported by Berzelius in 1826. J.F. Keggin with the use of X-ray diffraction experimentally determined the structure of Keggin anions in 1934. Keggin anions uses as catalysts in hydration, polymerization and oxidation.

Manganese, Technetium, Rhenium, Bohrium



MnO_2

O_2

MnX_2

X_2

$Mn(OH)_2$

H_2O

Mn

HX

MnX_2

C

Mn_3C

N_2

Mn_3N_2

Si

Mn_3Si

Mn chemical properties
(Tc, Re – similar)

Bohrium synthesis

$${}_{97}Np + {}_{20}Ca \rightarrow {}_{107}Bh$$

O.N.	-3	-2	-1	0
Compound	MnH_3	MnH_2	$H[Mn(CO)_5]$	$(CO)_5Mn\text{-}Mn(CO)_5$
Color	White/Colorless	White/Colorless	White /Colorless	🟨
O.N.	0	+1	+2	+3
Compound	$Mn(OH_2)_6$	$Br[Mn(CO)_5]$	$MnCl_2$	MnF_3
Color	🟪	🟧	🟪	🟪
O.N.	+4	+5	+6	+7
Compound	MnO_2	K_3MnO_4	K_2MnO_4	$KMnO_4$
Color	🟫	🟦	🟩	🟪

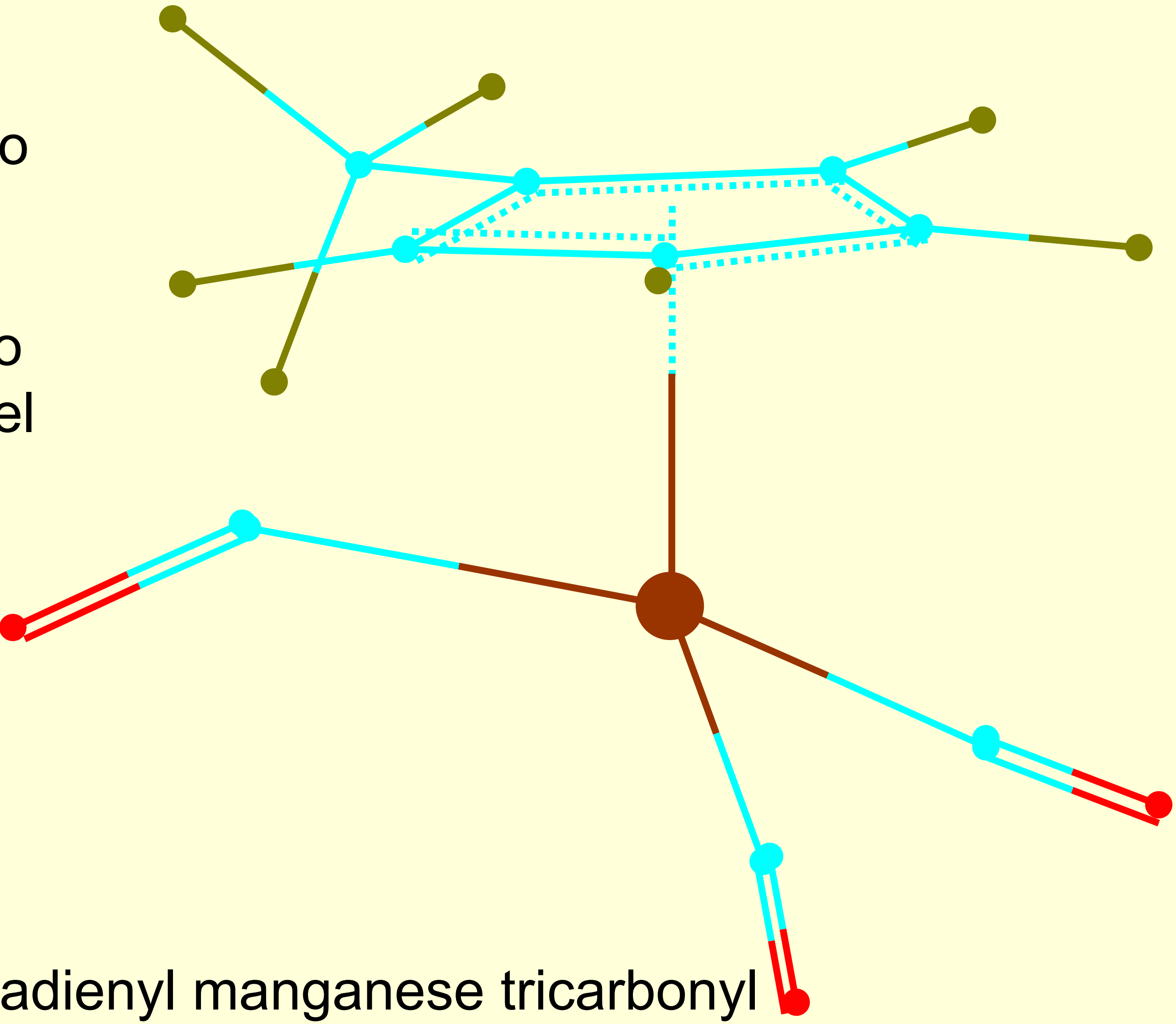
Manganese - uses

- The most of the manganese usage is in the industry producing ferroalloys (as additive for improving the properties, or for conducting different processes – ferromanganese - MnO_2+Fe_2O_3 - serves as deoxidizer for steel). Other uses are in construction, machinery, and transportation – with manganese demand of about 29%, 10%, and 10%, respectively (in US, in 2008). Other uses includes production of dry cell batteries, in plant fertilizers and animal feed, and as a brick colorant.

The corrosion-resistant aluminum alloys (with over 95% Al) have manganese content of 1-1.5% and are used for beverage pots.

Gasoline burn catalyst

A supplement to the gasoline additive tetraethyllead to increase the fuel octane rating



Methylcyclopentadienyl manganese tricarbonyl

Technetium and Rhenium - uses

- Technetium is the lowest atomic number element without any stable isotopes; every form of it is radioactive. From the 1860s through 1871, early forms of the periodic table proposed by Dimitri Mendeleev contained a gap (Tc, Z=43) between Mo (Z=42) and Ru (Z=44). The discovery of element 43 was finally confirmed only in December 1936.
- Tc is primarily artificial, only trace quantities existing in nature, even if its most stable isotope have the half-life greater than the second one of manganese ($T_{1/2}(^{98}Tc)=4.2$ mil. years > $T_{1/2}(^{53}Mn)=3.7$ mil. years).
- Tc use come from the following chain of nuclear reactions: $^{98}Mo + ^{1}n \rightarrow$ ^{99}Mo; $^{99}Mo \rightarrow {}^{99m}Tc$ (66h); $^{99m}Tc \rightarrow {}^{99}Tc+\gamma$ (6h); $\gamma=140500eV$. A lot of radiopharmaceuticals are based on technetium for imaging and functional studies of the brain, myocardium, thyroid, lungs, liver, gallbladder, kidneys, skeleton, blood, and tumors (an unstable isotope, ^{99}Mo decays in a stable one, ^{99}Tc ($T_{1/2}=210000$ years) without emitting dangerous particles, only a photon).
- Re free element has the third-highest melting point and highest boiling point of any element. Rhenium is added to high-temperature alloys for jet engine parts (70% of the worldwide rhenium production). Another major application is platinum-rhenium catalysts, which are primarily used in making lead-free, high-octane gasoline.

Lockheed Martin F-35B Lightning II

Single-seat, single-engine, fifth generation of multirole fighters under development to perform ground attack, reconnaissance, and air defense missions with stealth capability (Released on 18 December 2007).
Newer single-crystal third generation alloys contain 6% of rhenium; they are used in the F-35 engines.

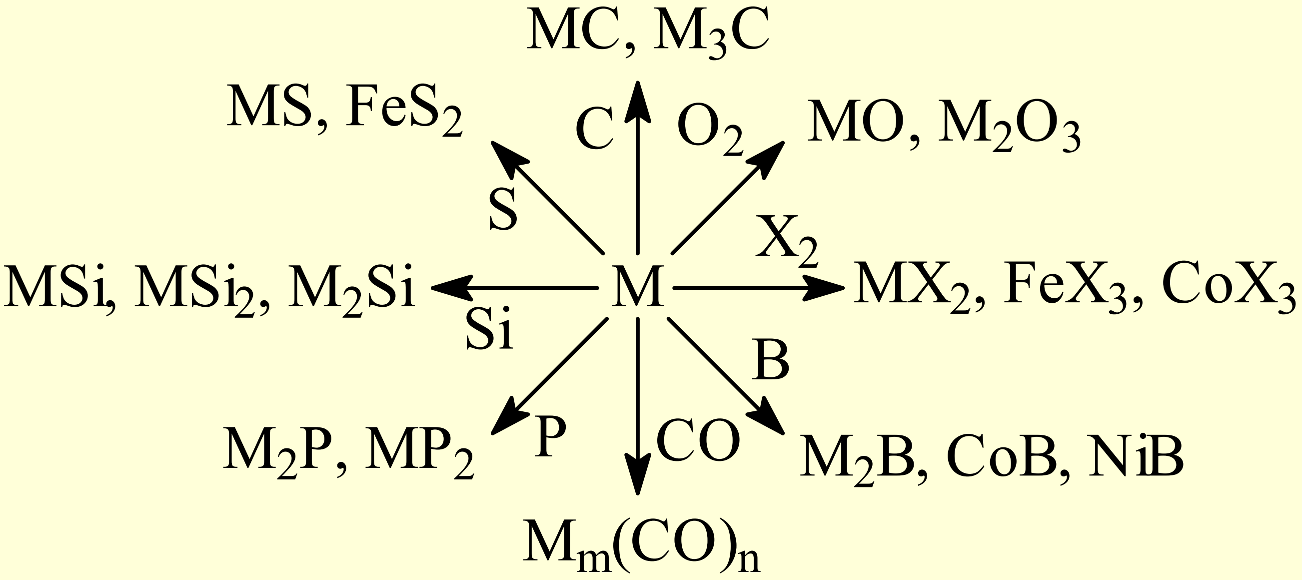
Course 8

“d^6-d^{10}” block

Iron, Ruthenium, Osmium, Hassium

Cobalt, Rhodium, Iridium, Meitnerium

Nickel, Palladium, Platinum, Darmstadtium



$M \xrightarrow{C} MC, M_3C$

$M \xrightarrow{O_2} MO, M_2O_3$

$M \xrightarrow{X_2} MX_2, FeX_3, CoX_3$

$M \xrightarrow{B} M_2B, CoB, NiB$

$M \xrightarrow{CO} M_m(CO)_n$

$M \xrightarrow{P} M_2P, MP_2$

$M \xrightarrow{Si} MSi, MSi_2, M_2Si$

$M \xrightarrow{S} MS, FeS_2$

Hassium synthesis

$_{96}Cm + _{12}Mg \rightarrow _{108}Hs$

Meitnerium synthesis

$_{83}Bi + _{26}Fe \rightarrow _{109}Mt$

Darmstadtium synthesis

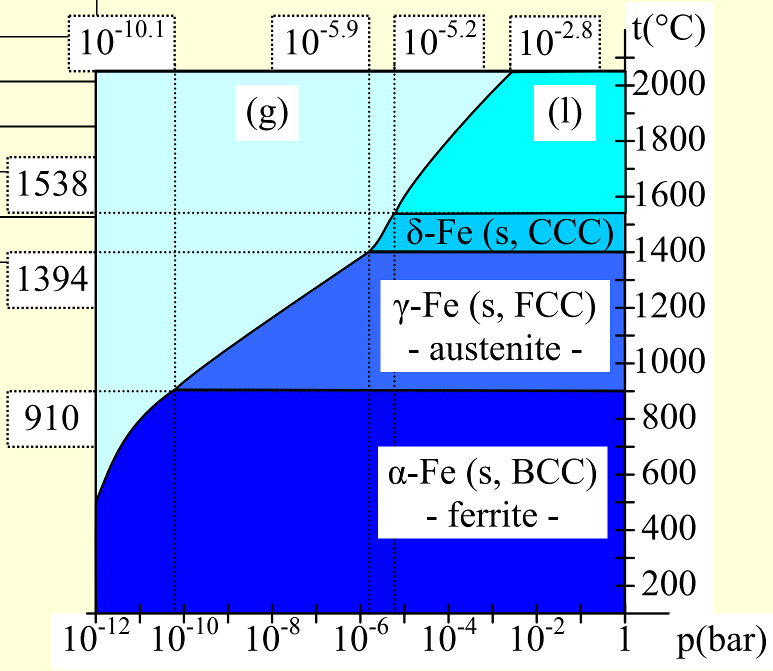
$_{82}Pb + _{28}Ni \rightarrow _{110}Ds$

Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt spread

- Inner core is mainly a Ni-Fe alloy. Fe is 4th element by spread in the crust (6%, as oxides, sulfides and carbonates): Fe_2O_3 - hematite, Fe_3O_4 - magnetite, FeS_2 - pyrite, $FeCO_3$ - siderite.
- Nickel is about 700 times less spread than Fe as $(Fe,Ni)_9S_8$ (pentlandite), NiS (millerite), NiAs (nickeline).
- Cobalt is about 3 times less spread than Nickel as CoAsS (cobaltite), $CoAs_2$(safflorite) and $CoAs_3$ (skutterudite).
- The rest of the elements (Ru, Rh, Pd, Os, Ir, Pt) may be found as free metals and rarely combined with S, Se, and Te.
- Palladium is about 5000 times less spread than Cobalt, Platinum is about 2 times less spread than Palladium, Osmium is about 2 times less spread than Platinum, Ruthenium is about 2 times less spread than Osmium, Rhodium is about 1.5 times less spread than Ruthenium, and Iridium is about 1.5 times less spread than Rhodium.

Iron + Carbon and Iron – phase diagrams

Name	Phases	Remarks
C	Graphite	100% carbon
Fe_2C	ε-Fe_2C	η-Fe_2C
$Fe_{2.2}C$	ε-$Fe_{2.2}C$	pseudo-hexagonal iron carbide
Fe_7C_3	Fe_7C_3	Ekström-Adcok iron carbide
$Fe_{2.4}C$	ε-$Fe_{2.4}C$	Fe_2C+Fe_3C
$Fe_{2.5}C$	Hägg carbide	χ-Fe_2C_5
Fe_3C	Cementite	θ-Fe_3C
Fe_3C	ε-Fe_3C	hexagonal iron carbide
Solid solutions ($C\%_{wt}$ ≤2%)		
γ-Fe+C	γ-Fe+C	Austenite (stable), face-centered cubic (FCC) Martensite (metastable), body-centered tetragonal (BCT)
Solid solutions or pure iron ($C‰_{wt}$≤0.3 at 723°C, $C‰_{wt}$≤0.06 at 20°C)		
Ferrite	α-Fe	body-centered cubic (BCC) 1400°C ≤ t
	β-Fe	obsolete term for the paramagnetic α-Fe
	γ-Fe	face-centered cubic (FCC)
	δ-Fe	body-centered cubic (BCC) t°C ≤ 912
ε-Fe	hexagonal close-packed (HCP), unstable, high pressure only	

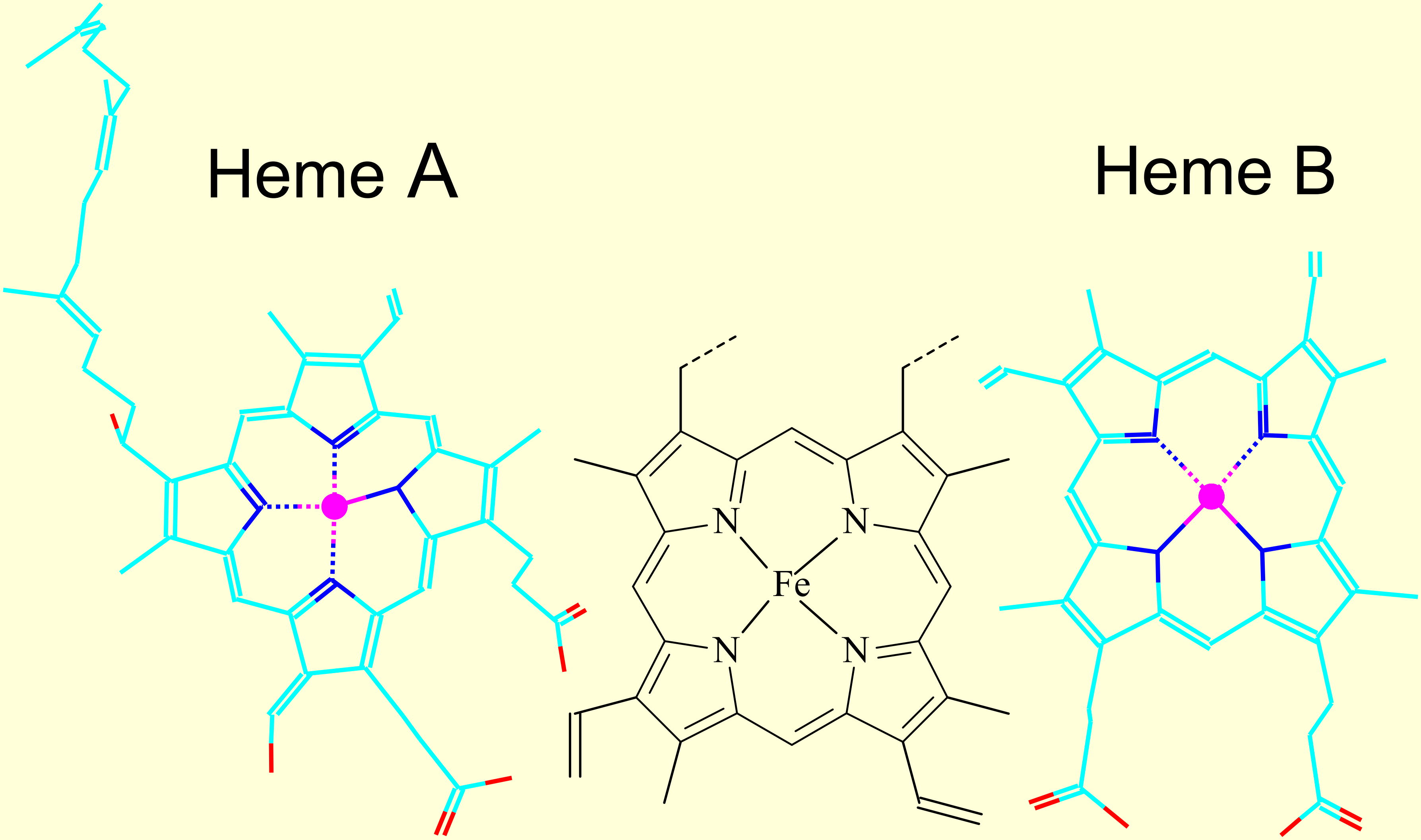


Hemoglobin and Myoglobin

- **Hemoglobin** (abbreviated Hb) is the iron-containing oxygen-transport metalloprotein in the red blood cells. Hemoglobin in the blood carries oxygen from the respiratory organs (lungs or gills) to the rest of the body where it releases the oxygen to burn nutrients to provide energy to power the functions of the organism, and collects the resultant carbon dioxide to bring it back to the respiratory organs to be dispensed from the organism. The hemoglobin molecule can bind & carry up to four oxygen molecules.
- **Myoglobin** (abbreviated Mb) is an iron-containing and oxygen-binding protein found in the muscle tissue and it is related to hemoglobin, which is the iron-containing and oxygen-binding protein in blood. Myoglobin is a single-chain globular protein of 153 or 154 amino acids, containing a **heme** (iron- containing porphyrin) and a mass of about 17,700 g/mol (with heme), and is the primary oxygen-carrying pigment of muscle tissues. High concentrations of myoglobin in muscle cells allow organisms to hold their breaths longer. Diving mammals such as whales and seals have muscles with particularly high myoglobin abundance.

Heme A

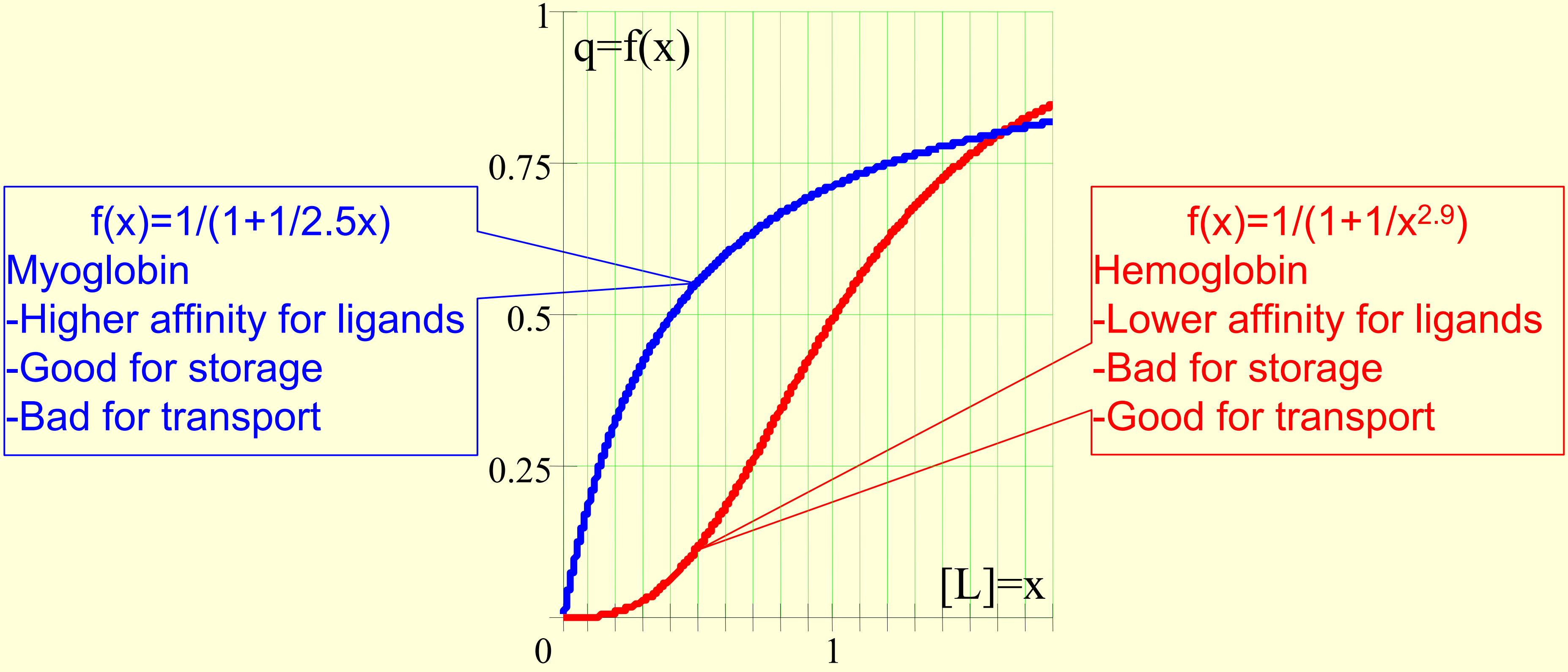
Heme B



A heme consists of an iron ion contained in the center of a large heterocyclic organic ring called porphyrin. Hemes are components of hemoglobin; they are also components of other hemoproteins (such as is Myoglobin).

Hb vs. Mb

- Hb carry 4 hemes and Mb store 1 heme. Each heme can bind one ligand (O_2, CO, CO_2, NO, etc.). H + mL ↔ HL_m; $m_{Hb} \approx 2.8\text{-}3.0$ (max.=4)
- $K_d = [H][L]^m/[HL_m]$; q = [binding sites occupied]/[total binding sites]; $q=[HL_m]/([HL_m]+[H])=\ldots=1/(1+K_d/[L]^m)$;
- $f(x) = 1/(1+a/x^m)$, a(Hb:Mb)≈2.5:1; m(Hb)≈2.9; m(Mb)=1



$f(x)=1/(1+1/2.5x)$

Myoglobin

-Higher affinity for ligands

-Good for storage

-Bad for transport

$f(x)=1/(1+1/x^{2.9})$

Hemoglobin

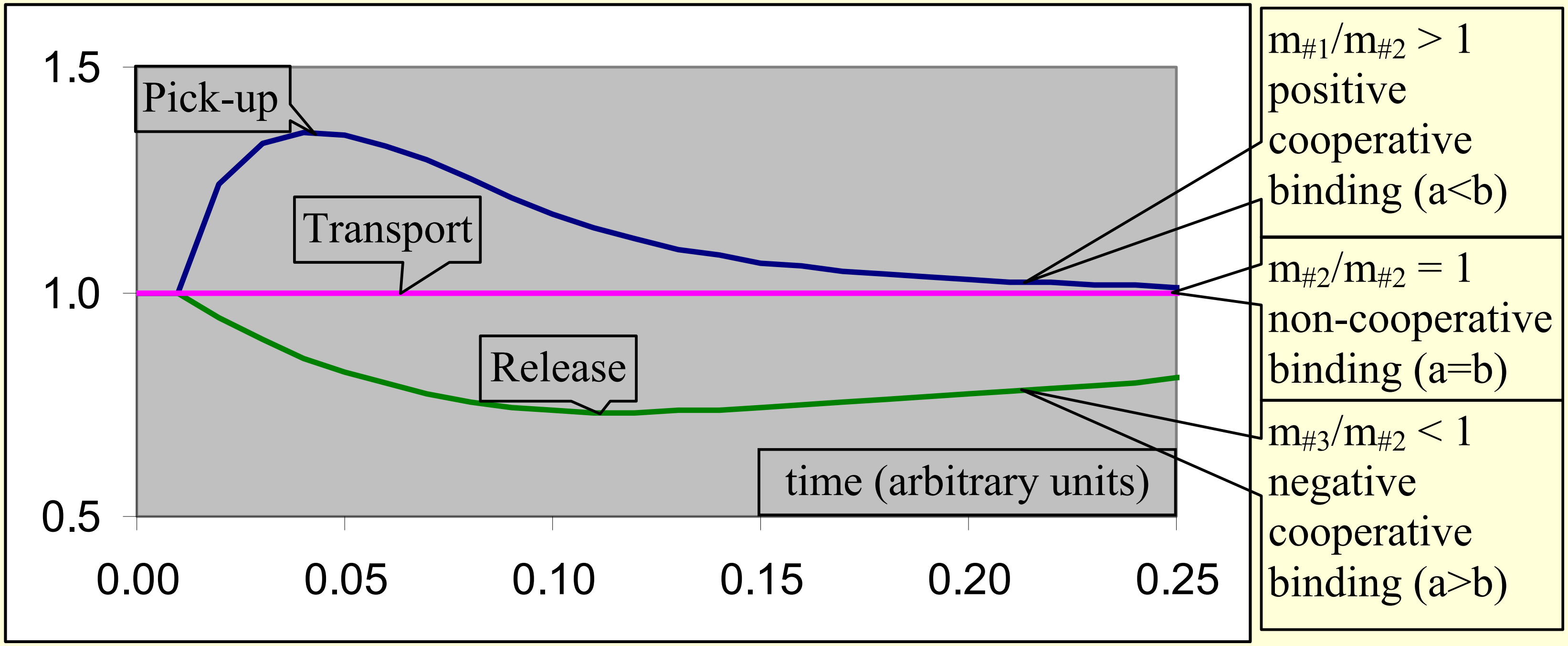
-Lower affinity for ligands

-Bad for storage

-Good for transport

Hemoglobin oxygen binding

$H + L \rightarrow HL$	k_1	$v_1=k_1\cdot[H][L]$	$[H]=x; [HL]=y; [HL_2]=z$
$HL + L \rightarrow HL_2$	k_2	$v_2=k_2\cdot[HL][L]$	$k_1=a; k_2=b; [L]=c$
H:	$d[H]/dt=-v_1$	$d[H]=-k_1\cdot[H][L]\cdot dt$	$\dot{x} = -acx$
HL:	$d[HL]/dt=v_1-v_2$	$d[HL]=(k_1\cdot[H][L]- k_2\cdot[HL][L])\cdot dt$	$\dot{y} = acx - bcy$
HL_2:	$d[HL_2]/dt=v_2$	$d[HL_2]=k_2\cdot[HL][L]\cdot dt$	$\dot{z} = bcy$
Cases	Initial	Iterative	$m = \frac{[HL]\cdot 1 + [HL_2]\cdot 2}{[H]+[HL]+[HL_2]}$
#1: $a=1<4=b$	$x_0=1; y_0=0; z_0=0;$	$x_{n+1}=x_n-ac\cdot\delta t$	
#2: $a=1=1=b$	$c=16$	$y_{n+1}=y_n+(acx_n-bcy_n)\cdot\delta t$	$m_n = \frac{y_n\cdot 1 + z_n\cdot 2}{x_n + y_n + z_n}$
#3: $a=4>1=b$	$\delta t=0.01$	$z_{n+1}=z_n+bcy_n\cdot\delta t$	
m: H saturation with L (simplified case, only 2 ligand sites)			

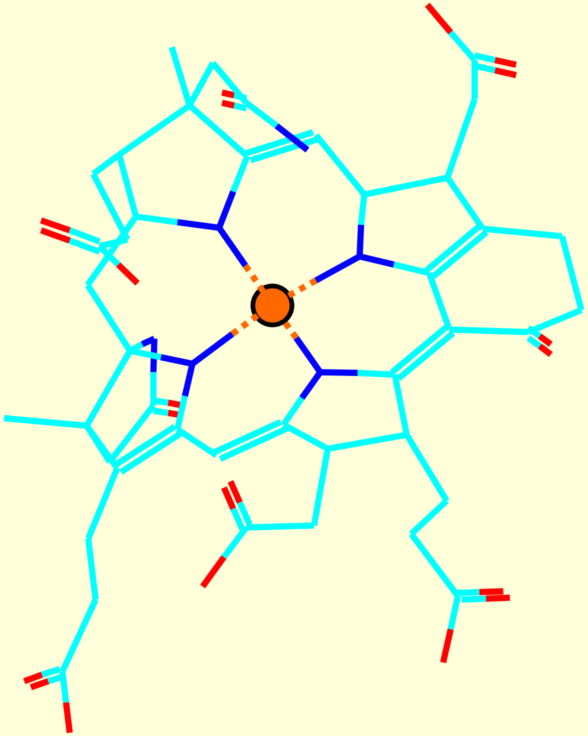


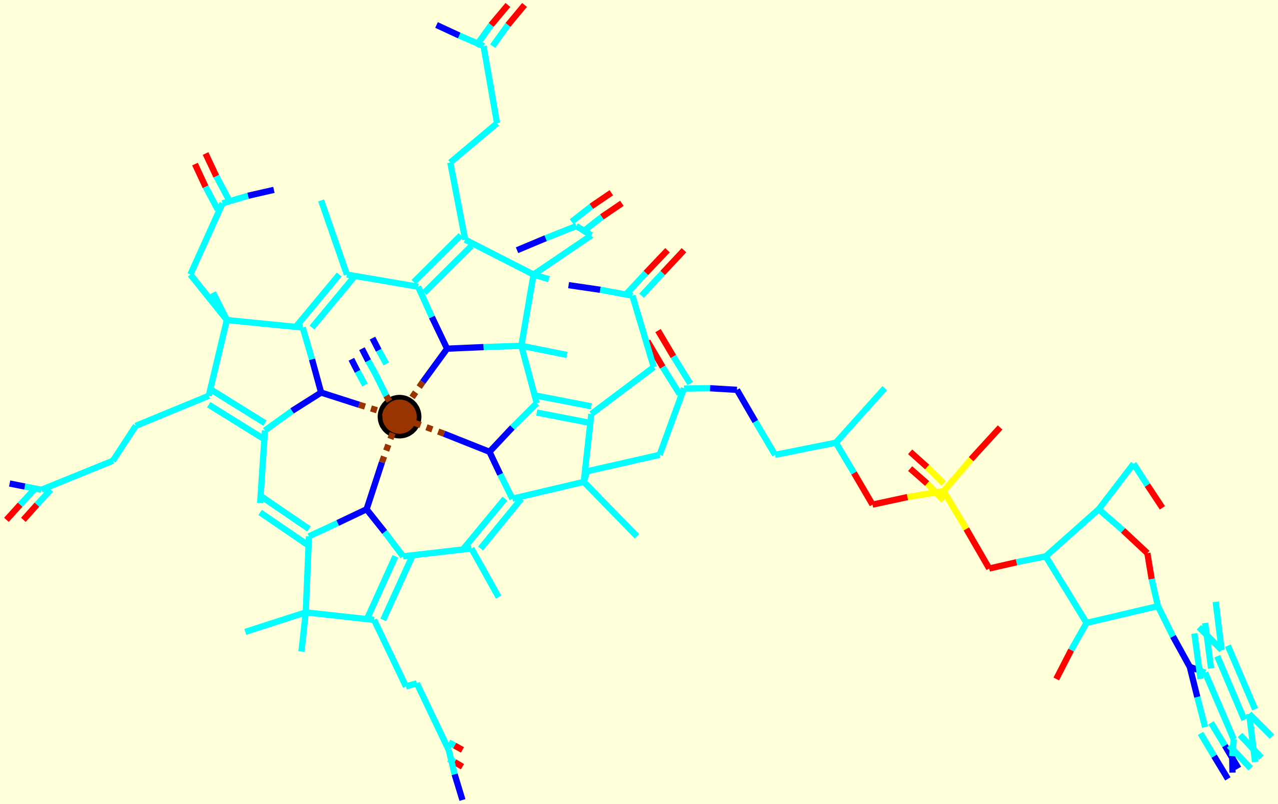
$m_{\#1}/m_{\#2} > 1$ positive cooperative binding (a<b)

$m_{\#2}/m_{\#2} = 1$ non-cooperative binding (a=b)

$m_{\#3}/m_{\#2} < 1$ negative cooperative binding (a>b)

Coenzyme F430 & B12 vitamin

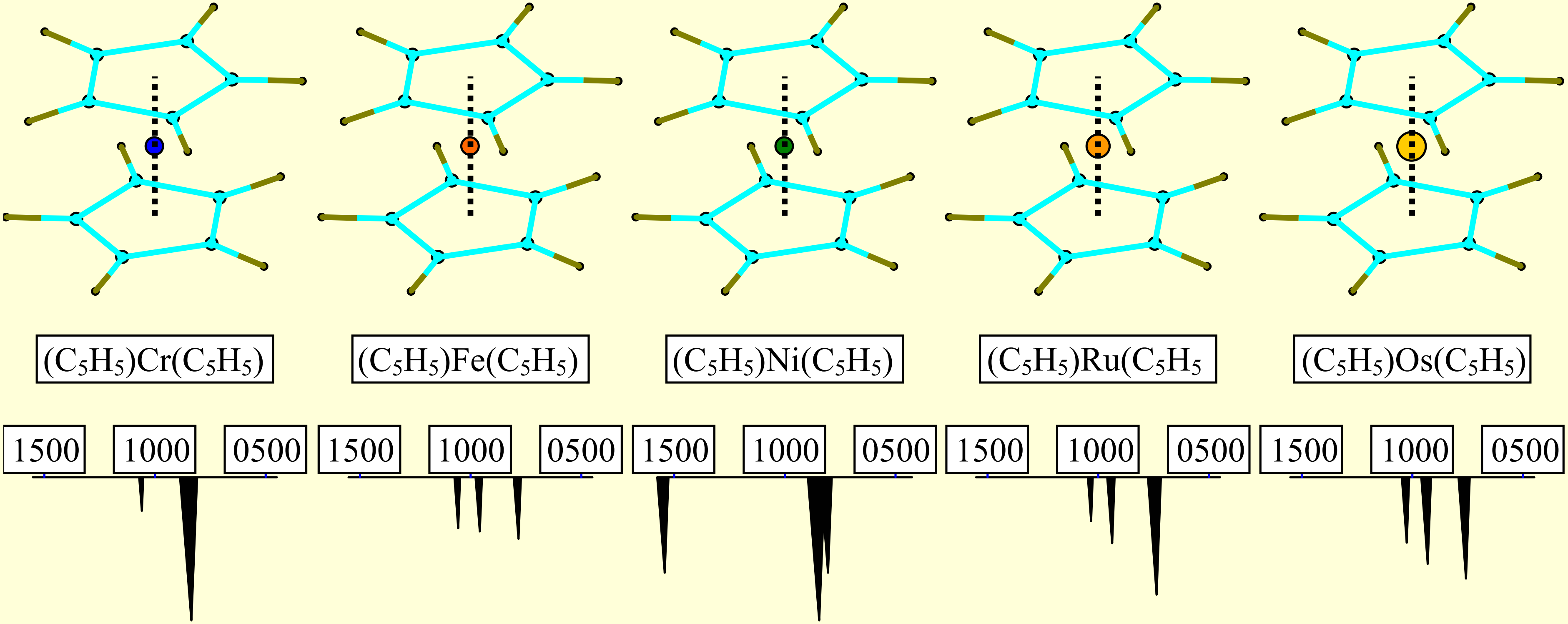




Ni$C_{42}N_6O_{13}H_{50}$

Co$C_{63}N_{14}O_{14}PH_{89}$

$(C_5H_5)M(C_5H_5)$ IR spectra (cm^{-1})



$(C_5H_5)M(C_5H_5)$ - molecular modeling & UV-VIS

$(C_5H_5)M(C_5H_5)$ properties (Spartan '10, DFT, RBLYP, 6-31G* + LANL2DZ>Kr, Vacuum)					
Formula	$C_5H_5CrC_5H_5$	$C_5H_5FeC_5H_5$	$C_5H_5NiC_5H_5$	$C_5H_5RuC_5H_5$	$C_5H_5OsC_5H_5$
Energy (a.u.)	-1427	-1650	-1891	-481	-478
E_{HOMO} (eV)	-8.62	-3.68	-2.50	3.69	8.43
E_{LUMO} (eV)	3.05	-0.86	-0.60	3.86	10.46
λ (nm)	106	440	653	7293	611
Absorbed light	⬜	🟪	🟧	⬛	🟨
Visible color	⬛	🟧	🟦	⬜	🟪
Dipole Moment (debye)	0.00	0.01	0.00	0.05	0.07
Pt. Group	D5d	D5	D5d	D5d	D5d
Area ($Å^2$)	192	180	198	196	195
Volume ($Å^3$)	171	170	173	174	174
Ovality (dimensionless)	1.29	1.21	1.32	1.30	1.29
Accessible Area ($Å^2$)	140	133	156	259	283
min(ElPot) (kJ/mol)	-118	-92	-143	-329	-460
min(LocIonPot) (kJ/mol)	48.5	34	17.4	2.6	7.1
Polarizability ($Å^3$)	52.5	54.5	55.0	55.5	55.0
Zero Point Energy (kJ/mol)	473	434	462	427	427
S^0 (J/mol, 298.15K)	350.1	348.5	378.9	363.5	368.3
H^0, G^0 (a.u., 298.15K)	-1427	-1650	-1890	-481	-478
Cv (J/mol, 298.15K)	143.5	156.5	161.9	165.9	166.2

Ru, Rh, Pd, Os, Ir, Pt, Ag, Au - extraction

- Finding the orebody and creating access to it
- Breaking the orebody and harvesting the ore by mining
- Transport the ore to the processing and refining site
- Processing
  - Refractory ore treatment:

    $$M_2S_n + nO_2 \rightarrow 2M + nSO_2$$
  - Solubilization (leaching):

    $$M_{(s)} + KCN_{(aq)} + O_{2(air)} + H_2O \rightarrow K[M(CN)_{n+1}]_{(aq)} + KOH$$
  - Concentrating:
    - Adsorption with carbon

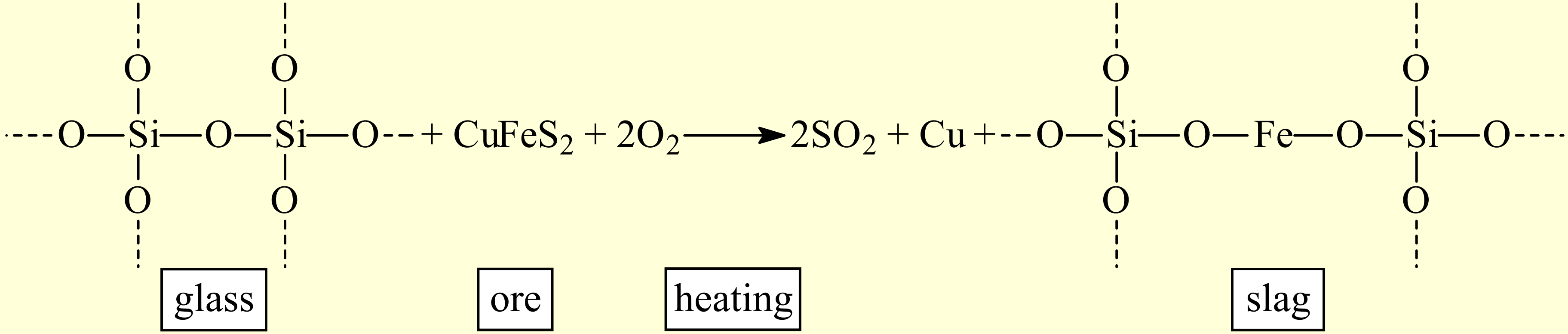
      $$C_{(s)}\text{-}K[M(CN)_{n+1}]_{(s)} \leftrightarrow K[M(CN)_{n+1}]_{(aq)}$$
    - Re-solubilization (re-leaching)
- Refining (>95%)
  - Reduction: $M^{n+}_{(aq)} + nH_{2(g)} \rightarrow M_{(s)} + 2nH^+_{(aq)}$
  - Solubilization (with aqua regia $3HCl+1HNO_3$, excepting Ru, Os, Ir):
    - $Ag_{(s)} + M_{(s)} + nH^+ + HNO_3 \rightarrow AgCl\downarrow + M^{n+} + NO_2 + H_2O$
    - $2Rh^{3+} + 6NaHSO_4 \rightarrow Rh_2(SO_4)_3 + 3Na_2SO_4 + 6H^+$
    - $Ru + Os + 8Na_2O_2 + 2H_2O \rightarrow Na_2[RuO_4(OH)_2] + Na_2[OsO_4(OH)_2] + 6Na_2O$
    - Iridium is the most corrosion-resistant metal known; $Ir + F_2 \rightarrow IrF_6$
- Electrolytic refining (>99%)

- Platinum Metals Reviews (http://platinummetalsreview.com) journal (open access)
  - Patents, January 2012 (Issue 1)
    - Producing Iridium-Containing Catalysts
    - Ruthenium-Based Carbene Catalyst
    - Platinum-Palladium in Exhaust System
    - Palladium-Bismuth Catalyst
    - Hydrogen Production Apparatus
    - Osmium in a Series of Penetrator Rods
    - Osmium(II) Arene Azo Anticancer Complexes
    - Palladium-Based Dental Alloy
    - Bridged Ring Metal Complexes for photoconversion
  - Patents, October 2012 (Issue 4)
    - Carbon Supported Palladium Catalyst
    - Ruthenium-Carbene Complexes
    - Manufacture of Vinyl Chloride
    - Saccharification of Biomass Materials
    - Hydrogenation of Vegetable Oil
    - Lean-Burn Engine Oxidation Catalyst
    - Oxygen Evolution Catalyst
    - Os and Ru Analyte Sensor
    - Novel Platinum Nanoparticles
    - Manufacturing Osmium Membrane

Ru, Rh, Pd, Os, Ir, Pt - uses

Copper – obtaining and use

- Copper can be found as native or combined (as CuS_2 - chalcocite, $CuFeS_2$ - chalcopyrite). Separating Cu from Fe is conducted with silica (see the image).
- Cu^{2+} are water-soluble, and serves at low concentration as bacteriostatics, fungicides, and wood preservatives as well as is an essential trace nutrient to all higher plant and animal life. At high concentrations are poisonous to higher organisms. The main places where copper is found in animals are liver, muscle and bone.
- Applications of copper includes electrical wires - 60%, roofing and plumbing (pipes) - 20%, and industrial machinery - 15%. When a higher hardness is required then are alloyed (5% of total use) in brass and bronze. A small part is used in production of nutritional supplements and fungicides in agriculture.



$$\text{---O—Si—O—Si—O--} + CuFeS_2 + 2O_2 \longrightarrow 2SO_2 + Cu + \text{--O—Si—O—Fe—O—Si—O---}$$

Copper, Silver, Gold – chemical properties

- Cu, Ag and Au have positive standard reduction potential, so they do not react with water and remove hydrogen from hydracids. Noble character grows from Cu to Au, while for alkali reactivity increases. Chemical inertness of Au is similar to that of platinoids.
- Cu reacts with HNO_3 differently depending on concentration (Ag only in concentrated):

$$3Cu + 8HNO_3 \text{ (diluted)} \rightarrow 2NO + 3Cu(NO_3)_2 + 4H_2O$$

$$Cu + 4HNO_3 \text{ (concentrated)} \rightarrow 2NO_2 + Cu(NO_3)_2 + 2H_2O$$

- Cu and Ag reacts with concentrated H_2SO_4 at heat:

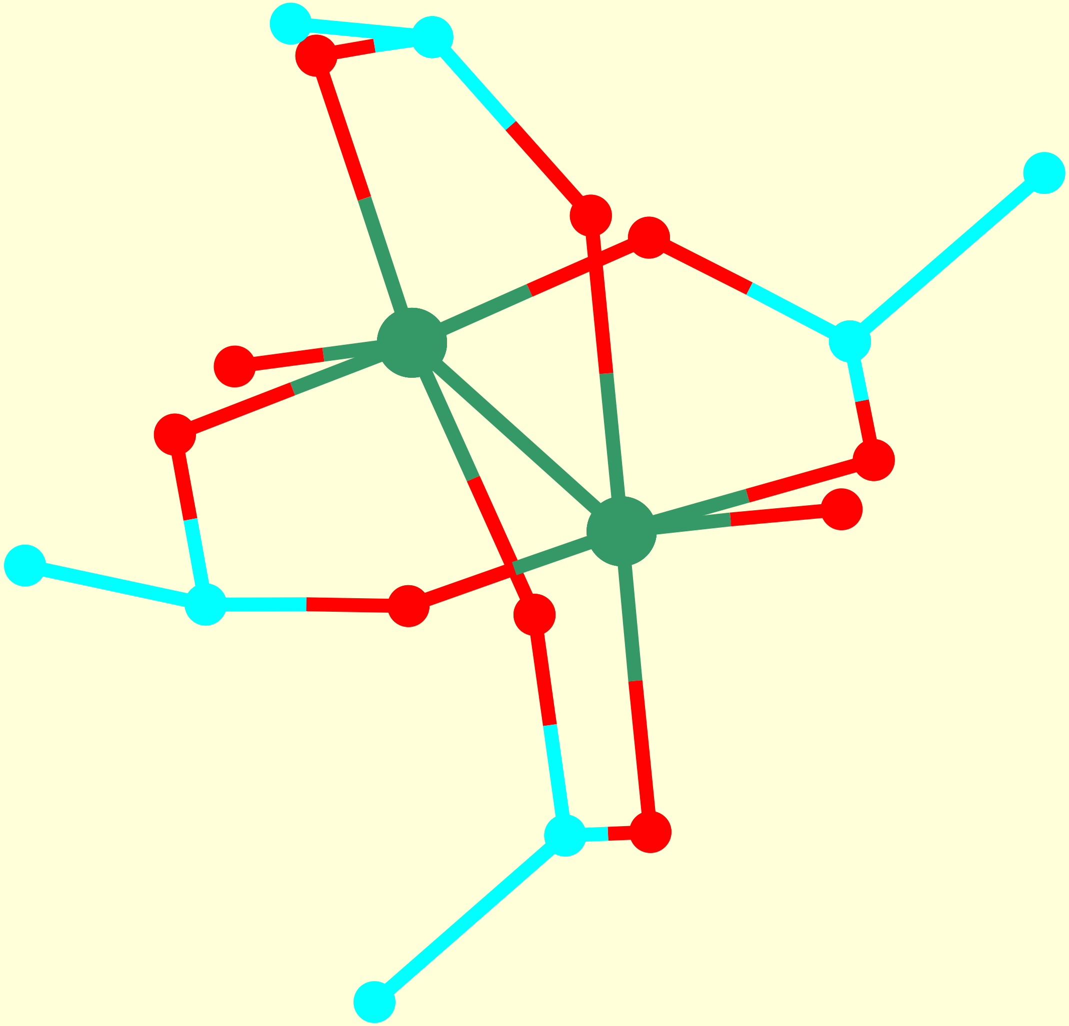
$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$$

- Cu oxidizes slowly in moist air covering herself with a greenish film:

$$2Cu + H_2O + O_2 + CO_2 \rightarrow CuCO_3 \cdot Cu(OH)_2$$

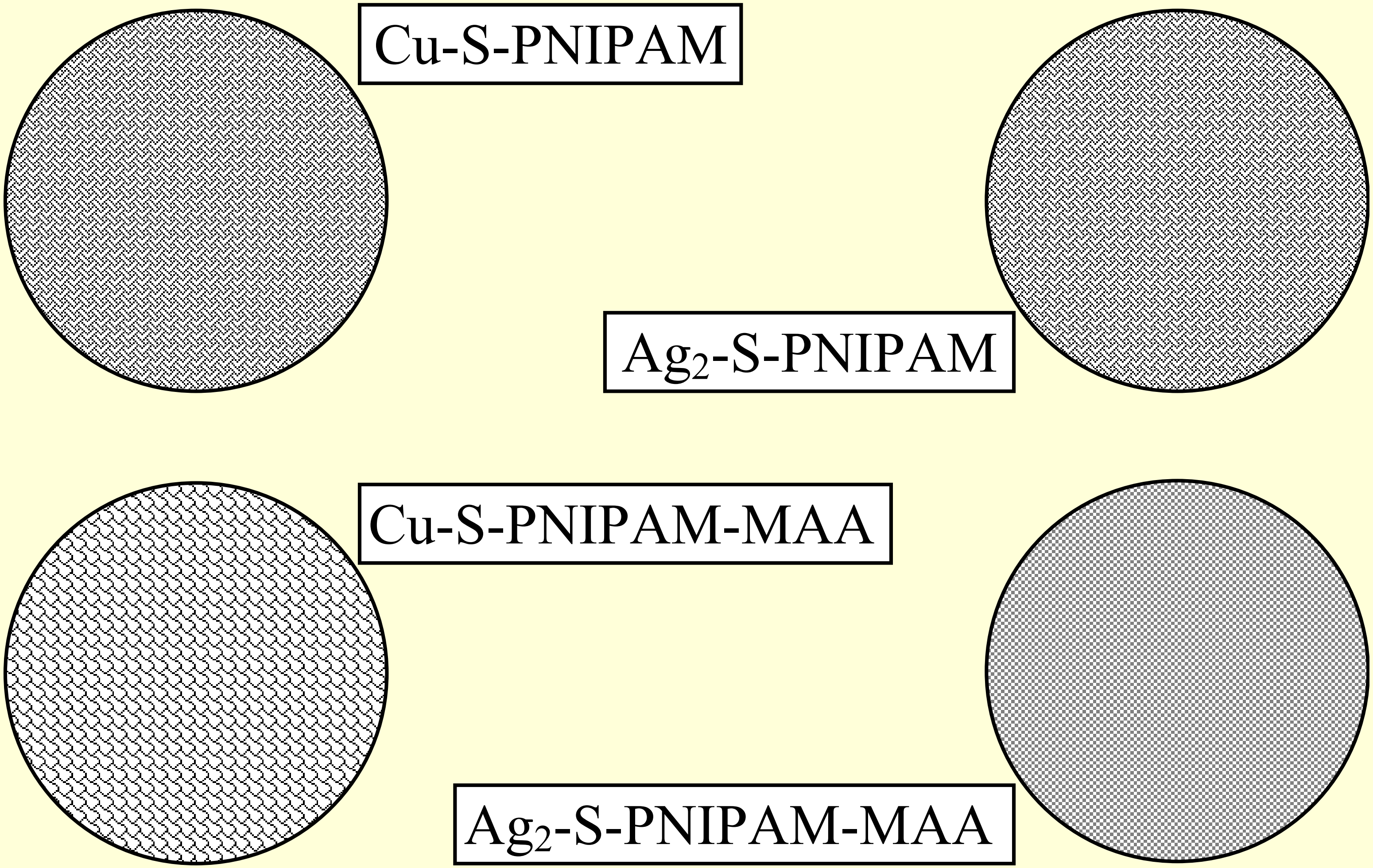
- Au reacts with HNO_3 and H_2SO_4 only in the presence of catalysts (HCl, MnO_2, HIO_3)
- With halogens: Cu(II), Ag(I), Au(III) + $X_2 \rightarrow CuX_2$, AgX, AuX_3

Cooper acetate



Copper acetate adopts the "paddle-wheel" structure seen also for Rh(II) and Cr(II) tetraacetates. The uses are as catalyst or oxidizing agent in organic syntheses.

Polymer composite textures design



Cu-S-PNIPAM

Ag_2-S-PNIPAM

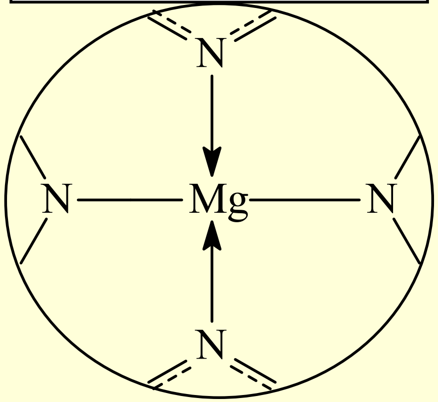
Cu-S-PNIPAM-MAA

Ag_2-S-PNIPAM-MAA

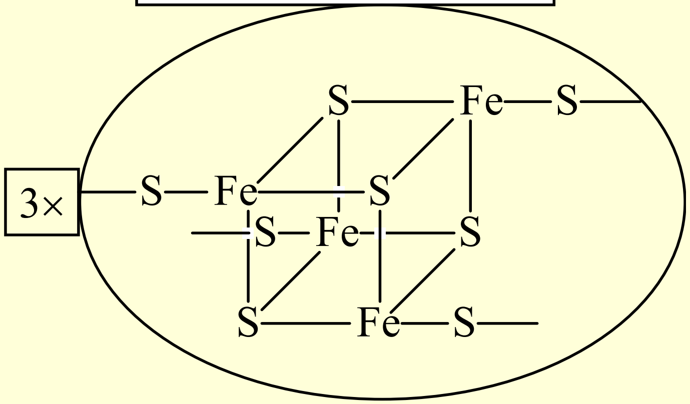
Cu & Ag: metal sulfide-polymer composite microspheres with different textures
P=poly; NIPAM-MAA=*N*-isopropylacrylamide-*co*-methacrylic acid

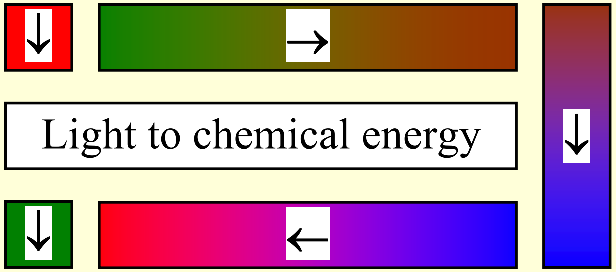
Fe, Cu, Mg – biological role

Chlorophyll

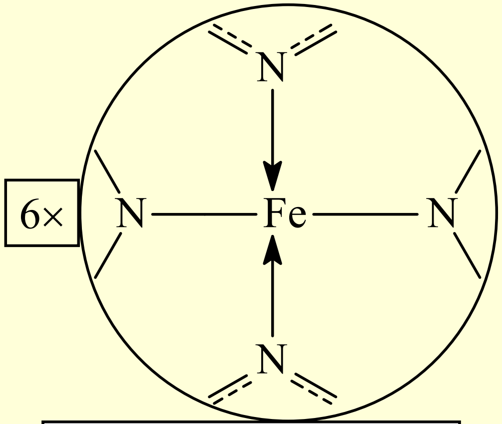


[Fe4S4]-ferredoxins

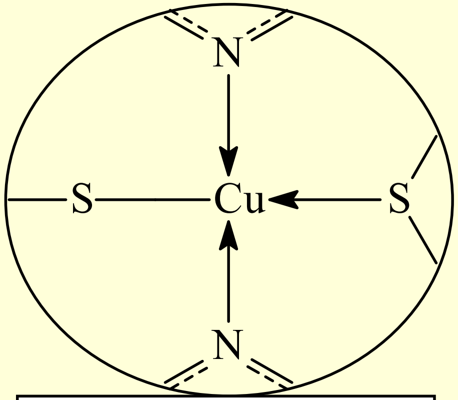




Light to chemical energy



Cytochrome f



Plastocyanin

Silver - uses

- AgCdO is withstand arcing and is used in high-voltage contacts. Small devices, such as hearing aids and watches, use AgO batteries (long life & high energy-to-weight ratio). Another usage is high-capacity Ag-Zn and Ag-Cd batteries.
- By sputtering along with other optically transparent layers, silver is applied to glass (layer of 10-15 nm thick), creating low emissivity coatings used in high-performance insulated glazing. Solar reflectors may use Ag as the reflective coating.
- Ag readily absorbs free neutrons and is used to make control rods regulating the fission chain reaction in nuclear reactors, as an alloy (80% Ag, 15% In, 5% Cd).
- Silver ions and silver compounds show a toxic effect on some bacteria, viruses, algae and fungi, but without the high toxicity to humans which gives a wide range of medical applications.

Gold - uses

- As gold is a good reflector of electromagnetic radiation such as infrared and visible light as well as radio waves and can be manufactured so thin that it appears transparent.
- Therefore it is used in some aircraft cockpit windows for de-icing or anti-icing by passing electricity through it, for the protective coatings on many artificial satellites, in infrared protective faceplates in thermal protection suits and astronauts helmets. Gold is used as the reflective layer on some high-end CDs and automobiles may use gold for heat shielding (such as in the engine compartment).
- Some gold salts do have anti-inflammatory properties and are used as pharmaceuticals in the treatment of arthritis and other similar conditions. Gold based injections have been explored as a means to help to reduce the pain and swelling of rheumatoid arthritis and tuberculosis.
- Gold alloys are used in restorative dentistry, especially in tooth restorations, such as crowns and permanent bridges. The gold alloys slight malleability facilitates the creation of a superior molar mating surface with other teeth and produces results that are generally more satisfactory than those produced by the creation of porcelain crowns.

Zinc, Cadmium, Mercury, Copernicium

- (M=Zn, Cd):
  - $M + 2HX \rightarrow MX_2 + H_2$
  - $2M + O_2 \text{ (t°C)} \rightarrow 2MO$
- $Zn + NaOH + H_2O \rightarrow Na_2[Zn(OH)_4] + H_2$
- Hg:

$$3Hg + 8HNO_3\text{(conc)} = 3Hg(NO_3)_2 + 2NO + 4H_2O$$

$$Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O$$

$$2Hg + O_2 \text{ (0-400°C)} \rightarrow 2HgO$$

$$2HgO \text{ (t>400°C)} \rightarrow 2Hg + O_2$$

Copernicium synthesis

$${}_{82}Pb + {}_{30}Zn \rightarrow {}_{112}Cn$$

Zn, Cd – properties

- Zinc is a bluish gray metal, which tarnishes in air, covering it with a protective layer of oxide. It is quite brittle at ordinary temperatures but becomes malleable at 100-150°C, it can be pulled sheets, but above 200°C becomes brittle again.
- Cadmium is similar to zinc, it differ in melting point (lower than cadmium). It begins to sublime at 160 °C. Reactivity is lower than cadmium zinc. Cadmium has a good capacity to alloying.
- Mercury is liquid at room temperature and emits vapor even at this temperature. Liquid mercury has a considerable vapor pressure at room temperature, therefore its surface should be protected, (with toluene) to avoid toxic fumes issue. Surprisingly, Hg is soluble both in polar solvents and non-polar (a saturated solution of Hg in water contains $6 \cdot 10^{-8}$ gHg/g). Mercury has the ability to form alloys with many metals, called amalgams. The easiest is amalgamates Na, K, Ag and Au, something harder Zn, Cd, Sn, Pb, Cu. Not amalgamate Mn, Fe, Co and Ni, so iron is used for making containers for mercury. Amalgamation is by simple mixing of cold metal.

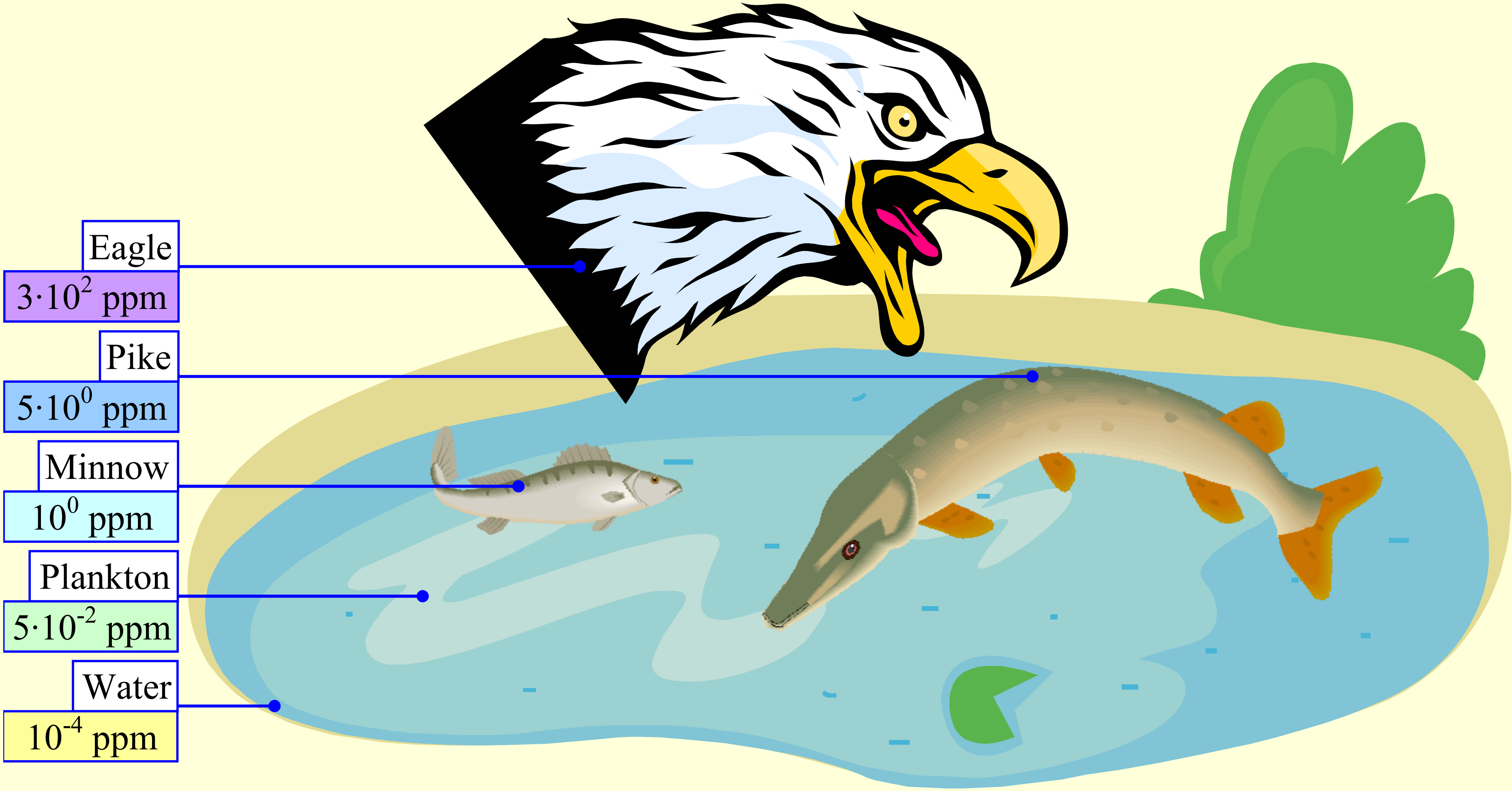
Zn, Cd, Hg - uses

- Zinc is produced in large quantities world production over 7 million tons / year and are mainly used to protect iron from corrosion. This can be done by plating (electroplating cover) by immersion in molten zinc metal (so-called "hot galvanizing"), or zinc powder coating and heating. Large quantities of zinc is used as sheet ("galvanized"). Use more objects cast zinc. Zinc alloys are also widely used, most notably brass (Cu-Zn with 20-50% Zn alloy). Electrodes of dry batteries are made of zinc. Of zinc compounds, zinc oxide, ZnO (zinc white) is used more as a pigment and zinc chloride, $ZnCl_2$, for treating textiles and cleaning metal surfaces (metal oxides dissolve).
- Cadmium is mainly used to protect steel against corrosion by galvanized. It is also used as a neutron absorber in nuclear reactors, batteries (Ni-Cd). With low melting point, cadmium uses for solders and fuses. CdS is a major yellow pigment used in painting.
- Mercury is used in the largest quantity as electrode in electrolytic cells for the production of NaOH and chlorine. It is also used in mercury vapor lamps in meters (thermometers, manometers), and in the extraction of precious metals (gold and silver). Organic-mercury compounds have fungicidal activity and is used in agriculture, being very toxic.

Cd, Hg - biochemistry

- While zinc is an important element for life, its congeners, Cd and Hg, are highly toxic. The main sources of cadmium zinc are their melts, from where cadmium gases can escape. By ingesting cadmium are accumulated in the kidneys causing its disorder and also can replace Zn in enzymes and preventing their function.
- Mercury combinations are considered among the most toxic minerals. Mercury vapors are toxic causing dizziness and disorders of the brain and/or lungs. Mercury is cumulative poison and having no biological role, no clearance mechanism in the body. It has both local corrosive action (the mouth, intestine, kidney) and general toxic action. The most important industrial sources of mercury are toxic acetaldehyde and vinyl chloride (monomer to manufacture PVC) factories, where Hg compounds are used as catalysts as well as on production of electrolytic NaOH and Cl_2, where the mercury use as cathodes.
- A greater toxicity are organic combinations of metallic mercury (alkyl and aryl mercury compounds).

Mercury accumulation



Eagle

$3 \cdot 10^2$ ppm

Pike

$5 \cdot 10^0$ ppm

Minnow

10^0 ppm

Plankton

$5 \cdot 10^{-2}$ ppm

Water

10^{-4} ppm

Chemical elements in human body

Rank		%	Elemental composition by mass											
1	O	65	9.5	Cl	0.15	19	Br	2.9E-4	28	As	2.6E-5	37	Sb	1.1E-5
2	C	18	11	Mg	0.05	20	Pb	1.7E-4	29	Sn	2.4E-5	38	Li	3E-6
3	H	10	12	Fe	6.0E-3	21	Nb	1.6E-4	30.5	Se	1.9E-5	40	Co	2E-6
4	N	3	13	F	3.7E-3	22	Cu	1.0E-4	30.5	Hg	1.9E-5	40	Cr	2E-6
5	Ca	1.4	14	Zn	3.2E-3	23	Al	8.7E-5	32	Mn	1.7E-5	40	Cs	2E-6
6	P	1.1	15	Si	2.0E-3	24	Cd	7.2E-5	33	I	1.6E-5	42	Ag	1E-6
7.5	S	0.25	16	Zr	6.0E-4	25	B	6.9E-5	34	Ni	1.4E-5			
7.5	K	0.25	17.5	Sr	4.6E-4	26	Ce	5.7E-5	35.5	Ti	1.3E-5			
9.5	Na	0.15	17.5	Rb	4.6E-4	27	Ba	3.1E-5	35.5	Mo	1.3E-5			

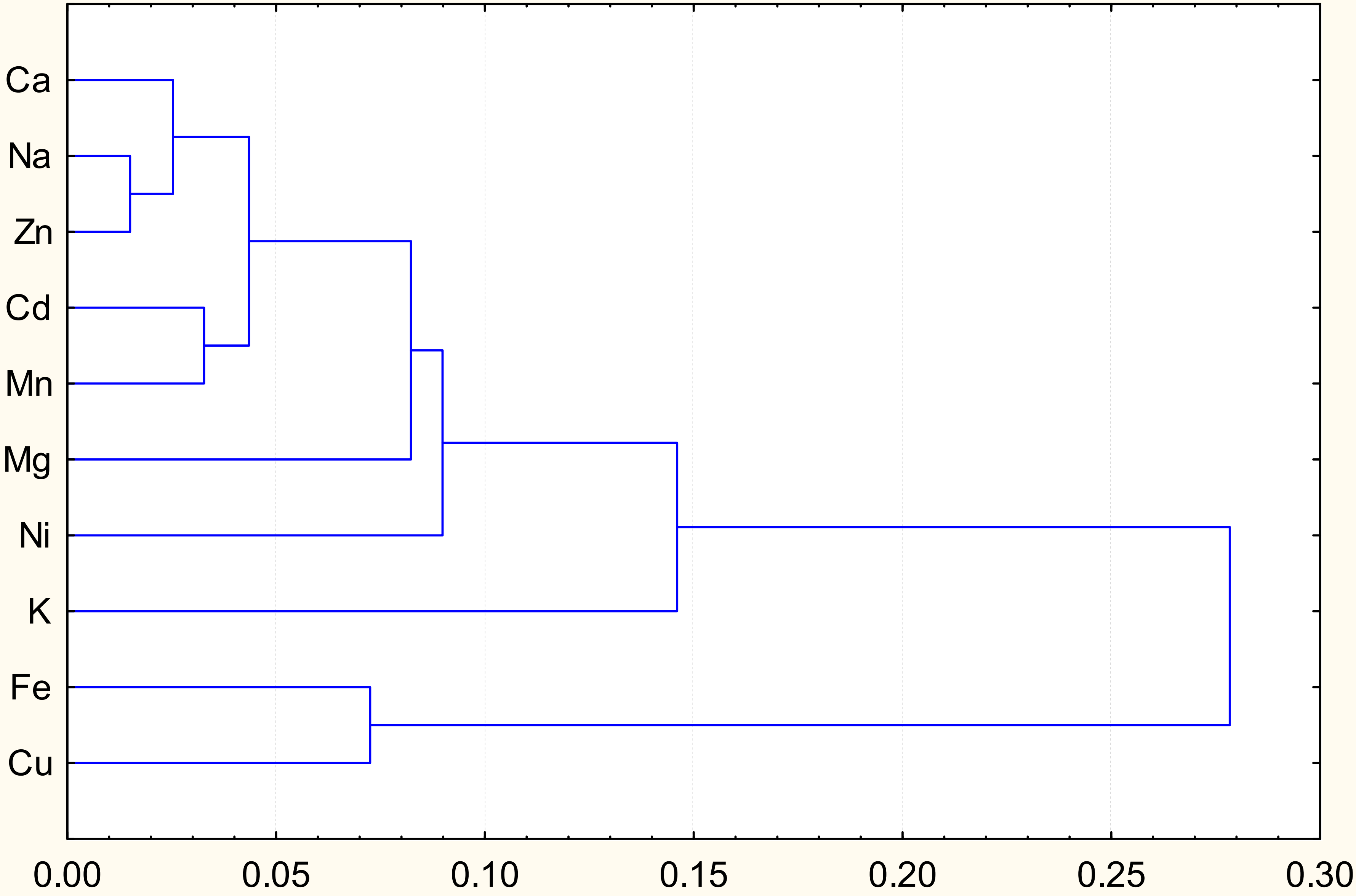
Rank		%	Elemental composition by atoms number											
1	H	63	10	Cl	0.024	19	Al	1.5E-5	28	Ba	1.2E-6	37.5	Cr	9E-8
2	O	24	11	Mg	0.007	20	Cu	1.0E-5	29	I	8E-7	37.5	As	9E-8
3	C	12	12	Si	5.8E-3	21.5	Pb	4.5E-6	30	Sn	6E-7	37.5	Sb	9E-8
4	N	0.58	13	F	1.2E-3	21.5	Cd	4.5E-6	31	Ce	4E-7	40.5	Se	5E-8
5	Ca	0.24	14	Fe	6.7E-4	23	B	3.0E-6	33	Zr	3E-7	40.5	Mo	5E-8
6	P	0.14	15	Zn	3.1E-4	24	Nb	1.7E-6	33	Ti	3E-7	42	Ag	9E-9
7	S	0.038	16.5	Sr	3.3E-5	26	Ni	1.5E-6	33	Co	3E-7			
8	Na	0.037	16.5	Rb	3.3E-5	26	Mn	1.5E-6	35	Cs	1E-7			
9	K	0.033	18	Br	3.0E-5	26	Li	1.5E-6	37.5	Hg	9E-8			

Metal containing enzymes

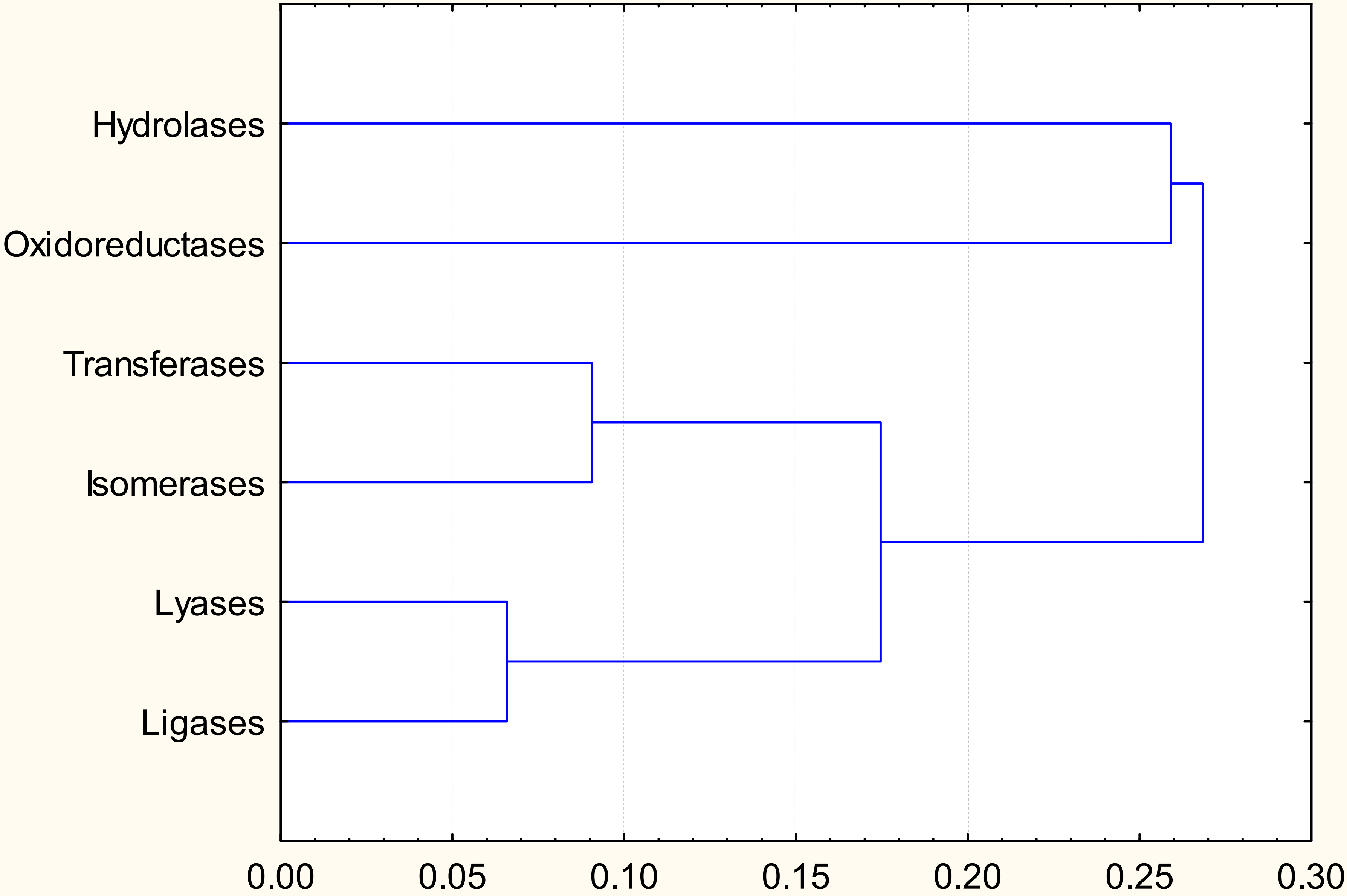
Enzymes\Element	Ca	Na	K	Mg	Fe	Zn	Sr	Rb	Al	Cu	Pb	Cd	Nb	Ni	Mn
Hydrolases	2752	1265	231	1437	184	2451	9	9	0	30	7	99	0	148	429
Transferases	593	553	213	1762	9	896	6	0	0	11	7	59	0	59	368
Oxidoreductases	545	413	217	394	412	758	6	0	0	473	5	41	0	105	203
Lyases	168	348	108	498	27	747	1	1	0	8	2	10	0	23	121
Ligases	36	35	25	263	0	327	0	0	0	0	0	3	0	18	51
Isomerases	47	90	14	203	7	87	0	0	3	1	1	8	0	19	117
The Research Collaboratory for Structural Bioinformatics (RSCB), www.rcsb.org Query on December 27, 2012															

See http://en.wikipedia.org/wiki/List_of_enzymes for their role

Single linkage tree diagram for 10 elements based on their occurence in enzymes
"1-Pearson r" distances (data from www.rscb.org on December 27, 2012)



Tree diagram for metal containing enzymes
"1-Pearson r" single linkage distances (www.rscb.org, Dec 27, 2012)



Q
&
R

In connection with the transitional elements:		
	0	Mercury is bioaccumulant because its concentration ([Hg]) in ecosystems tends to evolve in the progression: $[\mathrm{Hg}]_{\text{water}} \sim 500\cdot[\mathrm{Hg}]_{\text{plankton}}$; $[\mathrm{Hg}]_{\text{plankton}} \sim 20\cdot[\mathrm{Hg}]_{\text{minnow}}$; $[\mathrm{Hg}]_{\text{minnow}} \sim 5\cdot[\mathrm{Hg}]_{\text{pike}}$; $[\mathrm{Hg}]_{\text{pike}} \sim 60\cdot[\mathrm{Hg}]_{\text{eagle}}$
	1	Mercury is bioaccumulant because its concentration ([Hg]) in ecosystems tends to evolve in the progression: $[\mathrm{Hg}]_{\text{plankton}} \sim 500\cdot[\mathrm{Hg}]_{\text{water}}$; $[\mathrm{Hg}]_{\text{minnow}} \sim 20\cdot[\mathrm{Hg}]_{\text{plankton}}$; $[\mathrm{Hg}]_{\text{pike}} \sim 5\cdot[\mathrm{Hg}]_{\text{minnow}}$; $[\mathrm{Hg}]_{\text{eagle}} \sim 60\cdot[\mathrm{Hg}]_{\text{pike}}$
	0	FeO (iron white) is used as pigment
	1	ZnO (zinc white) is used as pigment
	1	Mg is present in chlorophyll
	0	Fe is present in chlorophyll
	0	Mg is present in myoglobin and haemoglobin
	1	Fe is present in myoglobin and haemoglobin
	0	Rh is about 2 times less spread than Ir, Ru is about 2 times less spread than Rh, Os is about 2 times less spread than Ru, Pt is about 1.5 times less spread than Os, and Pd is about 1.5 times less spread than Pt
	1	Pt is about 2 times less spread than Pd, Os is about 2 times less spread than Pt, Ru is about 2 times less spread than Os, Rh is about 1.5 times less spread than Ru, and Ir is about 1.5 times less spread than Rh
	0	Co is about 700 times less spread than Pd, Ni is about 3 times less spread than Co, Fe is about 5000 times less spread than Ni
	1	Ni is about 700 times less spread than Fe, Co is about 3 times less spread than Ni, Pd is about 5000 times less spread than Co

Q

&

R

In connection with the transitional elements:		
	0	Al alloys with the addition of Mg are used for beverage pots
	1	Al alloys with the addition of Mn are used for beverage pots
	0	The Cr-W-Co-C super hard high-speed tool steel is a Al-based alloy
	1	The Cr-W-Co-C super hard high-speed tool steel is a Fe-based alloy
	0	Zr_2O is a good catalyst for oxidation reactions (such as for obtaining of H_2SO_4 - catalyst for oxidation of SO_2 to SO_3)
	1	V_2O_5 is a good catalyst for oxidation reactions (such as for obtaining of H_2SO_4 - catalyst for oxidation of SO_2 to SO_3)
	0	Approximately 10% of current production of titanium is used in the construction of supersonic aircrafts and spaceships
	1	Approximately 90% of current production of titanium is used in the construction of supersonic aircrafts and spaceships
	0	Zinc alloy with 6% Al and 4% V has good mechanical properties and is used for gas tanks (H_2, O_2, F_2) and missiles
	1	Titanium alloy with 6% Al and 4% V has good mechanical properties and is used for gas tanks (H_2, O_2, F_2) and missiles
	0	Ti, Zr and Hf are very few resistant to chemical agents at moderate temperatures due to the formation of unproductive oxide layer on the surface
	1	Ti, Zr and Hf are very resistant to chemical agents at moderate temperatures due to the formation of a protective oxide layer on the surface
	0	Lutetium tantalate ($LuTa_4$) is the densest known stable white material (9.81 g/cm^3)
	1	Lutetium tantalate ($LuTaO_4$) is the densest known stable white material (9.81 g/cm^3)

Course 9

“f” block

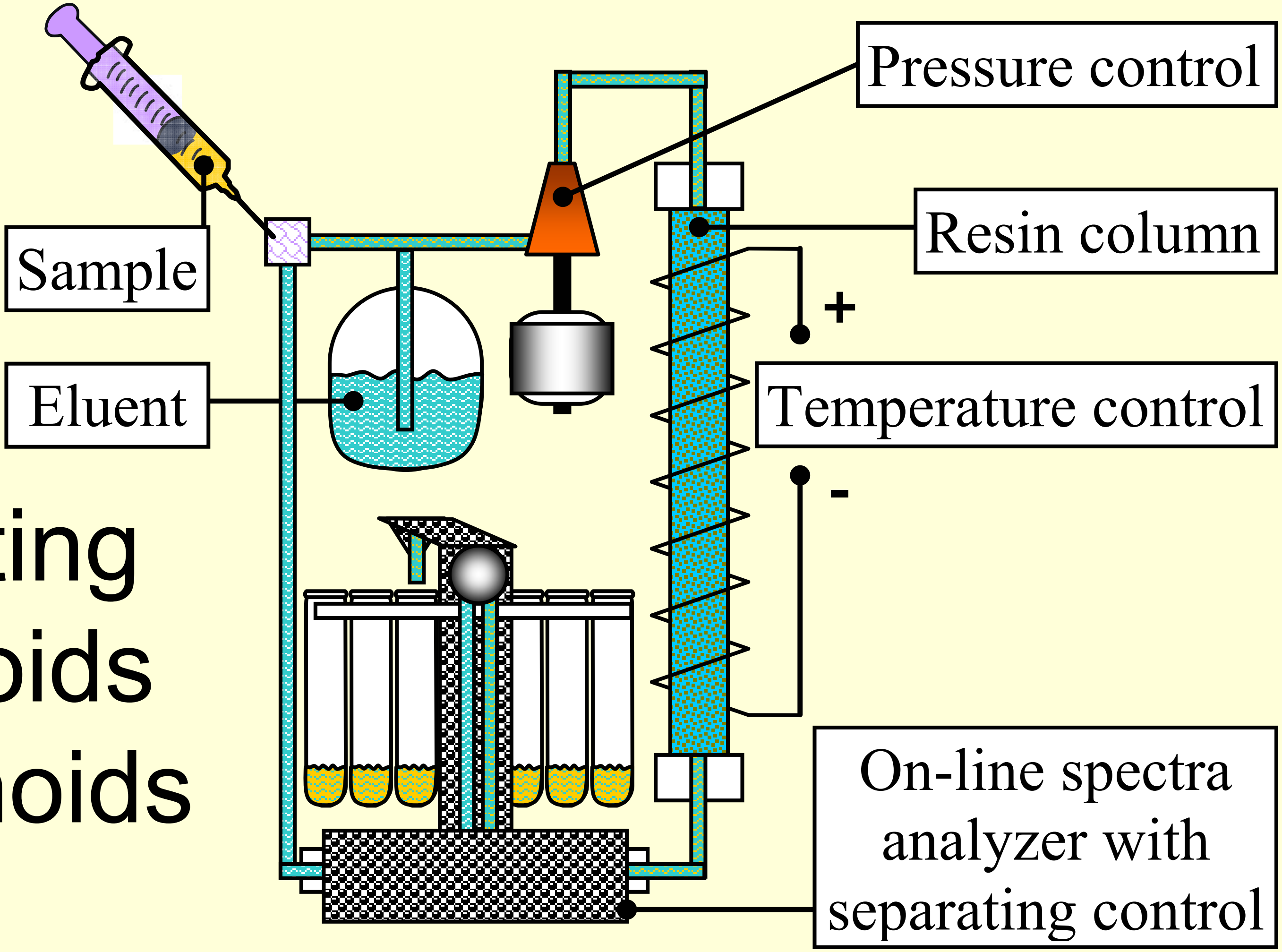
Lanthanoids and actinoids - separating

- Because almost perfect likeness of the chemical and electrochemical properties, lanthanides and actinides separation, one by one, pure, is very difficult. Earliest attempts were based on separation by fractional crystallization of double salts of nitrates, hydroxides or decomposition of fractional oxalate - these processes were long and about 20,000 operations required to obtain pure samples from a single element. Today, the separation is made easier due to the emergence of ion exchangers. Thus, a column of cathion, RH, apply a solution consisting of a mixture of salts of all lanthanides. Heavier ions are less bulky stronger will be complexed by citrate ion and will spend a period of time in solution and obviously, a shorter phase resin. In other words, less bulky ions will migrate faster along the column, coming first in the column.

Separating lanthanoids and actinoids

Problems:
Similar mass
Similar charge

Sample: mixture of lanthanoids and actinoids



Sample

Eluent

Pressure control

Resin column

Temperature control

+

-

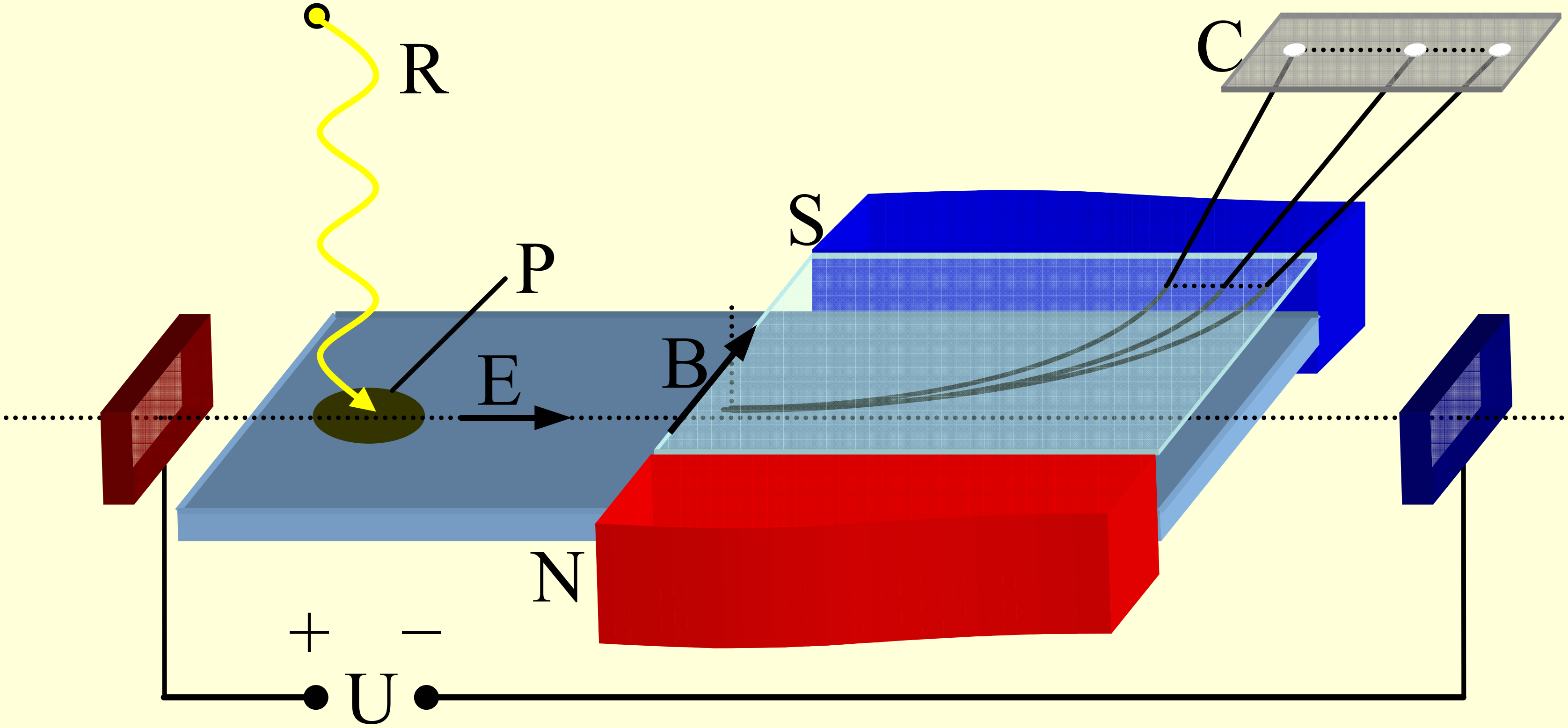
On-line spectra analyzer with separating control

Solution:
Process optimization

Eluent: Alcohol + HCl/HNO_3 mixture

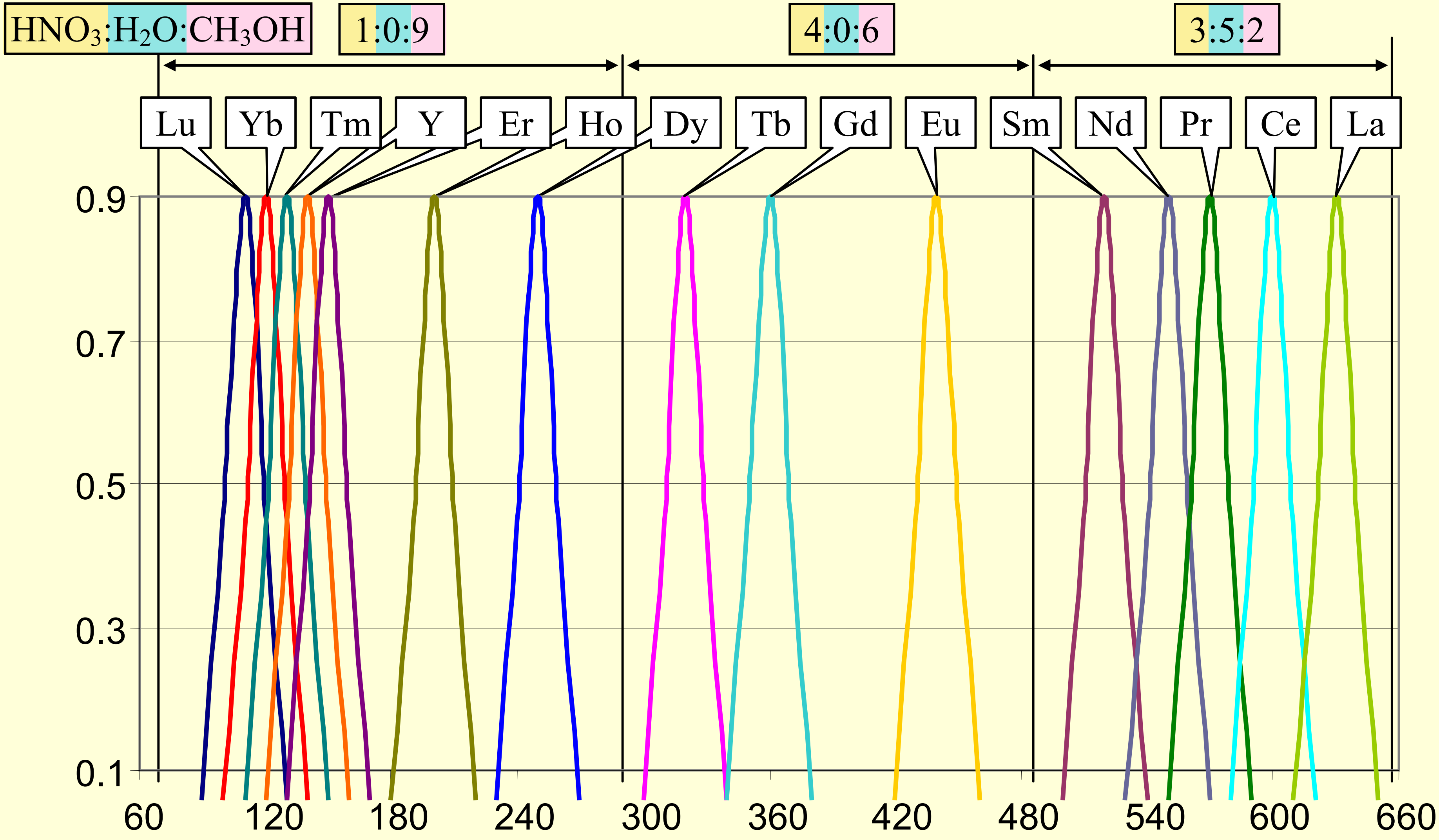
Resin: alternate copolymer of phenylene and substituted pyridine rings

Mass spectrometry

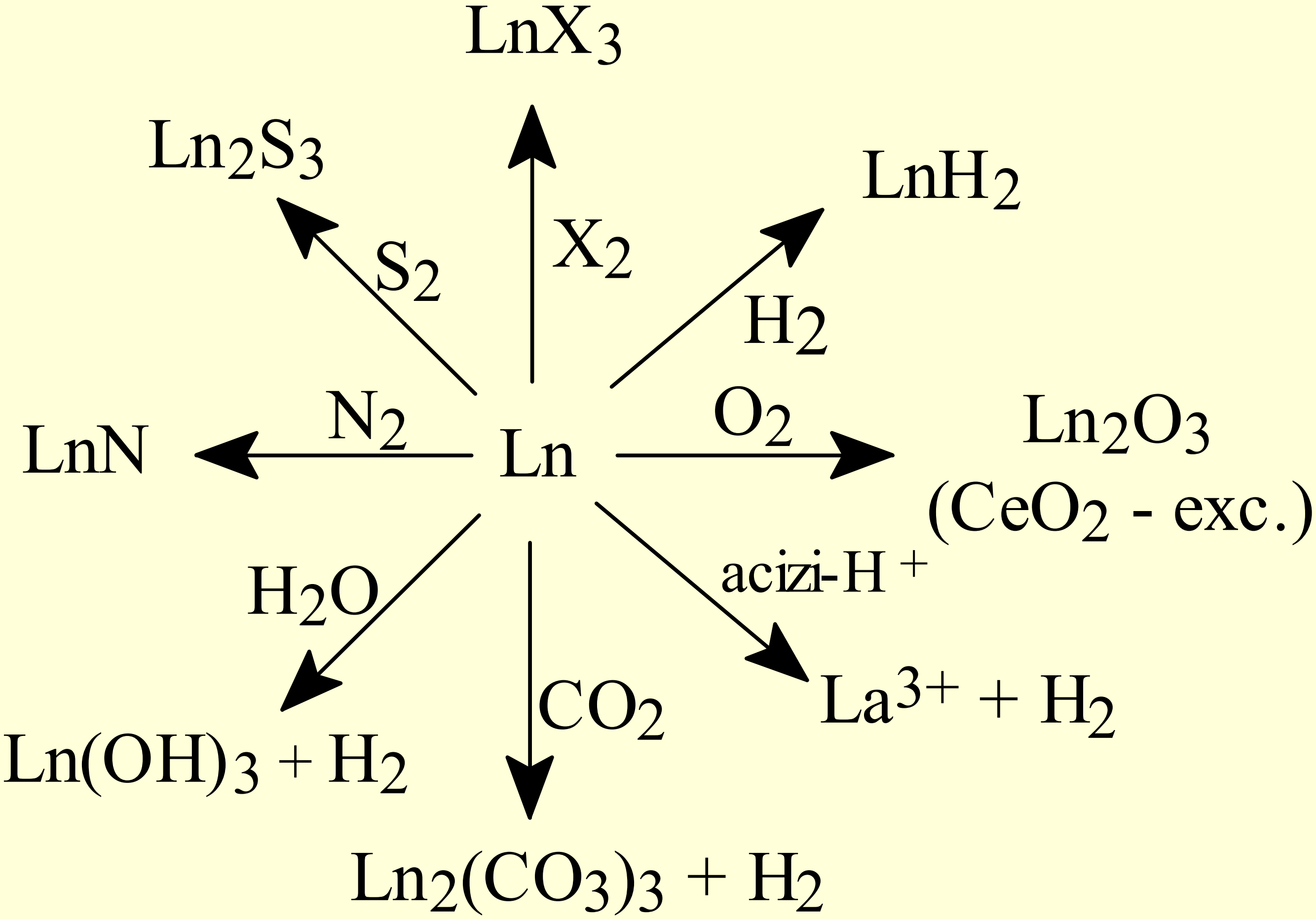


Applying an electric potential U can create a flow of positive ions to the negatively charged electrode and a flow of electrons to positively charged electrode, the flow of positive ions is passed through a region of magnetic field B and suffer deviations from the straight path, the screen photosensitive C positive electrical charge carriers are separated according to the ratio m/q where m is the mass and q is the charge of the wearer. The method used to determine the quantitative composition of samples.

Mobile phase (eluent) optimization



Lanthanoids – chemical properties



$Ln \xrightarrow{X_2} LnX_3$

$Ln \xrightarrow{H_2} LnH_2$

$Ln \xrightarrow{O_2} Ln_2O_3$ (CeO_2 - exc.)

$Ln \xrightarrow{\text{acizi-}H^+} La^{3+} + H_2$

$Ln \xrightarrow{CO_2} Ln_2(CO_3)_3 + H_2$

$Ln \xrightarrow{H_2O} Ln(OH)_3 + H_2$

$Ln \xrightarrow{N_2} LnN$

$Ln \xrightarrow{S_2} Ln_2S_3$

La’s & Ac’s – thermodynamic properties

Symbol	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Z	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
6s	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
4f	0	1	3	4	5	6	7	7	9	10	11	12	13	14	14
5d	1	1	0	0	0	0	0	1	0	0	0	0	0	0	1
Radius CN=6 (pm)	103	101	99	98	97	96	95	94	92	91	90	89	88	87	86
Radius CN=8 (pm)	122	120	118	116	114	113	112	111	110	108	107	106	105	104	103
ΔH_{sub} (kJ/mol)	431	420	357	327	318	207	177	398	389	290	301	312	232	156	428
ΔG_{sub} (kJ/mol)	323	318	257	227	157	108	81	288	277	188	198	215	134	61	313
$M \rightarrow M^{3+}$ (kJ/mol)	3456	3530	3633	3701	3709	3871	4036	3749	3802	3899	3823	3934	4045	4194	3887
Symbol				U	Np	Pu	Am	Cm							
Z				92	93	94	95	96							
6s				2	2	2	2	2							
4f				3	4	6	7	7							
5d				1	1	0	0	1							
Radius CN=6 (pm)				103	101	100	98	96							
Radius CN=8 (pm)				116	114	112	111	109							
ΔH_{sub} (kJ/mol)				531	465	343	284	387							
ΔG_{sub} (kJ/mol)				425	358	237	178	281							
$M \rightarrow M^{3+}$ (kJ/mol)				3627	3702	3769	3847	3774							

Ln^{3+}	4f^{n}	ground level	**colour**	g [J(J+1)]$^{1/2}$	μ_{obs}
Ce	1	$^{2}F_{5/2}$	colourless	2.54	2.3-2.5
Pr	2	$^{3}H_{4}$	green	3.58	3.4-3.6
Nd	3	$^{4}I_{9/2}$	lilc	3.62	3.5-3.6
Pm	4	$^{5}I_{4}$	pink	2.68	-
Sm	5	$^{6}H_{5/2}$	yellow	0.85	1.4-1.7
Eu	6	$^{7}F_{0}$	pale pink	0	3.3-3.5
Gd	7	$^{8}S_{7/2}$	colourless	7.94	7.9-8.0
Tb	8	$^{7}F_{6}$	pale pink	9.72	9.5-9.8
Dy	9	$^{6}H_{15/2}$	yellow	10.65	10.4-10.6
Ho	10	$^{5}I_{8}$	yellow	10.6	10.4-10.7
Er	11	$^{4}I_{15/2}$	rose-pink	9.58	9.4-9.6
Tm	12	$^{3}H_{6}$	pale green	7.56	7.1-7.5
Yb	13	$^{2}F_{7/2}$	colourless	4.54	4.3-4.9
Lu	14	$^{1}S_{0}$	colourless	0	0

Lanthanides apps

- Superconductors: $LaO_{1-x}F_xFeAs$ become superconductor at T ranging from 26K to 43K(at 4GPa); $SmO_{1-x}F_xFeAs$ at 55K; most of the discovered superconductors are copper-based;
- Strong permanent magnets: $SmCo_5$, ~150 kJ/m^3 (maximum energy density); Sm_2Co_{17}, ~160 kJ/m^3; $Nd_2Fe_{14}B$, ~270 kJ/m^3; comparing: SrFe, ~35 kJ/m^3; AlNiCo – HDD (8–12% Al, 15–26% Ni, 5–24% Co, up to 6% Cu, up to 1% Ti, Fe is the rest) ~ 35 kJ/m^3;
- Optoelectronics: the incorporation of Eu^{3+} & Dy^{3+} ions to heavy metal glass materials increases red & yellow/blue luminescence;
- Tunable microwave resonators: $(x)A_{1/2}Ln_{1/2}TiO_3 \cdot (1-x)NaNbO_3$ (A = Na, Li; Ln = La, Nd, Sm) tunable as microwave resonators through changing the values of x;
- X-ray screens, neutron detectors, alpha particle scintillators; for X, n^0, & γ detectors: Gd_2O_2S:Ln, Ln = Tb - green (peak at 545 nm), Ln = Eu - red (627 nm), Ln = Pr - green (513 nm)

Rare-earth magnets

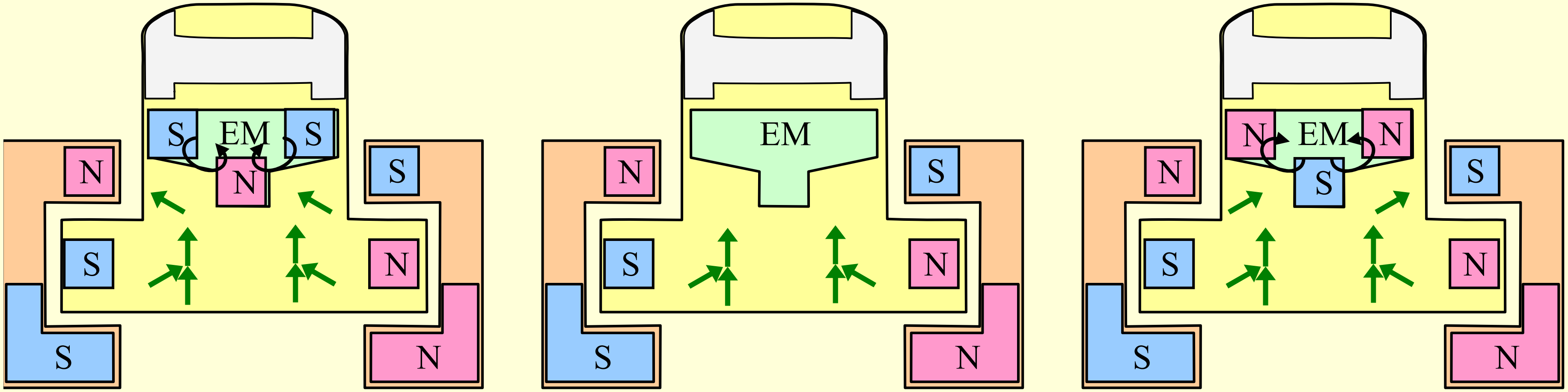
NdFeB strong permanent magnets

$Nd_2Fe_{14}B$	Remanence	Coercivity	Intrinsic H	B_H max	t max
(std)	(B_r, T)	H_{cB} (kA/m)	H_{cJ} (kA/m)	kJ/m^3	°C
N35	1.17-1.21	868	955	263-287	80
N38	1.21-1.25	899	955	287-310	80
N40	1.25-1.28	923	955	302-326	80
N42	1.28-1.32	923	955	318-342	80
N45	1.32-1.38	876	955	332-366	80
N48	1.38-1.42	835	876	366-396	80
N50	1.38-1.45	835	876	374-406	80
N52	1.44-1.48	836	876	390-422	80
N35M	1.17-1.21	868	1114	263-287	100
N38M	1.21-1.25	899	1114	287-310	100
N40M	1.25-1.28	923	1114	302-326	100
N42M	1.28-1.32	963	1114	318-342	100
N45M	1.32-1.38	995	1114	332-366	100
N48M	1.37-1.42	1018	1114	358-390	100
N50M	1.40-1.45	1042	1114	374-406	100
N28AH	1.04-1.10	772	2786	207-231	220
N30AH	1.08-1.17	812	2786	223-255	220
N33AH	1.14-1.22	851	2786	247-279	220
N35AH	1.17-1.25	876	2786	263-295	220

Comparison

Magnet	kA/m	T
$BaFe_{12}O_{19}$	360	0.4
$Co_{10}Fe_7Ni_4Ti_2CuAl$	50-150	0.6
$Fe_{50}Ni_{10}Al_2Nb$	50	1.2
MnBi	370	0.5
$Ce(CuCo)_5$	450	0.7
$SmCo_5$	1000	0.8
Sm_2Co_{17}	600	1.1
$Nd_2Fe_{14}B$	1100	1.2

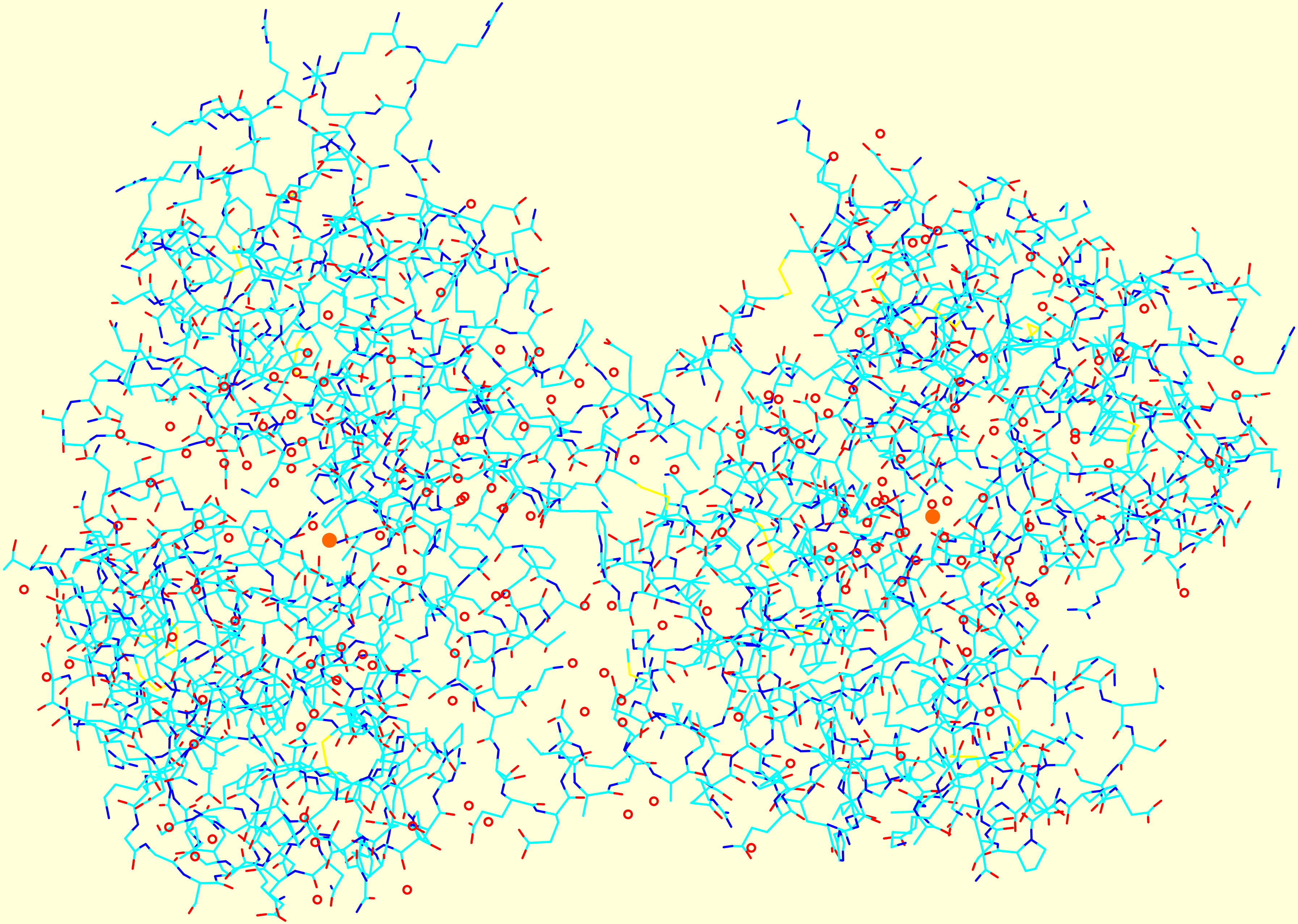
Magnetic levitation apps



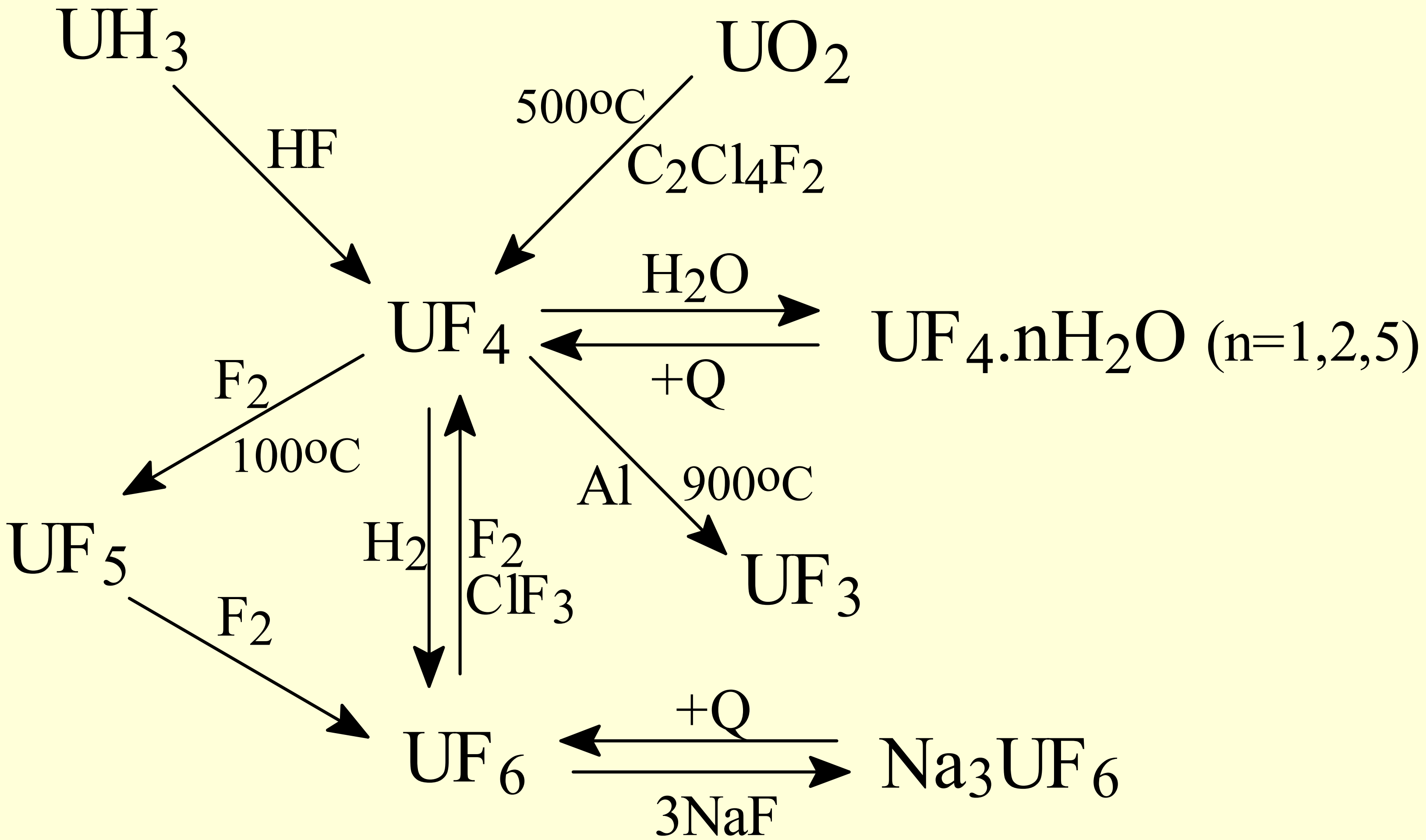
Car	Max. Speed	Weight	Load	Magnets	Power supply
"MagneMotion"	160 km/h	5000 kg	2000 kg (40%)	PM & EM	480V AC
"MagLev GA"	160 km/h	11350 kg	5250 kg (46%)	PM	600V DC
"CDOT 200"	160 km/h	25370 kg	12172 kg (48%)	EM	3000V DC

http://www.fta.dot.gov/documents/FTA_LowSpeedMaglev_LessonsLearned.pdf

Diceric human lactoferrin



UF_4 – separating of ^{235}U and ^{238}U isotopes



UH_3

UO_2

HF

500°C

$C_2Cl_4F_2$

UF_4

H_2O

$UF_4.nH_2O$ (n=1,2,5)

+Q

F_2

100°C

Al

900°C

UF_5

H_2

F_2

ClF_3

UF_3

F_2

+Q

UF_6

Na_3UF_6

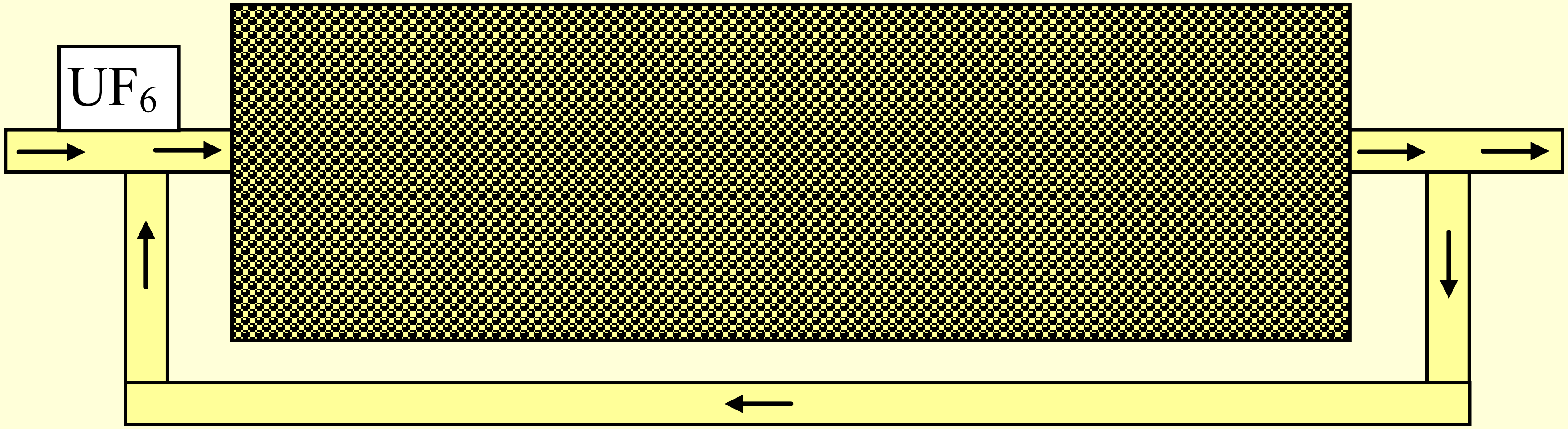
3NaF

U extraction

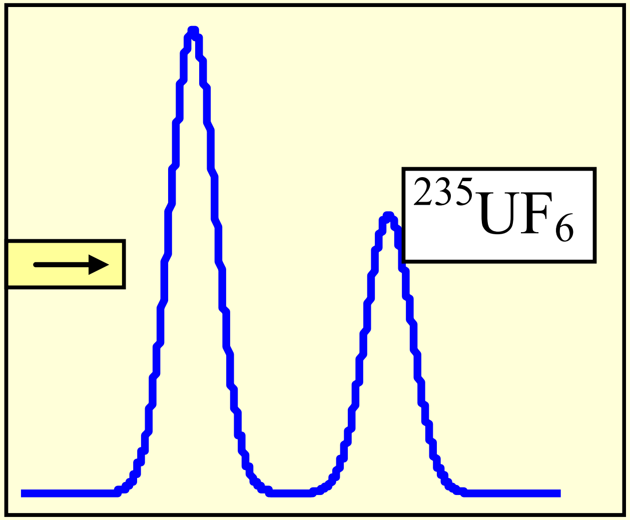
- In the dry process, uranium oxide concentrates are first calcined (heated strongly) to drive off some impurities, then agglomerated and crushed. For the wet process, the concentrate is dissolved in HNO_3. The resulting solution of $UO_2(NO_3)_2{\cdot}6H_2O$ is fed into a countercurrent solvent extraction process, using tributyl phosphate dissolved in kerosene or dodecane. The uranium is collected by the organic extractant, from which it can be washed out by diluted HNO_3 and then concentrated by evaporation. The solution is then calcined in a fluidised bed reactor to produce UO_3.
- Purified U_3O_8 from the dry process and UO_3 from the wet process are then reduced in a kiln by hydrogen to UO_2:

  $U_3O_8 + 2H_2 \rightarrow 3UO_2 + 2H_2O$ & $UO_3 + H_2 \rightarrow UO_2 + H_2O$
- This reduced oxide is then reacted in another kiln with HF to UF_4: $UO_2 + 4HF \rightarrow UF_4 + 2H_2O$
- The UF_4 is then fed into a fluidised bed reactor or flame tower with $F_{2(g)}$ to produce UF_6: $UF_4 + F_2 \rightarrow UF_6$

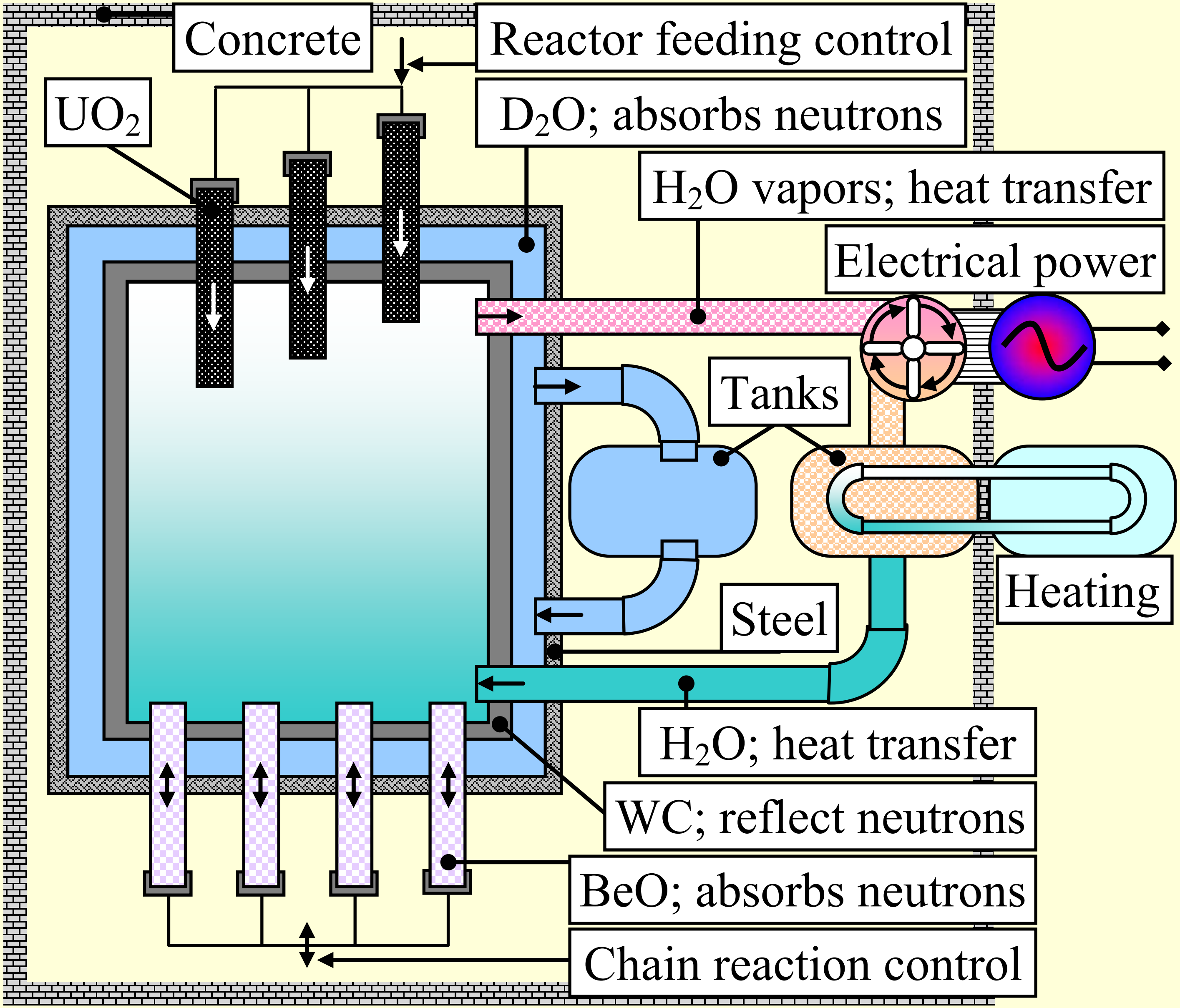
^{235}U enrichment



UF_6 is passed through a porous barrier material; the lighter molecules containing ^{235}U penetrate the barrier slightly more rapidly, and with enough stages significant separation can be accomplished



Actinides apps: nuclear power



Concrete

Reactor feeding control

UO_2

D_2O; absorbs neutrons

H_2O vapors; heat transfer

Electrical power

Tanks

Heating

Steel

H_2O; heat transfer

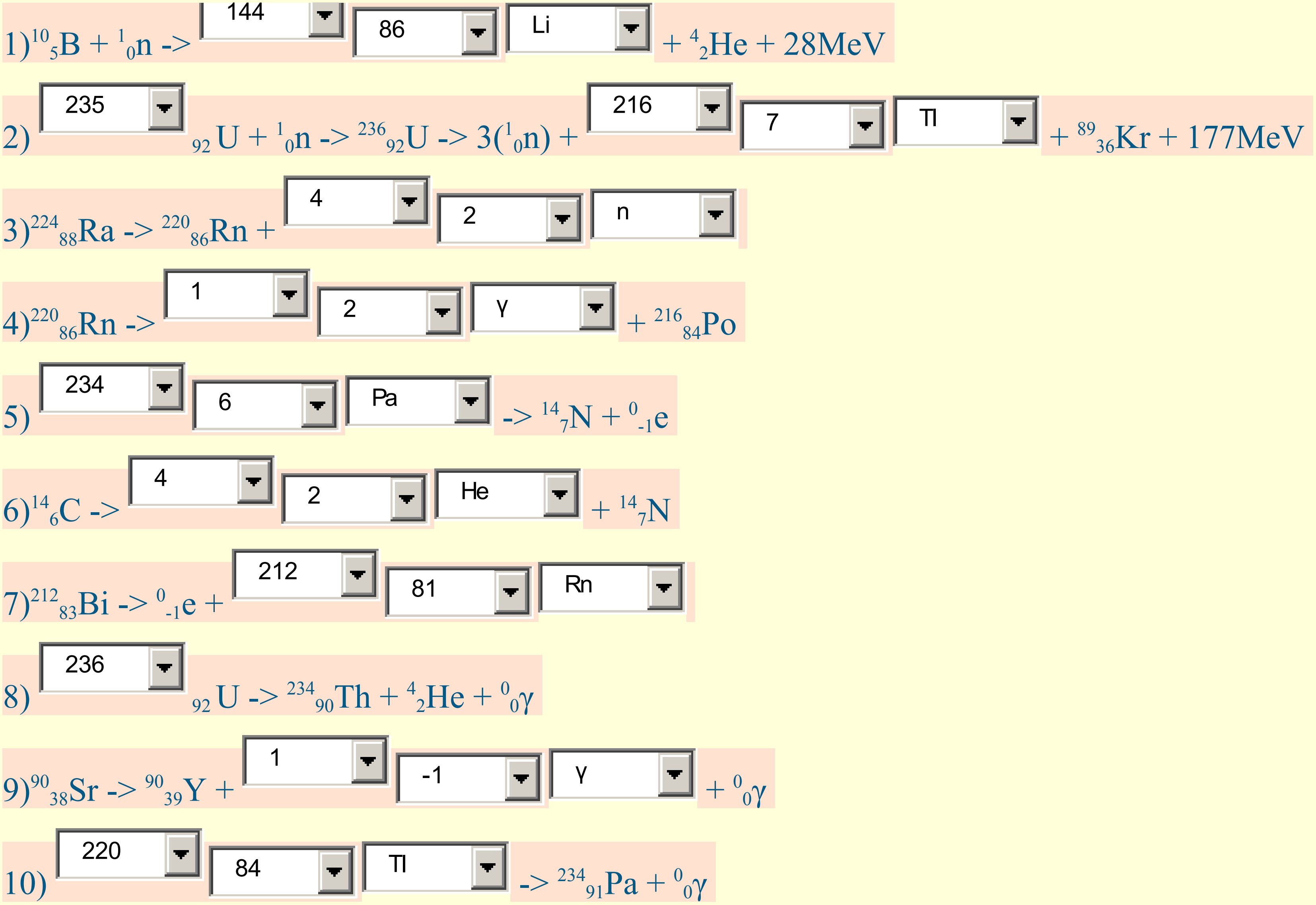
WC; reflect neutrons

BeO; absorbs neutrons

Chain reaction control

Radiochemistry

http://l.academicdirect.org/Education/Training/Geiger/test2/



1) $^{10}_{5}$B + $^{1}_{0}$n -> 144 86 Li + $^{4}_{2}$He + 28MeV

2) 235 $_{92}$U + $^{1}_{0}$n -> $^{236}_{92}$U -> 3($^{1}_{0}$n) + 216 7 Tl + $^{89}_{36}$Kr + 177MeV

3) $^{224}_{88}$Ra -> $^{220}_{86}$Rn + 4 2 n

4) $^{220}_{86}$Rn -> 1 2 γ + $^{216}_{84}$Po

5) 234 6 Pa -> $^{14}_{7}$N + $^{0}_{-1}$e

6) $^{14}_{6}$C -> 4 2 He + $^{14}_{7}$N

7) $^{212}_{83}$Bi -> $^{0}_{-1}$e + 212 81 Rn

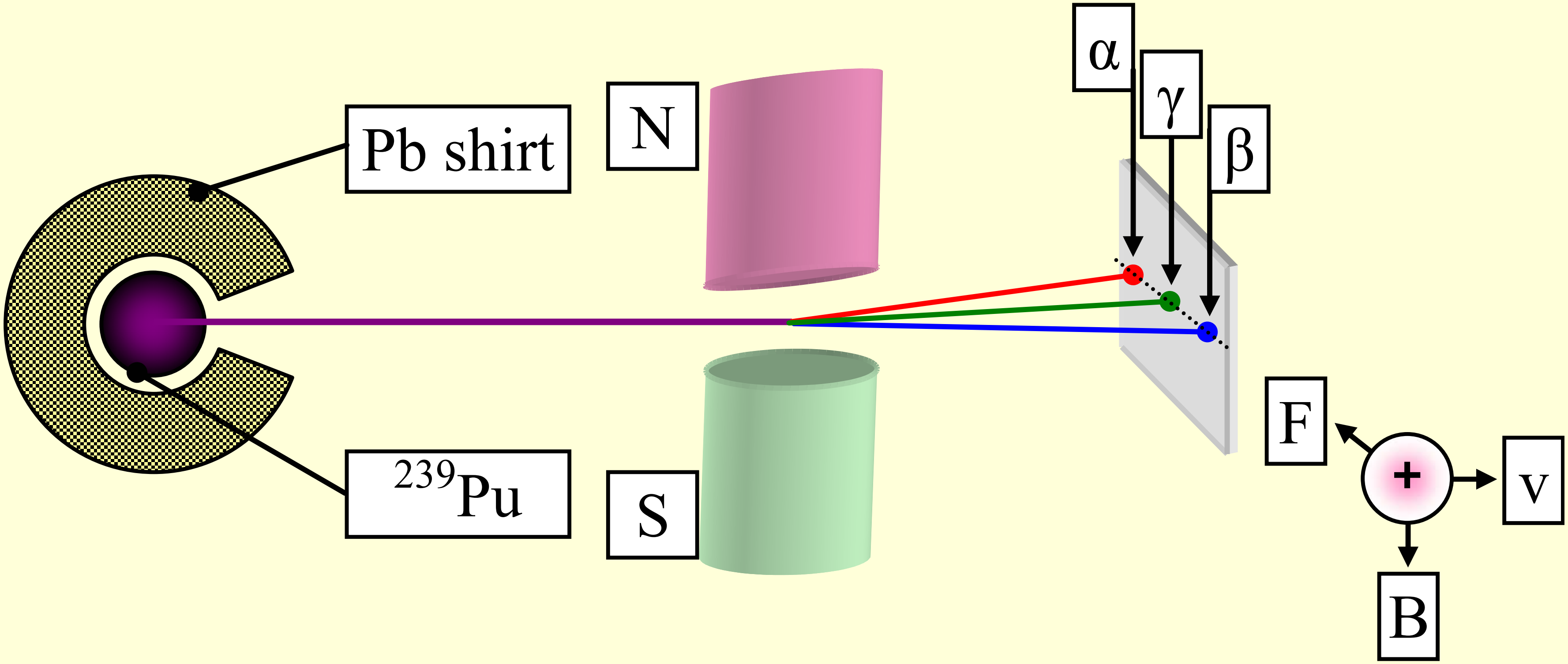
8) 236 $_{92}$U -> $^{234}_{90}$Th + $^{4}_{2}$He + $^{0}_{0}\gamma$

9) $^{90}_{38}$Sr -> $^{90}_{39}$Y + 1 -1 γ + $^{0}_{0}\gamma$

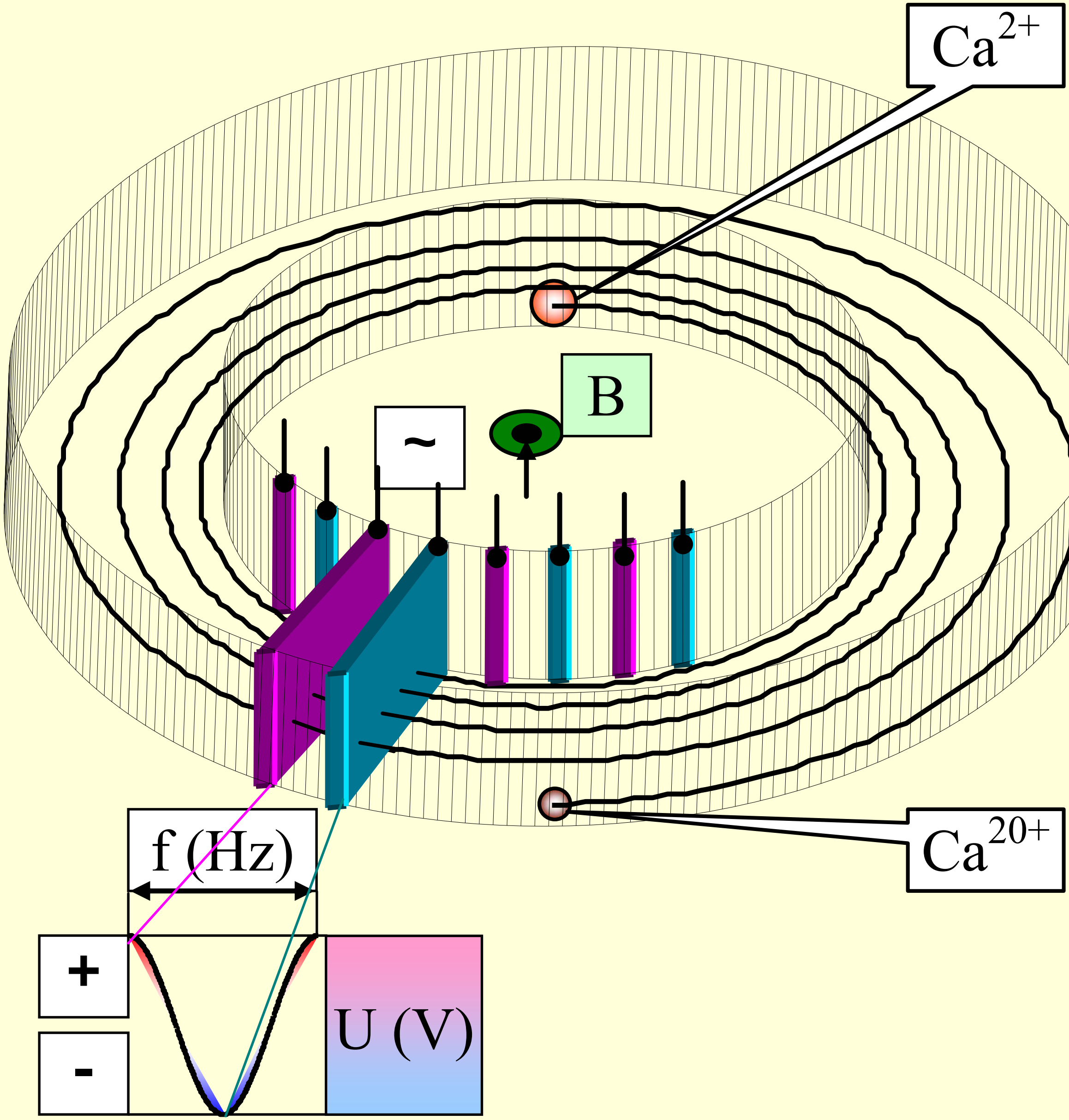
10) 220 84 Tl -> $^{234}_{91}$Pa + $^{0}_{0}\gamma$

Radiations

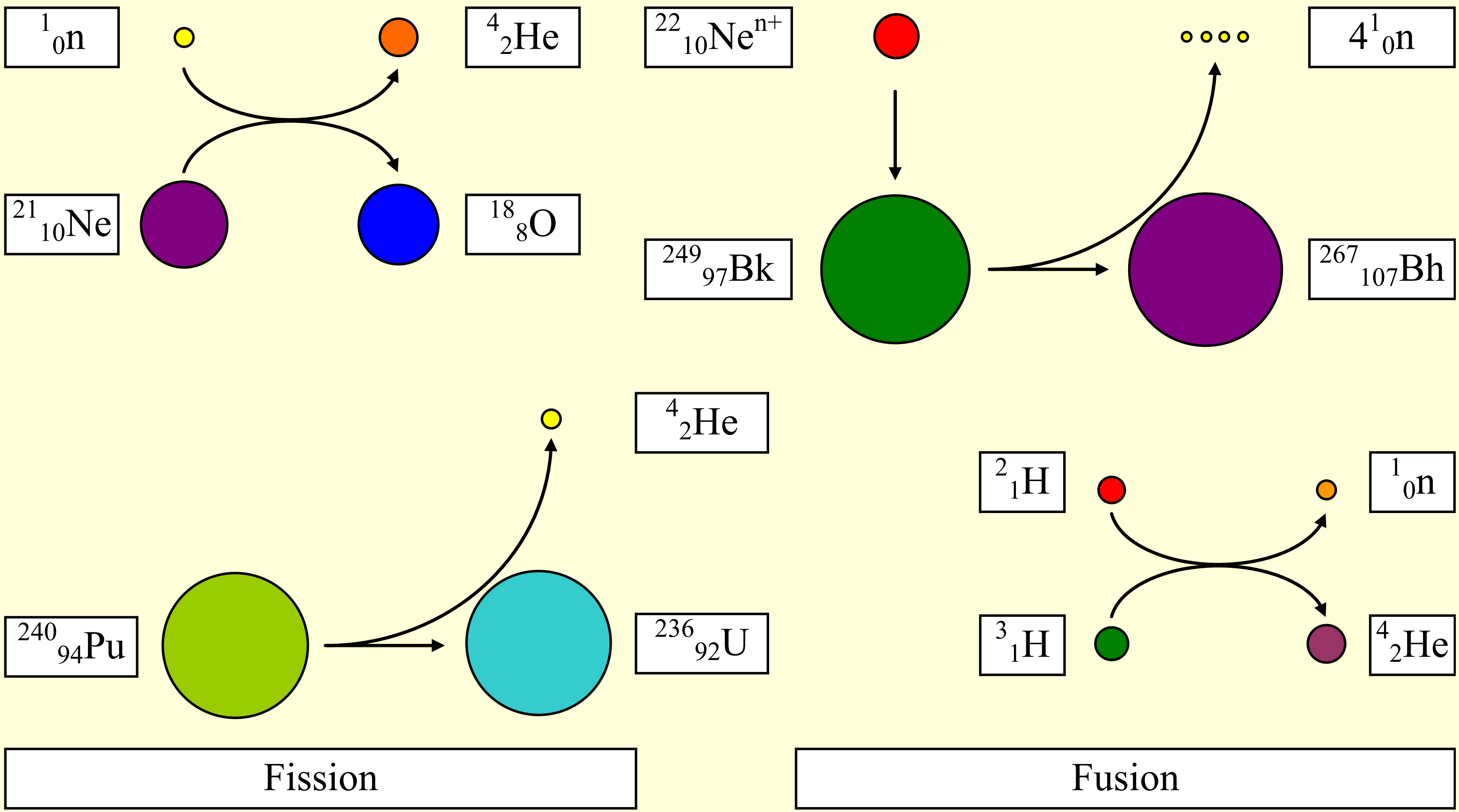
- *α radiations* –He^{2+};
- *β* radiations – e^- (β^-; positrons, β^+);
- *γ* radiations – electromagnetic (such is the light), with λ much smaller than X rays;



Cyclotron



Fission & fusion



$^{1}_{0}n$

$^{4}_{2}He$

$^{21}_{10}Ne$

$^{18}_{8}O$

$^{22}_{10}Ne^{n+}$

$4\,^{1}_{0}n$

$^{249}_{97}Bk$

$^{267}_{107}Bh$

$^{4}_{2}He$

$^{240}_{94}Pu$

$^{236}_{92}U$

$^{2}_{1}H$

$^{1}_{0}n$

$^{3}_{1}H$

$^{4}_{2}He$

Fission

Fusion

Q
&
R

In connection with lanthanides and actinides:	
0	In nuclear reactions mass is converted into energy ($\Delta E=c^2\cdot\Delta m$)
1	Mass is conserved in nuclear reactions ($\Delta m = 0$)
0	The isotope of U with Z = 92 and A = 135 has applications in energy production
1	The isotope of U with Z = 92 and A = 235 has applications in energy production
0	Examples of combinations of uranium are UH_6, UO_4, UF_7, UF_8
1	Examples of combinations of uranium are UH_3, UO_2, UF_5, UF_6
0	Lanthanides have applications in metallurgy, cosmetics and medical recovery
1	Lanthanides have applications in supraconductibility, magnetics and optoelectronics
0	Lanthanides (Ln) forms in reaction with oxygen compounds in LnO_2 form excepting Cerium (Ce_2O_3)
1	Lanthanides (Ln) forms in reaction with oxygen compounds in $Ln2O_3$ form, excepting Cerium (CeO_2)
1	Are difficult to separate lanthanides
0	Are easy to separate lanthanides
0	Lanthanides have very different chemical and electrochemical properties
1	Lanthanides have very similar chemical and electrochemical properties
0	Lanthanides tend to form 1+ ions
0	Lanthanides tend to form 2+ ions
1	Lanthanides tend to form 3+ ions

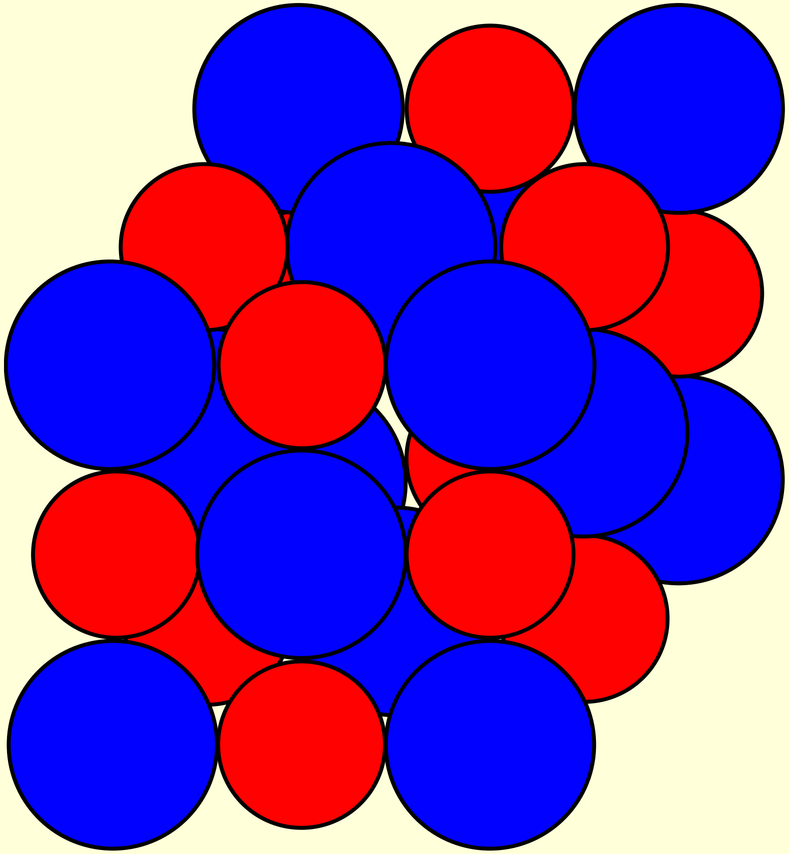
Crystallography

- In the growth of a crystal particles are arranged in rows and orderly and symmetrical networks. The shortest distance between corresponding points of an infinite sequence is called shifting the shortest or fundamental translation. In the crystal structure, it is the distance between atoms.
- Strings, flat networks and three-dimensional networks are considered infinite. In most crystals, the distance between atoms is 3-5Å and in only 1 mm^3 volume is then about 10^{21} particles, which provides practical infinity assumption. Considering a linear displacement of a point (source) until observable and measurable properties of that point are again the same (destination) get a basic translation. One of the features of a basic shift is that it is the lowest point translation that makes repeating properties. Constant movement is usually marked with a.

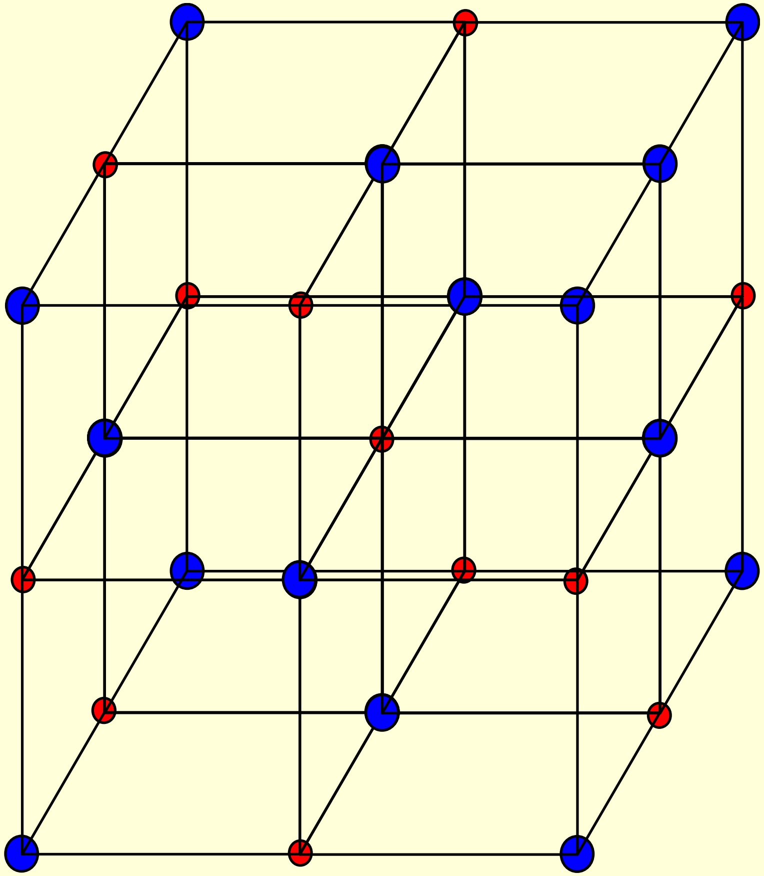
Crystalline nets

Structure of halite (NaCl)

model

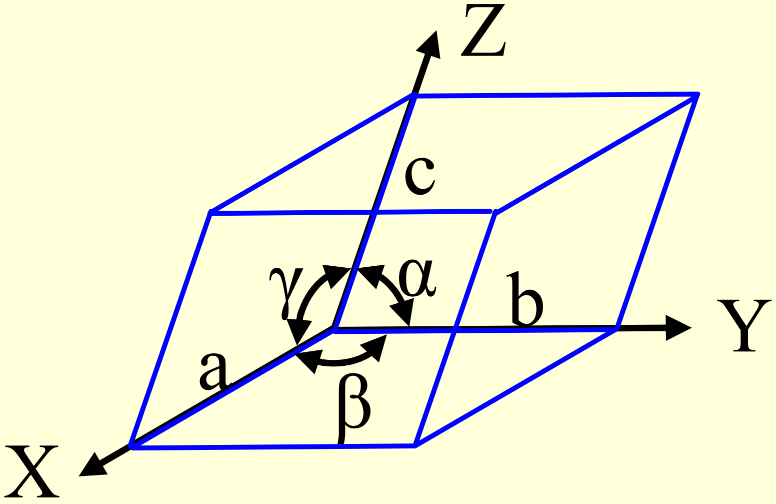


scheme

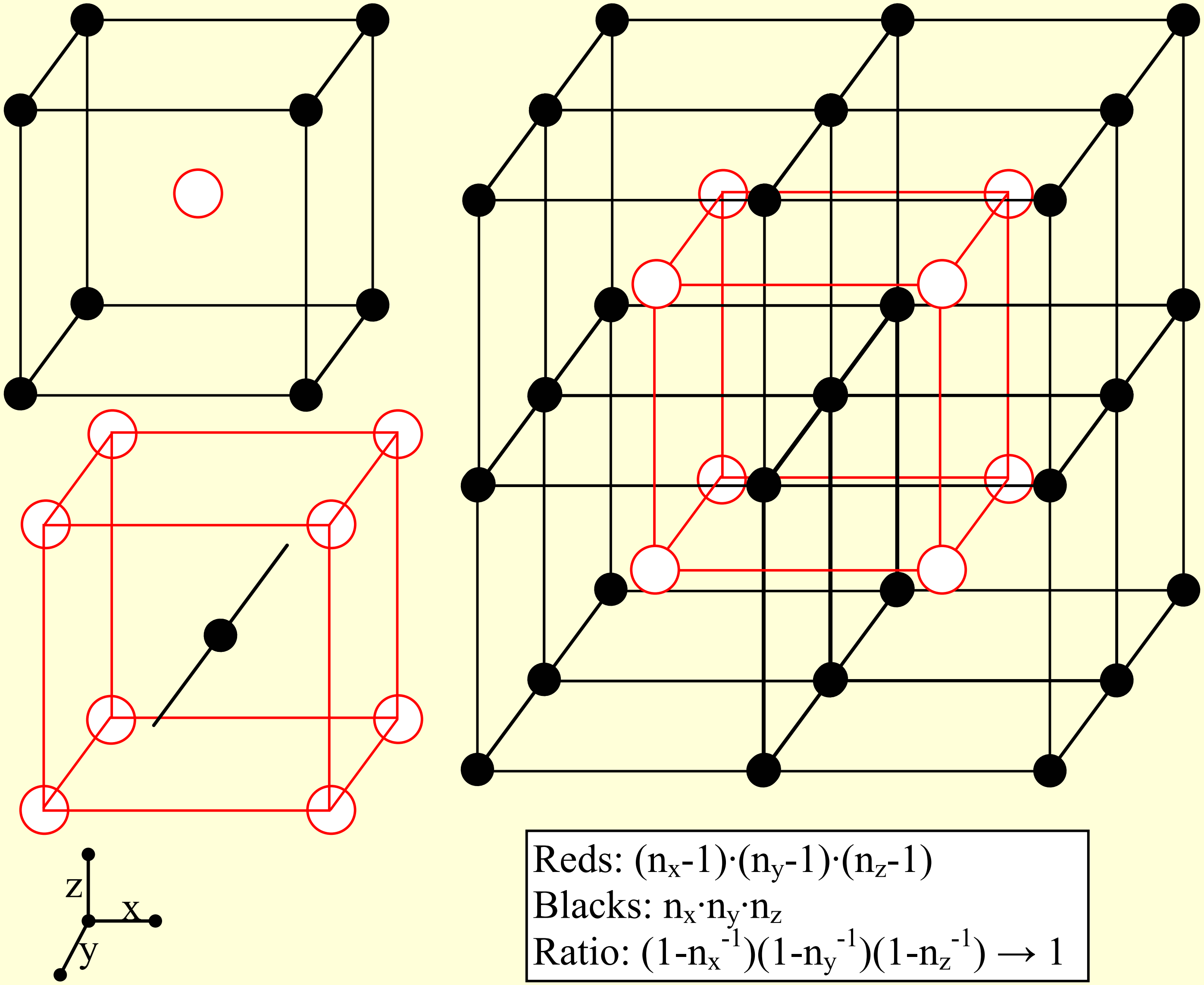


Elementary cells

- A pair of elementary translations nonparallel iteration scheme defines homologous points in a plane. A 3-necoplanară basic translation of the first 2 generates a three-dimensional network of homologous points. Constants of the 3 basic movements usually is denoted a_1, a_2 and a_3. Parallelepiped of elementary translations (a_1, a_2, a_3) form the basic cell, $(a_1, a_2, a_3) = (a, b, c)$.



Chemical formula vs. crystal structure



Reds: $(n_x\text{-}1)\cdot(n_y\text{-}1)\cdot(n_z\text{-}1)$
Blacks: $n_x\cdot n_y\cdot n_z$
Ratio: $(1\text{-}n_x^{-1})(1\text{-}n_y^{-1})(1\text{-}n_z^{-1}) \rightarrow 1$

Polyhedra

Polyhedra count for given number of vertices (or faces)

4	1	9	2606	14	1496225352
5	2	10	32300	15	23833988129
6	7	11	440564	16	387591510244
7	34	12	6384634	17	6415851530241
8	257	13	96262938	18	107854282197058

Polyhedra count for given number of edges

6	1	12	12	18	4199	24	5623571	30	10204782956
7	0	13	22	19	13384	25	19358410	31	36249143676
8	1	14	58	20	43708	26	67078828	32	129267865144
9	2	15	158	21	144810	27	233800162	33	462669746182
10	2	16	448	22	485704	28	819267086	34	1661652306539
11	4	17	1342	23	1645576	29	2884908430	35	5986979643542

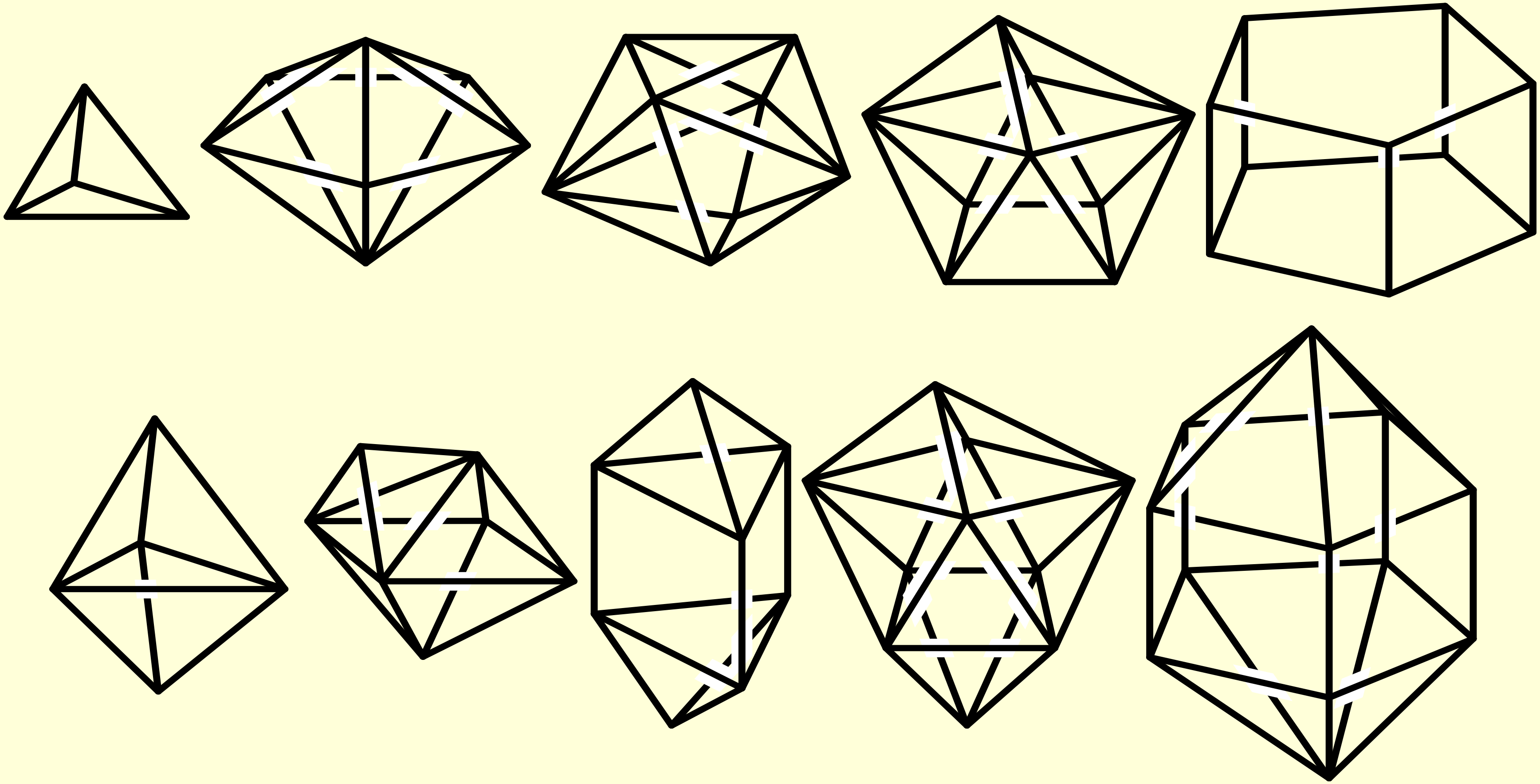
“Counting Polyhedra”, Gérard P. Michon & Stuart E. Anderson, © 2000-2001, upd. 2002 http://home.att.net/~numericana/data/polycount.htm

Polyhedra count depending on vertices and faces number

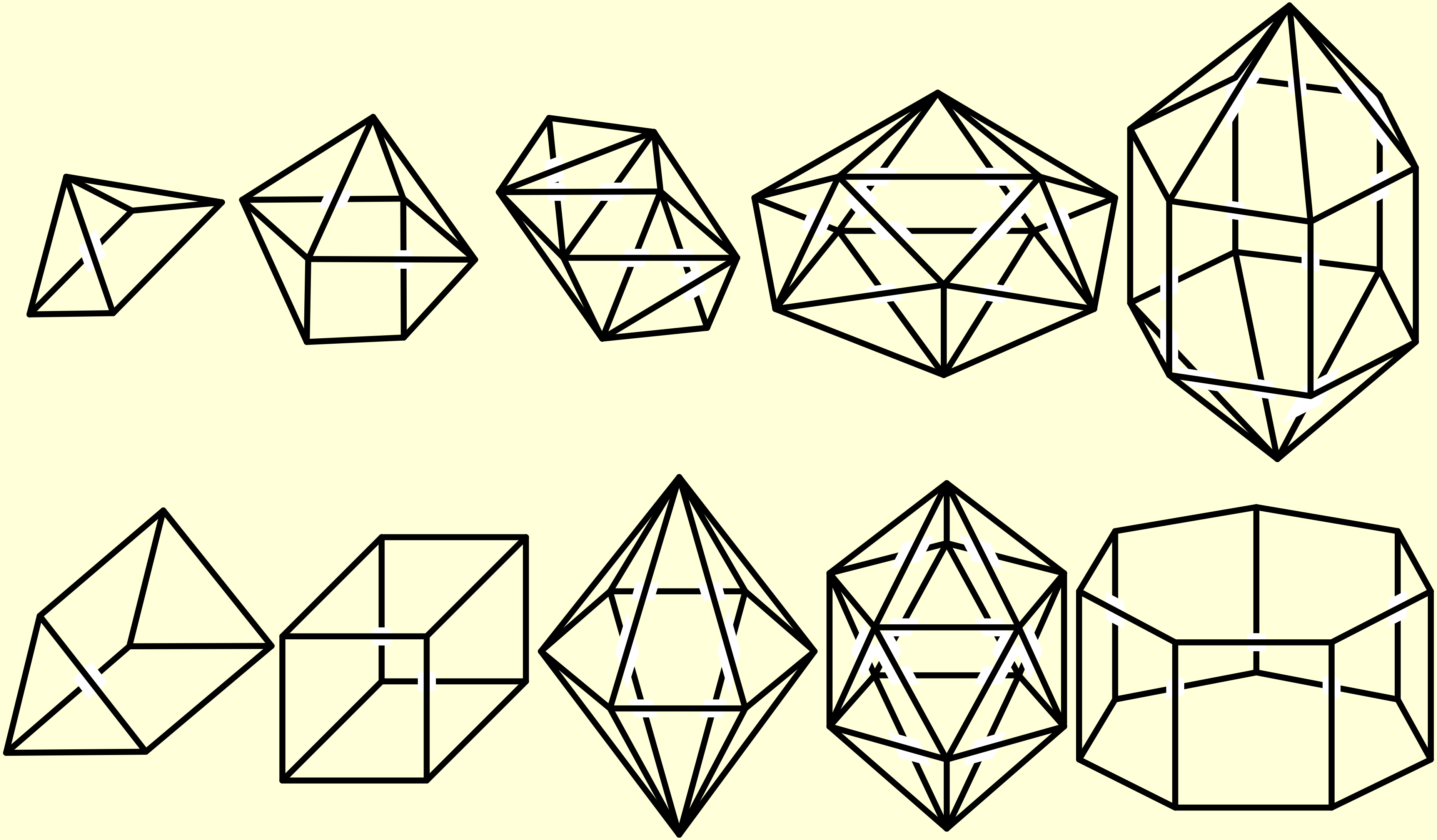
edges =
vertices +
faces - 2

	4	5	6	7	8	9	10	11
4	1							
5		1	1					
6		1	2	2	2			
7			2	8	11	8	5	
8			2	11	42	74	76	38
9				8	74	296	633	768
10				5	76	633	2635	6134
11					38	768	6134	25626

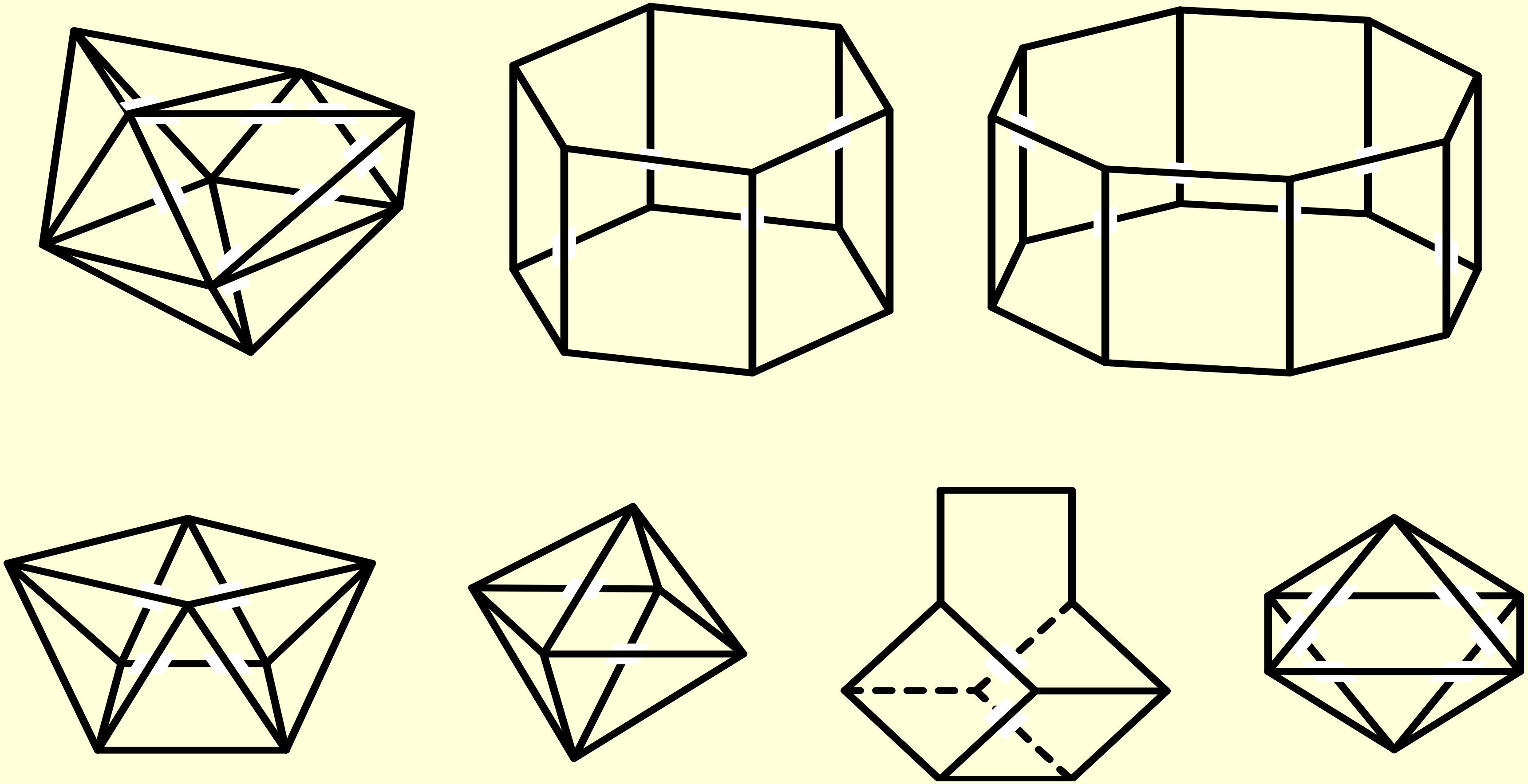
Polihedra (1)



Polihedra (2)



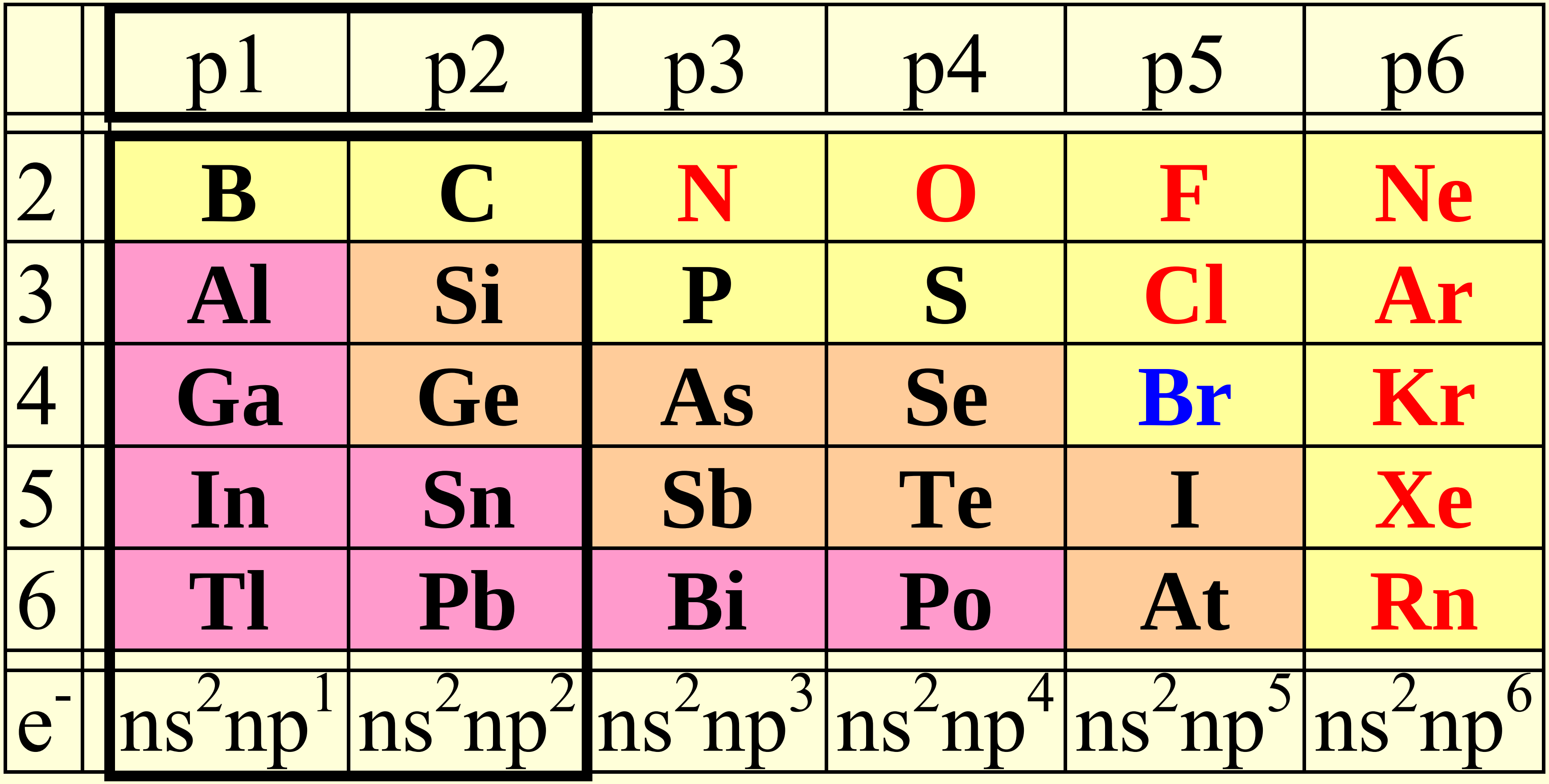
Polihedra (3)



Course 10

Boron group
Carbon group

“p” block



	p1	p2	p3	p4	p5	p6
2	**B**	**C**	**N**	**O**	**F**	**Ne**
3	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
4	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
5	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
6	**Tl**	**Pb**	**Bi**	**Po**	**At**	**Rn**
e^-	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6

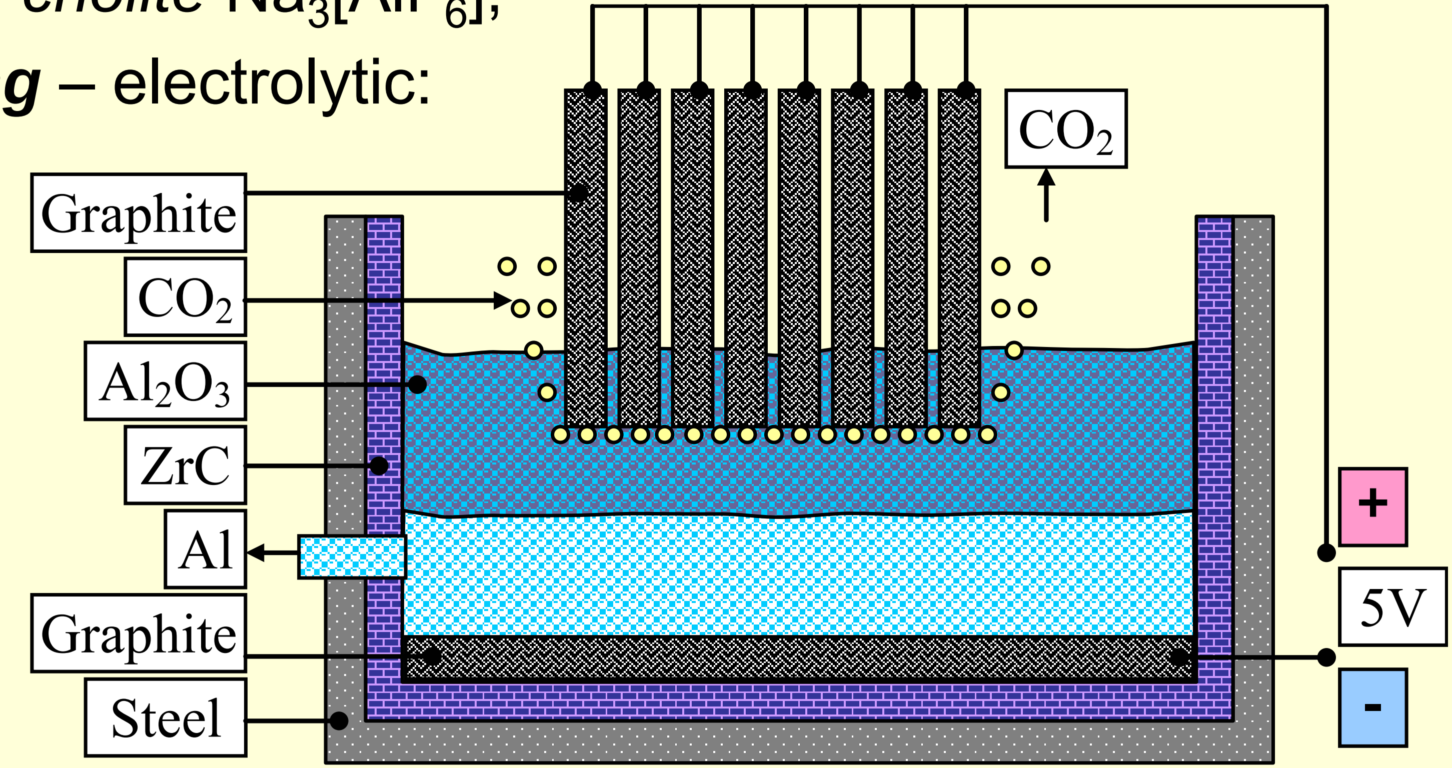
Boron

- ***Crystalline structure***: a structure repeating a *icosahedra* (12 vertices and 20 faces); 7 allotropic forms, binding different the icosahedra;
- ***Natural state***: Clark: $5 \cdot 10^{-3}\%$. It's presence is essential to plant growing; minerals: *borax* $Na_2B_4O_7 \cdot 10H_2O$, *kernite* $Na_2B_4O_7 \cdot 4H_2O$, *borocalcite* $CaB_4O_7 \cdot 4H_2O$ and *colemanite* $Ca_2B_6O_{11} \cdot 5H_2O$
- **Obtaining**: $Na_2B_4O_7 \ {}_{HCl}{\rightarrow}_{NaCl} \ H_3BO_3 \ {}_{Q}{\rightarrow}_{H2O} \ B_2O_3 \ {}_{Mg}{\rightarrow}_{MgO} \ B$ - a brown amorphous solid solution of boron and boron oxide are obtained. High purity boron are obtained from electrolysis of kalium tetrafluoroborate KBF_4 or thermal decomposition of diborane: $B_2H_6 \ {}_{Q}{\rightarrow} \ 2B + 3H_2$
- **Purification**: procedure "Van Arkel" – "de Boer":

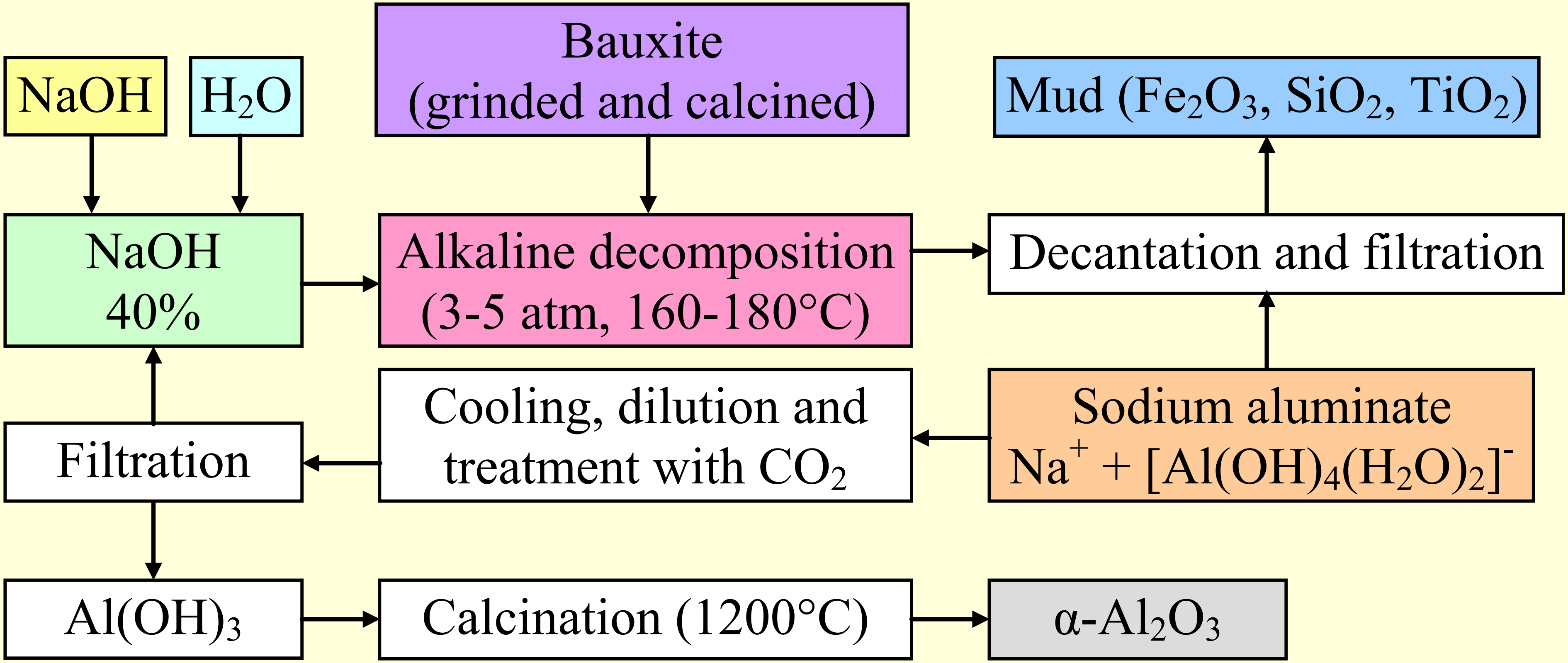
$$B + I_2 \ {}_{Q}{\rightarrow} \ BI_3\uparrow \ {}_{Q}{\rightarrow} \ B + I_2$$

Aluminum

- ***Crystalline structure***: metal, hexagonal-compact;
- ***Natural state***: Clark: 7.45%; many minerals; *bauxite*, AlO(OH) – industrial way to obtain aluminum; *corindon*, Al_2O_3 and its colored varieties (due to ions impurities): *rubine* (Cr), *saphire* (Ti), *topaz* (Ni); *hydrargilite* $Al(OH)_3$; *spinel* $MgAl_2O_4$; *criolite* $Na_3[AlF_6]$;
- ***Obtaining*** – electrolytic:



Obtaining of alumina (Al_2O_3)



$NaOH$

H_2O

Bauxite (grinded and calcined)

Mud (Fe_2O_3, SiO_2, TiO_2)

$NaOH$ 40%

Alkaline decomposition (3-5 atm, 160-180°C)

Decantation and filtration

Filtration

Cooling, dilution and treatment with CO_2

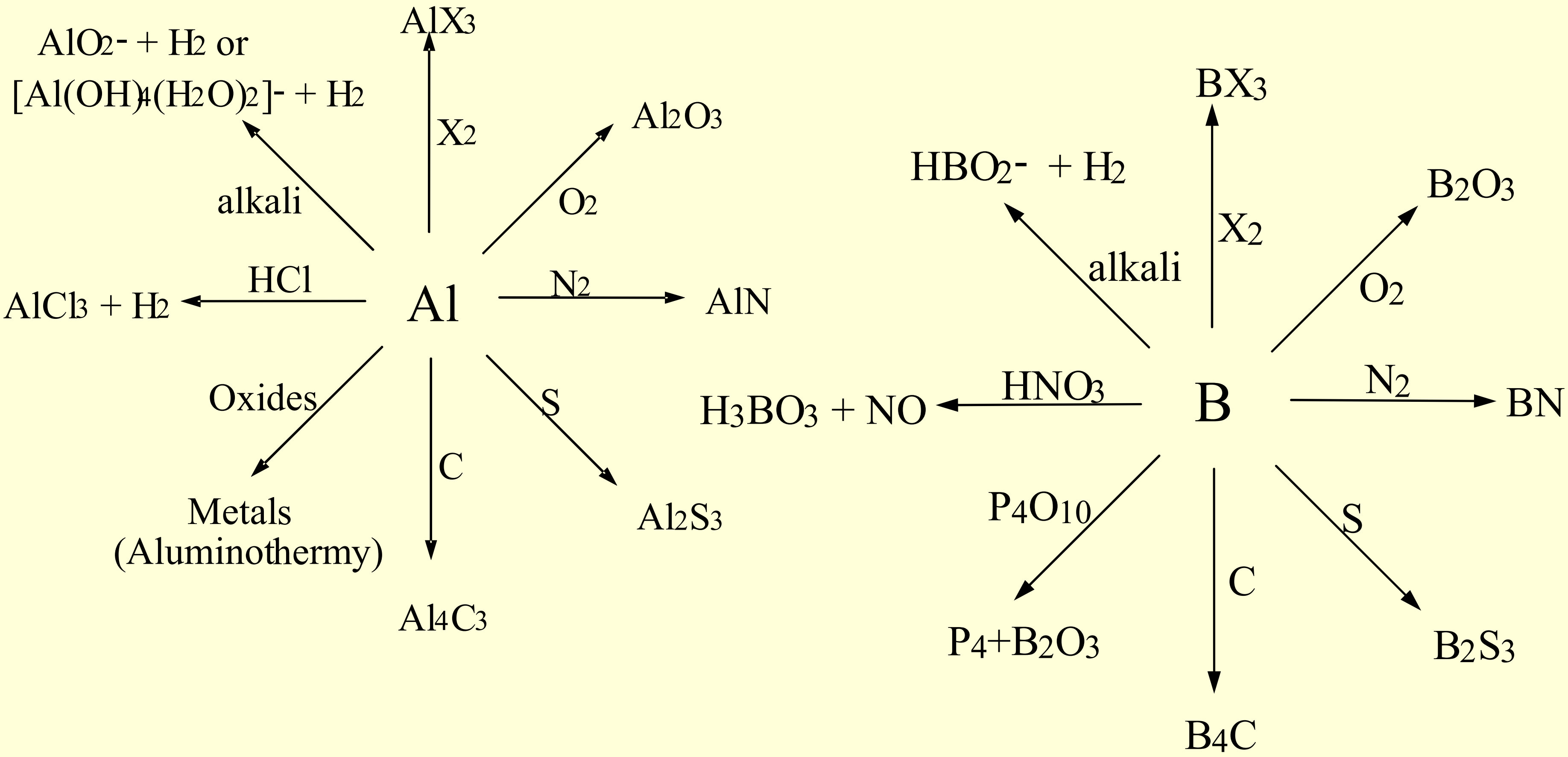
Sodium aluminate $Na^+ + [Al(OH)_4(H_2O)_2]^-$

$Al(OH)_3$

Calcination (1200°C)

α-Al_2O_3

Boron and aluminum – chemical properties



$Al \xrightarrow{alkali} AlO_2^- + H_2$ or $[Al(OH)_4(H_2O)_2]^- + H_2$

$Al \xrightarrow{X_2} AlX_3$

$Al \xrightarrow{O_2} Al_2O_3$

$Al \xrightarrow{HCl} AlCl_3 + H_2$

$Al \xrightarrow{N_2} AlN$

$Al \xrightarrow{Oxides}$ Metals (Aluminothermy)

$Al \xrightarrow{C} Al_4C_3$

$Al \xrightarrow{S} Al_2S_3$

$B \xrightarrow{alkali} HBO_2^- + H_2$

$B \xrightarrow{X_2} BX_3$

$B \xrightarrow{O_2} B_2O_3$

$B \xrightarrow{HNO_3} H_3BO_3 + NO$

$B \xrightarrow{N_2} BN$

$B \xrightarrow{P_4O_{10}} P_4 + B_2O_3$

$B \xrightarrow{C} B_4C$

$B \xrightarrow{S} B_2S_3$

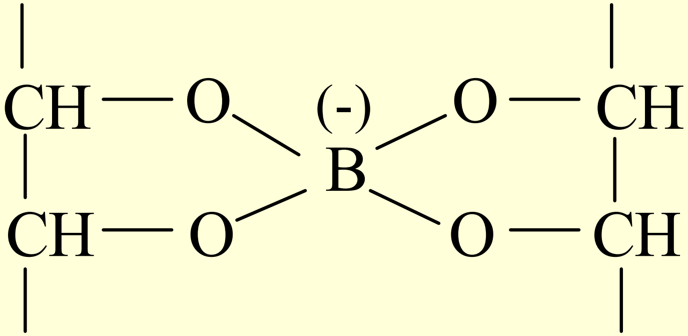
Boron and aluminum – physical properties

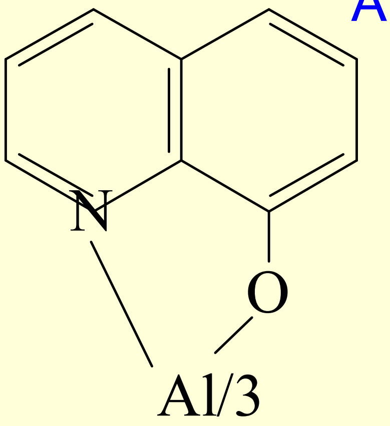
Property	B	Al
I.P.(1), eV	8.30	5.95
I.P.(2), eV	25.15	18.82
I.P.(3), eV	37.92	28.44
$\varepsilon^0 M^{3+}/M$ (V)	-0.73	-1.67
ρ (g/cm^3)	2.4	2.7
M.p. (°C)	2300	660
B.p. (°C)	2550	2500
Atomic radius (pm)	90	143
Covalent radius (pm)	84±3	121±4
Van der Waals radius (pm)	192	184

Boron and aluminum - uses

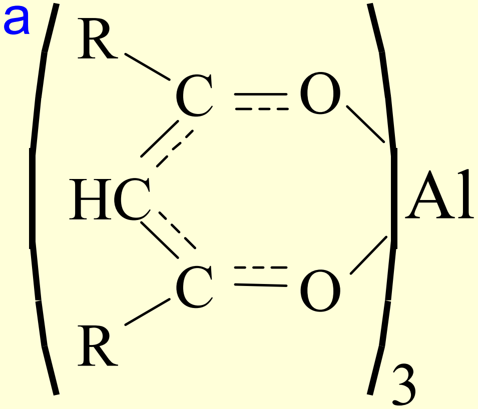
- **Boron**: uses as alloying element in steels (giving a increasing of impact resistance); in alloys provide hardness and corrosion resistance; metal borides have good mechanical and chemical properties; in nuclear plants is used to control fission neutrons energy;
- **Aluminum**: after iron most used element; cheep, light, corrosion resistant, keeps in time its properties, may be can be drawn into sheets and wires, good thermal conductivity; at relative to the density is the best electrical conductor;
- From aluminum light and mechanical resistant alloys are designed and used in constructions and vehicles. Have good alloying properties with iron, silicium, magnesium, copper and zinc.

Boron and aluminum – complex combinations





Al ↔ Ga

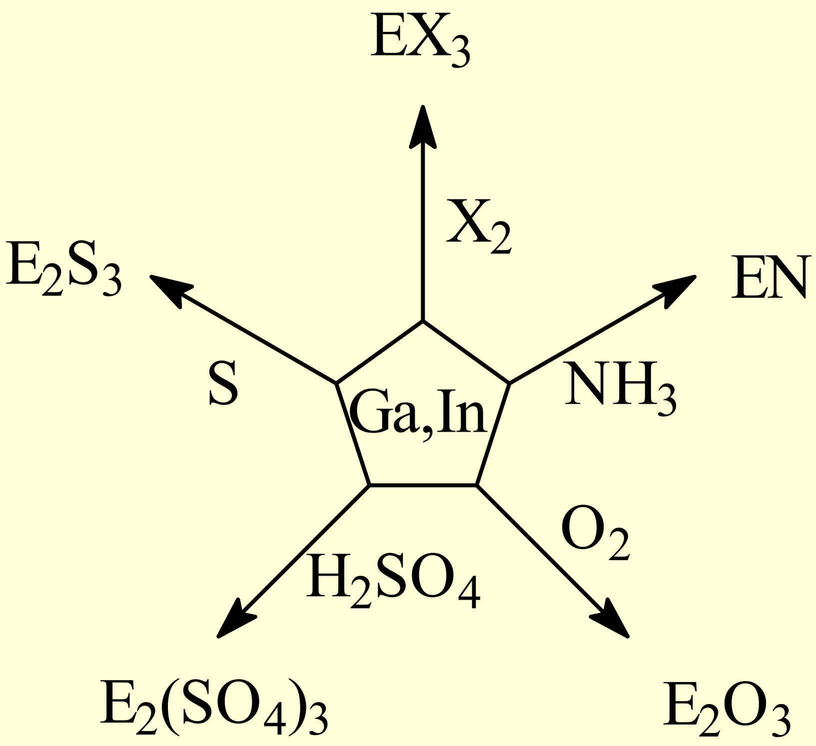


- ***Boron*** likely provide tetra-covalent combinations; have a series of di-hydroxyl and poly-hydroxyl combinations such as glycerol or mannitol (6 -OH); ***Aluminum*** provides complexes with β-di-ketones;
- ***Borazole*** $B_3N_3H_6$ – named inorganic *benzene:*

$$3LiBH_4 + 3NH_4Cl \rightarrow B_3N_3H_6 + 3LiCl + 12H_2$$

- ***Boron nitride*** BN – some of its allotropes possess properties diamond-like;

Ga, In, Tl – chemical properties



EX_3

X_2

E_2S_3

EN

S

Ga,In

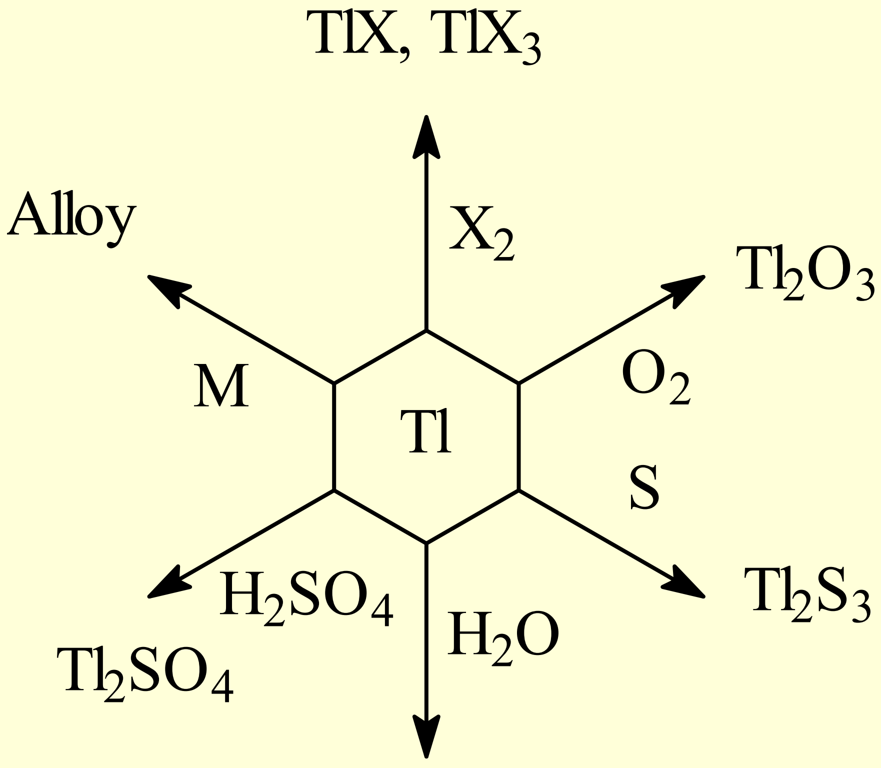
NH_3

O_2

H_2SO_4

$E_2(SO_4)_3$

E_2O_3



TlX, TlX_3

Alloy

X_2

Tl_2O_3

M

Tl

O_2

S

H_2SO_4

H_2O

Tl_2S_3

Tl_2SO_4

Ga, In, Tl – physical properties

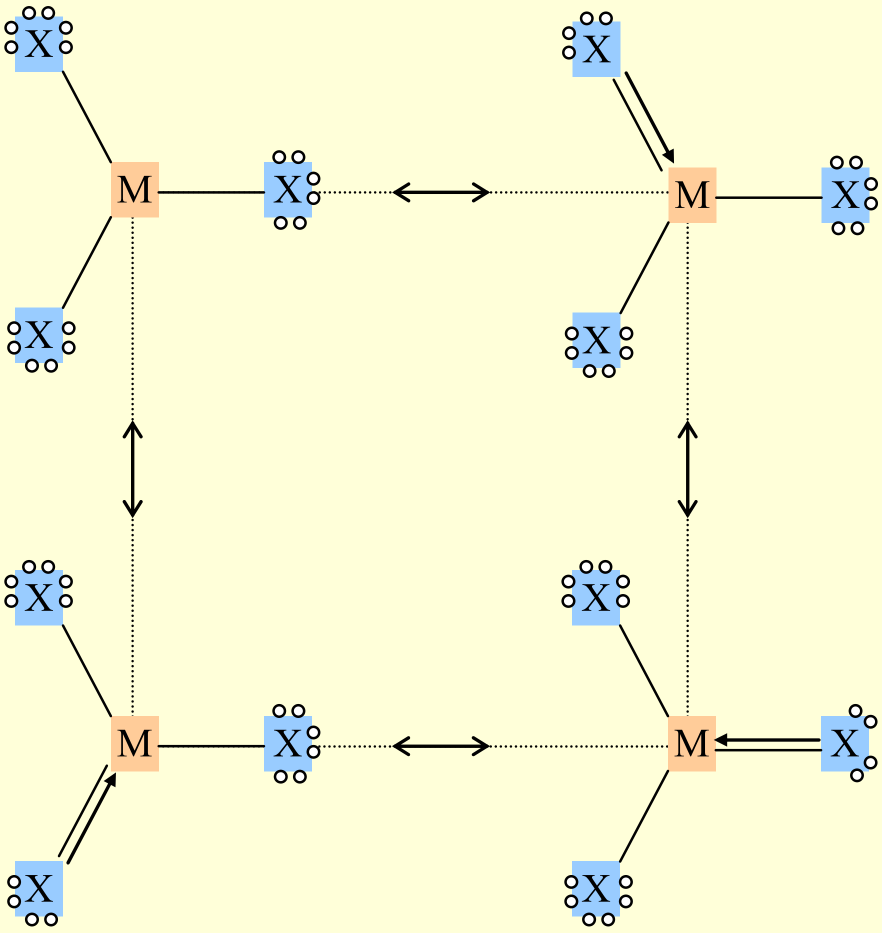
Property	Ga	In	Tl
I.P.(1), eV	6.0	5.8	6.1
I.P.(2), eV	20.4	18.8	20.3
I.P.(3), eV	30.6	27.9	29.7
$\varepsilon^0 M^{3+}/M$ (V)	-0.52	-0.34	0.72
$\varepsilon^0 M^{+}/M$ (V)	-	-0.25	-0.34
ρ (g/cm^3)	5.93	7.29	11.85
M.p. (°C)	29.8	156	449
B.p. (°C)	2070	2100	1390
Atomic radius (pm)	135	167	170
Covalent radius (pm)	122±3	142±5	145±7
Van der Waals radius (pm)	187	193	196

Ga, In, Tl - uses

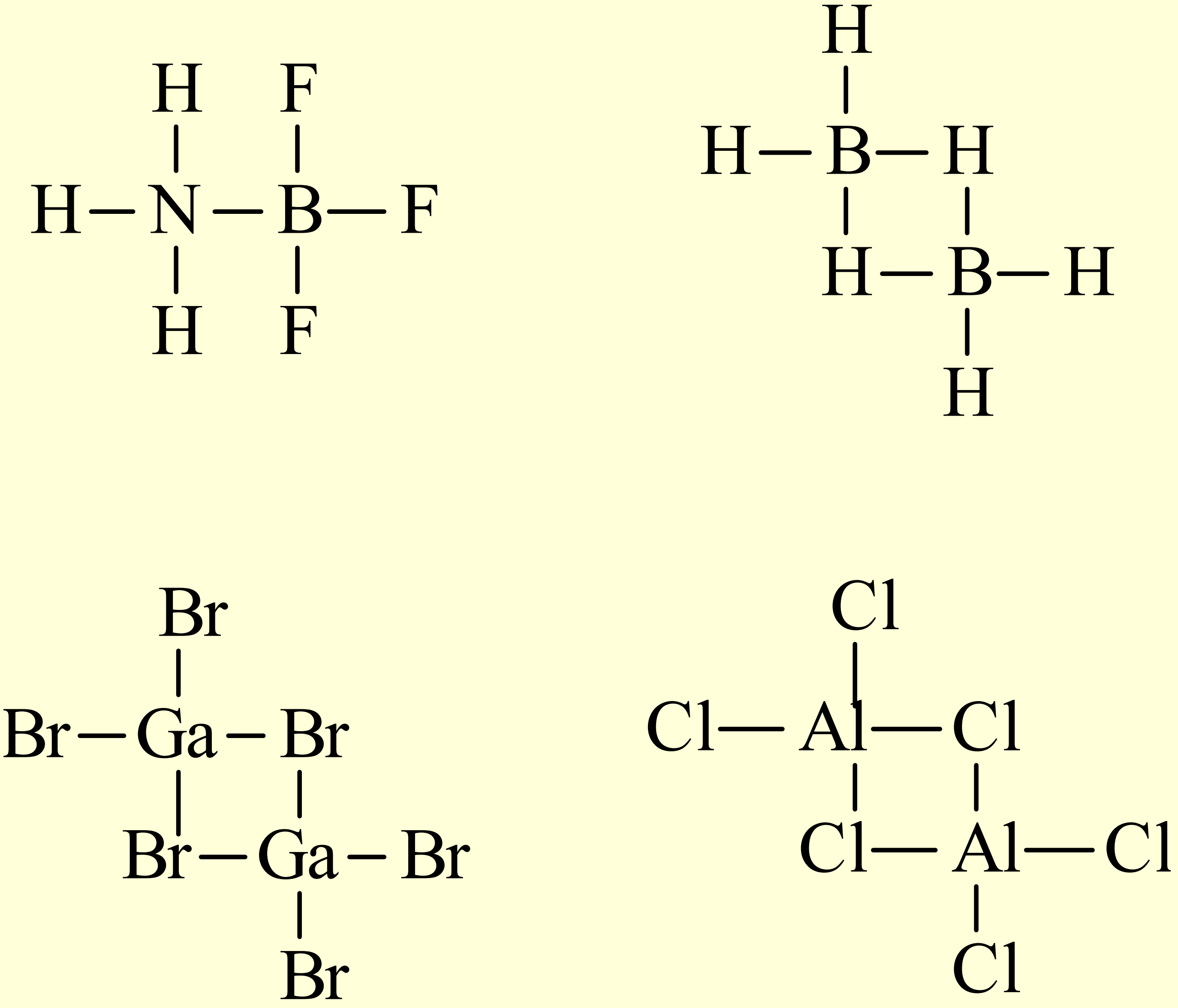
- Galium: obtaining low-melting alloys used as electrical fuses. Being non-toxic and melting down, it also serves as heat transfer medium in nuclear industry heat exchangers as liquid thermometers for high temperatures and as a means of vacuum sealing technique. Also used to obtain compound semiconductors GaAs and GaP.
- Indium: have the property to reflect most of the visible spectra – very useful for mirrors in this range. Production of alloys for bearings (self-lubricating eg, In-Pb), some power of reflection mirrors (similar to Ag, but more resistant to corrosion).
- Talium: obtaining special bottles, increasing the refractive index of the glass or the manufacture of catalysts.

Group 13. Chemical bonds

- Group 13 gives compounds with covalent bonds MX_3 (M = B, Al, …) which are ***deficient in electrons*** – are not quite stable and stabilization occurs through electrons transfer from inside or outside of the molecule. If the electrons comes from atoms of same type, it results dimers or polymers; if comes from atoms of other type then *donor-acceptor* compounds are obtained and have Td or Oh symmetry.



Coordinative compounds and dimers



$$\begin{array}{ccccccc} & & H & & F & & \\ & & | & & | & & \\ H & - & N & - & B & - & F \\ & & | & & | & & \\ & & H & & F & & \end{array}$$

$$\begin{array}{ccccccc} & & H & & & & \\ & & | & & & & \\ H & - & B & - & H & & \\ & & | & & | & & \\ & & H & - & B & - & H \\ & & & & | & & \\ & & & & H & & \end{array}$$

$$\begin{array}{ccccccc} & & Br & & & & \\ & & | & & & & \\ Br & - & Ga & - & Br & & \\ & & | & & | & & \\ & & Br & - & Ga & - & Br \\ & & & & | & & \\ & & & & Br & & \end{array}$$

$$\begin{array}{ccccccc} & & Cl & & & & \\ & & | & & & & \\ Cl & - & Al & - & Cl & & \\ & & | & & | & & \\ & & Cl & - & Al & - & Cl \\ & & & & | & & \\ & & & & Cl & & \end{array}$$

Q & R

In connection with the elements of group 13 (B, Al, Ga, In, Tl) and 14 (C, Si, Ge, Sn, Pb):		
	0	Length of covalent bonds decreases with decreasing electronegativity and bond order
	0	Length of covalent bonds increases with increasing electronegativity and bond order
	1	Length of covalent bonds increases with decreasing electronegativity and bond order
	1	Length of covalent bonds decreases with increasing electronegativity and bond order
	0	Group 13 gives compounds with covalent bonds MX (BF, AlCl) which are in excess of electrons
	1	Group 13 gives compounds with covalent bonds MX_3 (BF_3, $AlCl_3$) which are deficient in electrons

Group 14. Physical properties

Element	Covalent radius (nm)	Oxidation state	Electronegativity (Pauling)	M.p. K	B.p. K
C	7.7	-IV, II, IV	2.55	3800	4300
Si	11.7	- IV, IV	1.90	1687	3173
Ge	12.2	- IV, II, IV	2.01	1211	3093
Sn	14.0	- IV, II, IV	1.96	505	2875
Pb	14.6	- IV, II, IV	2.33	601	2022

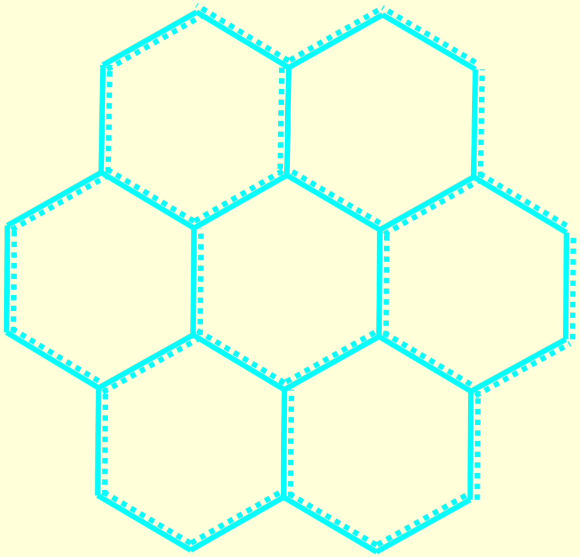
Group 14: Bond lengths

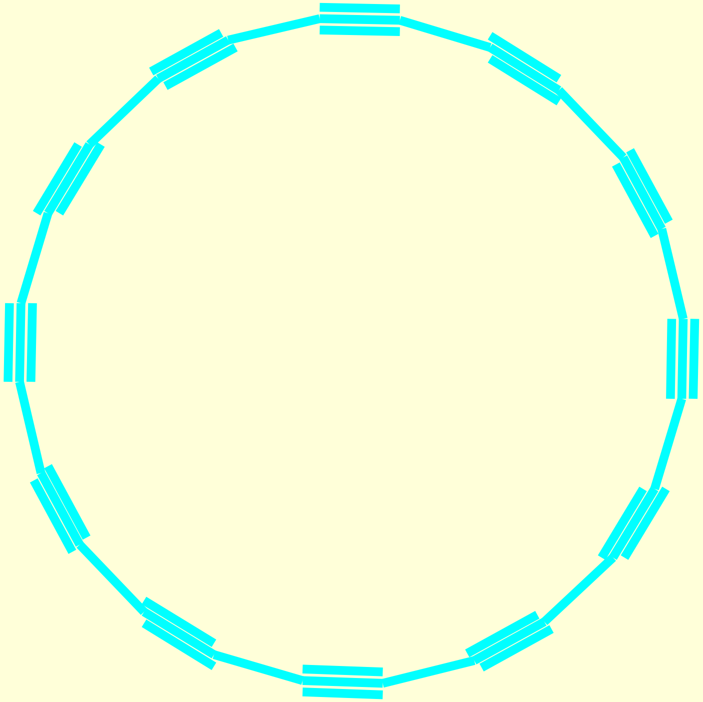
Bond	Length (pm)		Bond	Length (pm)		Bond	Length (pm)
N≡N	110		F-H	92		C-H	109
C≡N	116		O-H	96		Si-H	148
C≡C	120		N-H	101		Ge-H	153
C=O	123		C-H	109		C-O	143
C=N	128		F-C	135		Si-O	163
C=C	134		O-C	143		Ge-O	173
C-O	143		N-C	147		C-Si	186
N-N	145		C-C	154		Si-Si	326
C-N	147						
O-O	148						
C-C	154						

Carbon allotropes

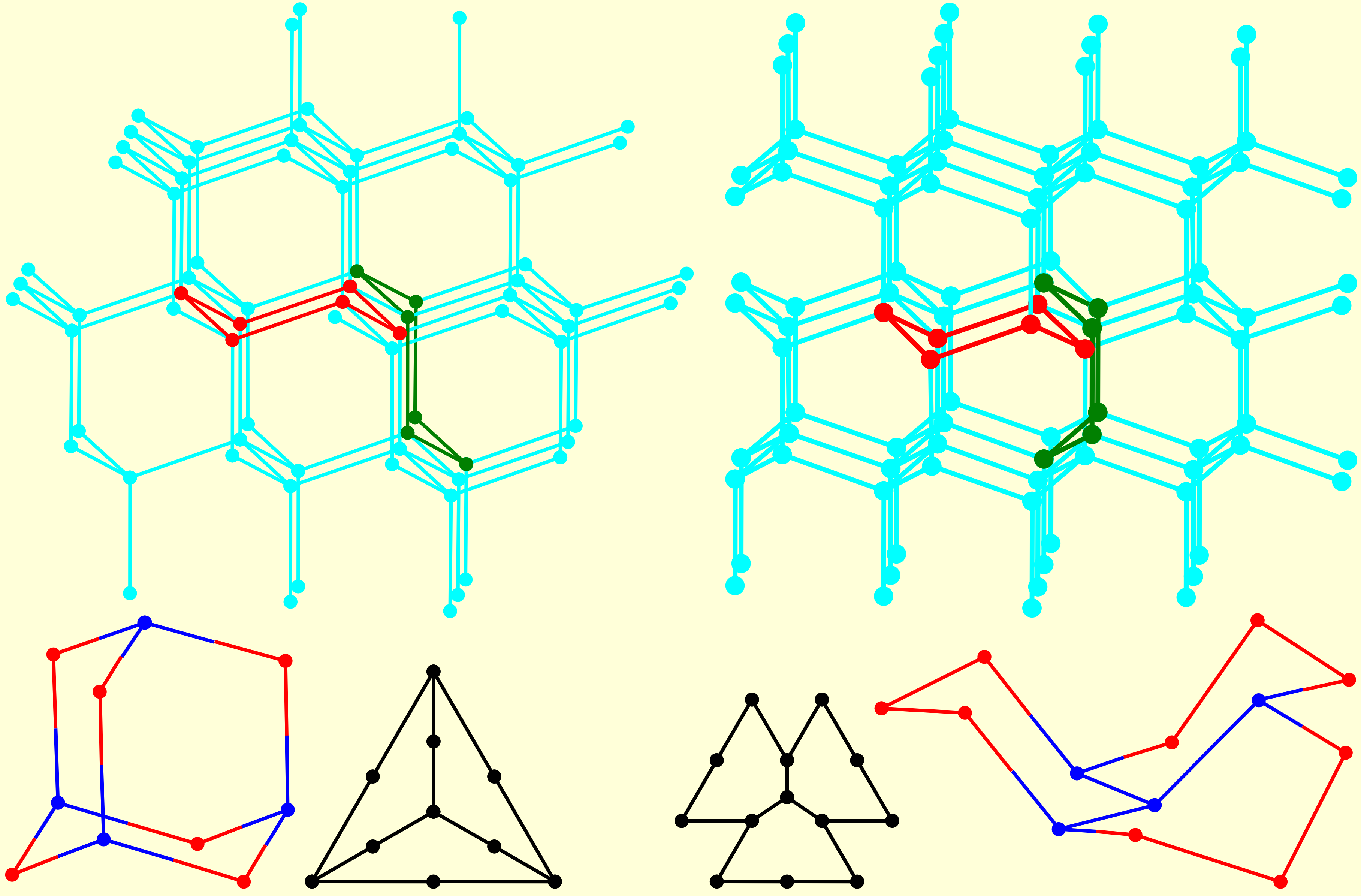
- Natural
  - Amorphous
  - Graphite
  - Cubic diamond
- Synthetic
  - Polyyne (-C≡C- polymer)
  - Graphene (single layer of graphite)
  - Hexagonal diamond (also found in meteorites)
  - Fullerenes (pentagons and hexagons of carbon atoms)
  - Nanotubes (hexagons of carbon atoms)
  - Carbon nanofoam (hexagons and heptagons of carbon atoms)
  - Glassy carbon (spatial disordered hexagons of carbon atoms)

Graphene & Polyyne

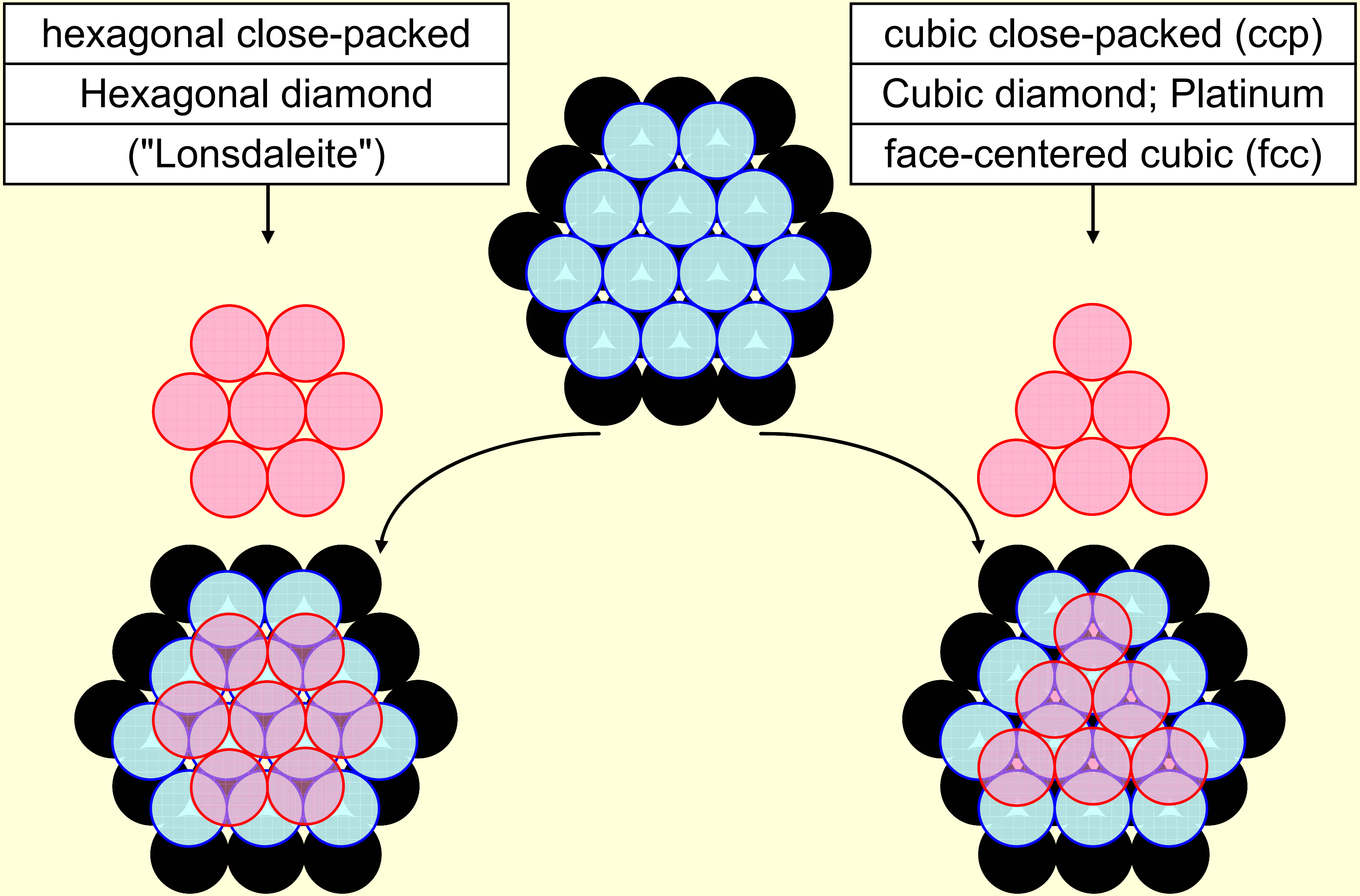




Diamond: cubic & hexagonal



Diamond: close-packed

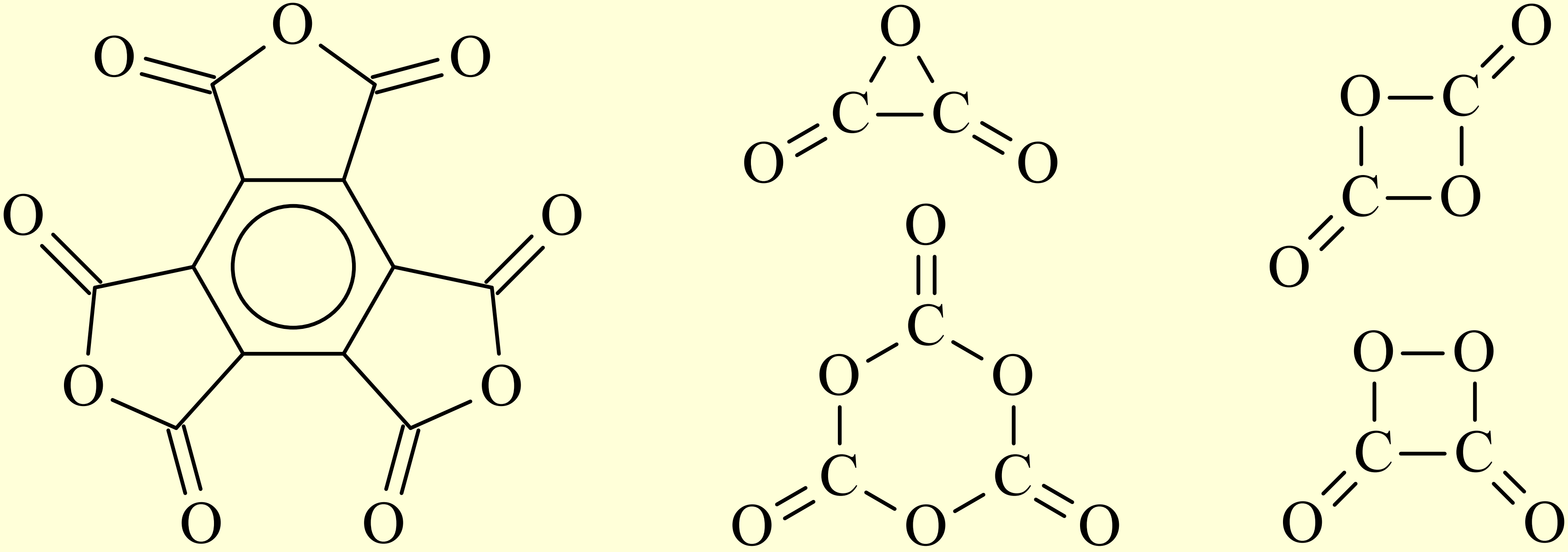


hexagonal close-packed
Hexagonal diamond
("Lonsdaleite")

cubic close-packed (ccp)
Cubic diamond; Platinum
face-centered cubic (fcc)

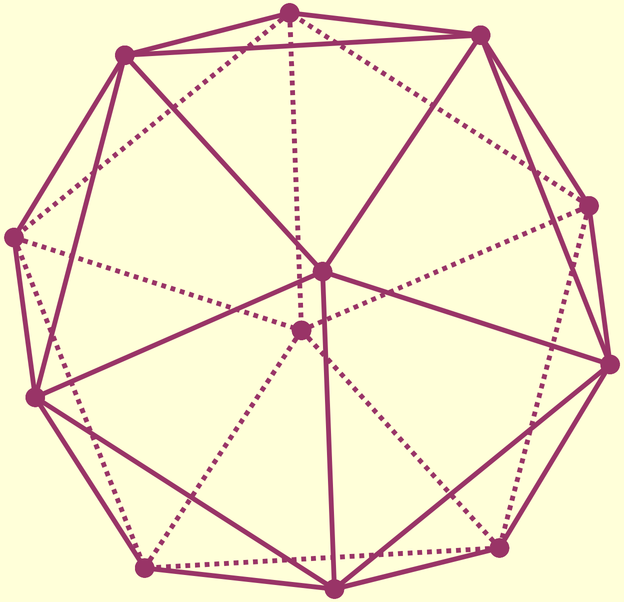
Carbon and oxygen

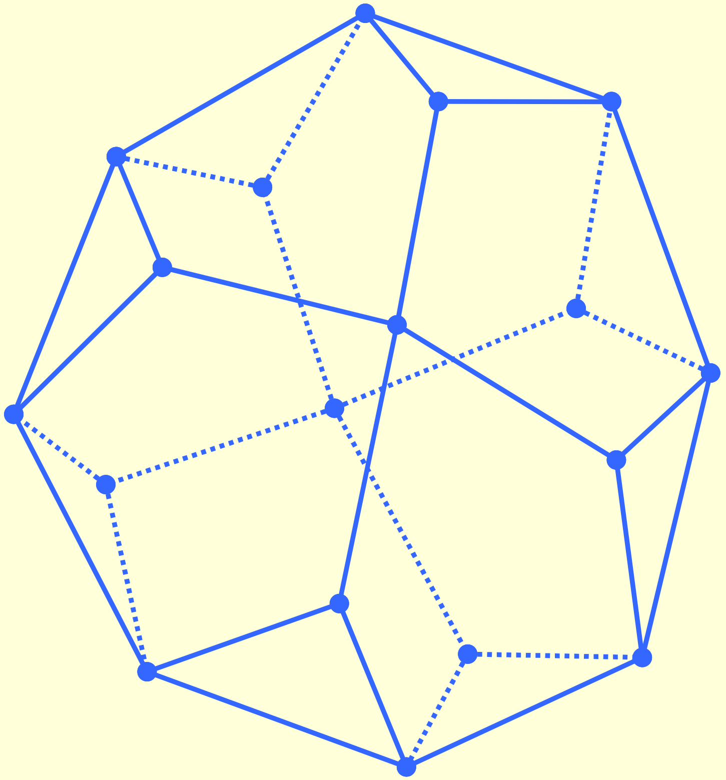
- It forms a series of gaseous components with the oxygen: carbon monoxide, C=O, carbon dioxide, O=C=O, carbon suboxide, O=C=C=O, tricarbon dioxide O=C=C=C=O, and tetracarbon dioxide O=C=C=C=C=O. It has also been obtained by flash vapor pyrolysis of 2,4,6-tris(diazo)cyclohexane-1,3,5-trione ($C_6N_6O_3$) the pentacarbon dioxide O=C=C=C=C=C=O which is stable up to -96 °C, when it polymerizes. Other non-linear molecules are depicted:



- **Boron Carbide** is one of the hardest materials known, ranking **third** behind diamond and boron nitride. It is the hardest material produced in tonnage quantities. It has no clear repetitive structure. It have a ratio Boron:Carbon varying from 23:2 to 19:6. Below are given two possible arrangements in which a part of boron atoms are replaced by carbon atoms.

B:C
12:0
11:1
10:2

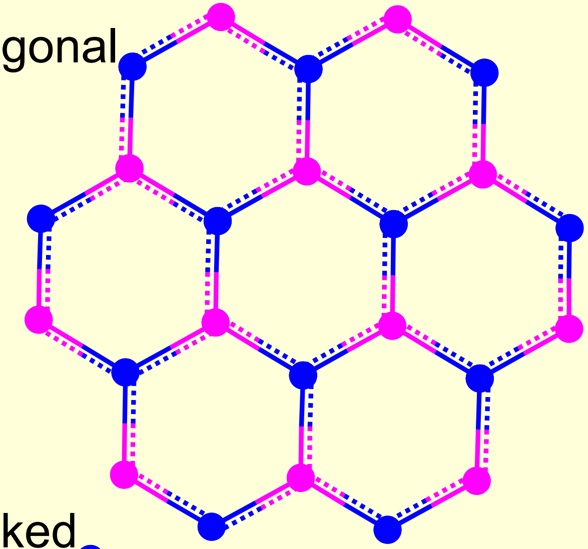




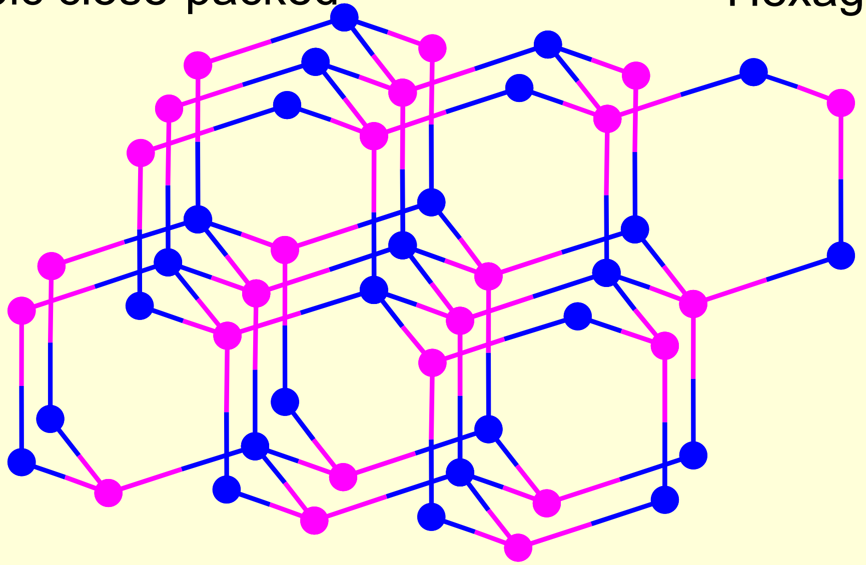
B:C
18:0
16:2
14:4

Boron nitride

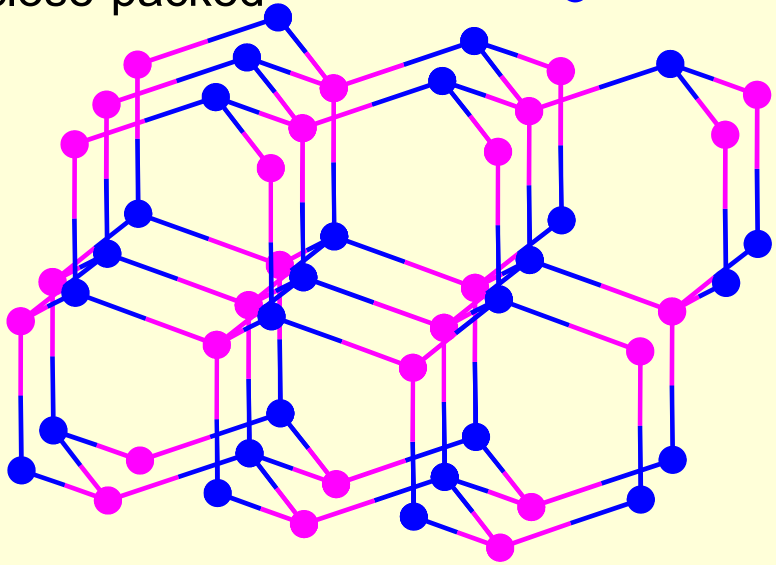
- Hexagonal form is a good lubricant
- Cubic close-packed form is thermal and chemical stable; hardness inferior only to diamond
- Hexagonal close-packed has never been synthesized but is likely to be harder than the cubic close-packed form



Hexagonal

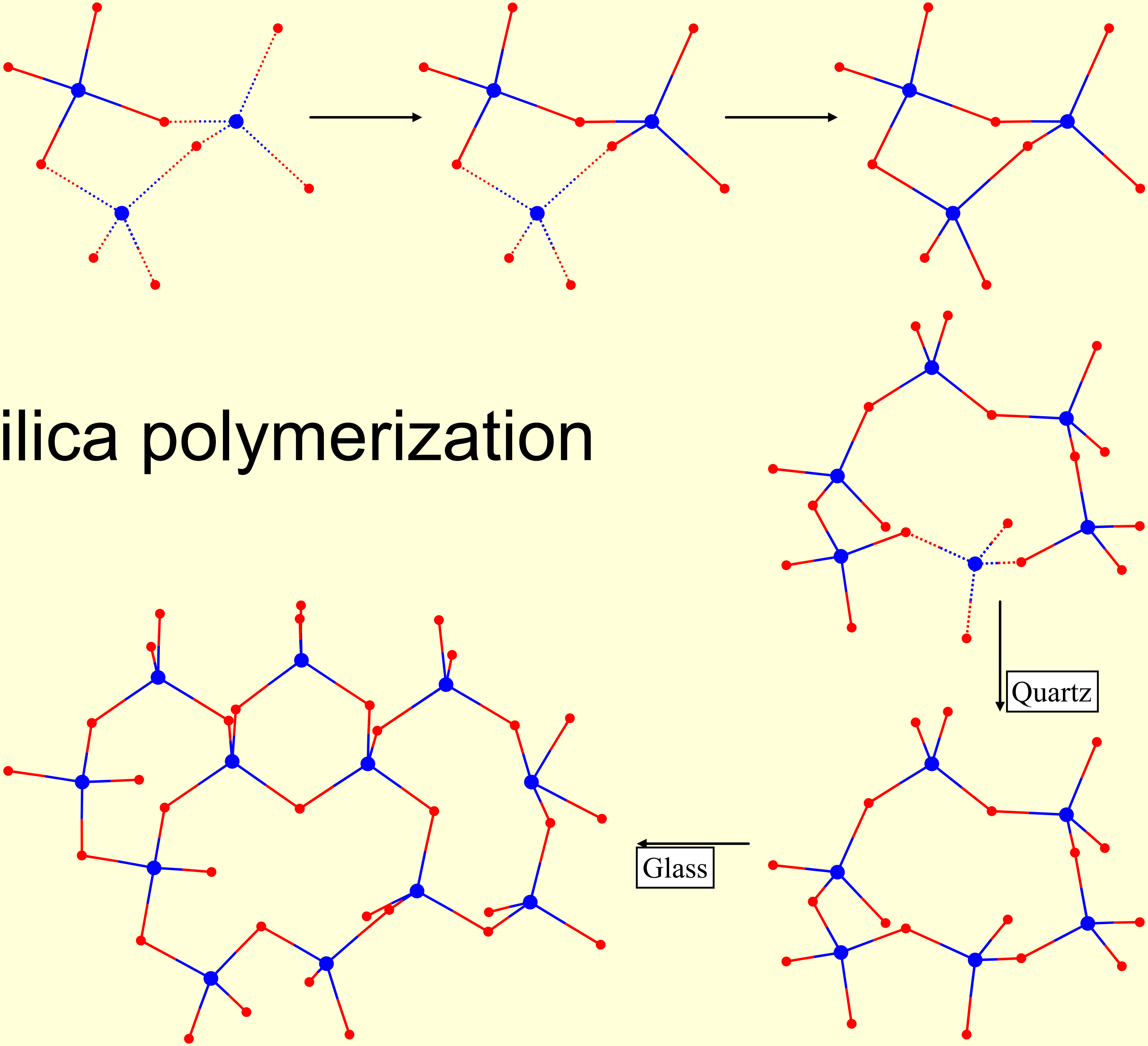


Cubic close-packed

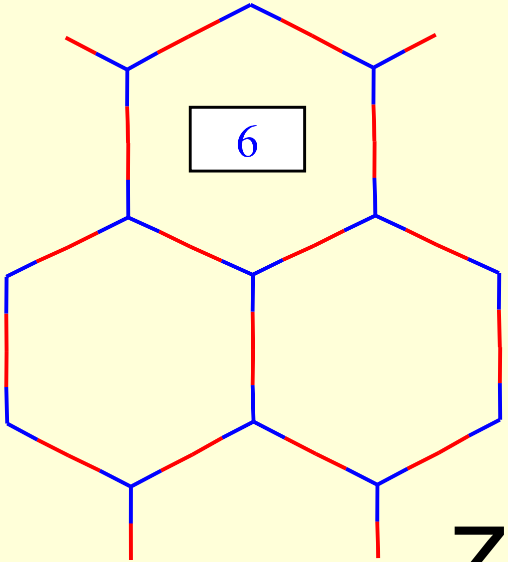


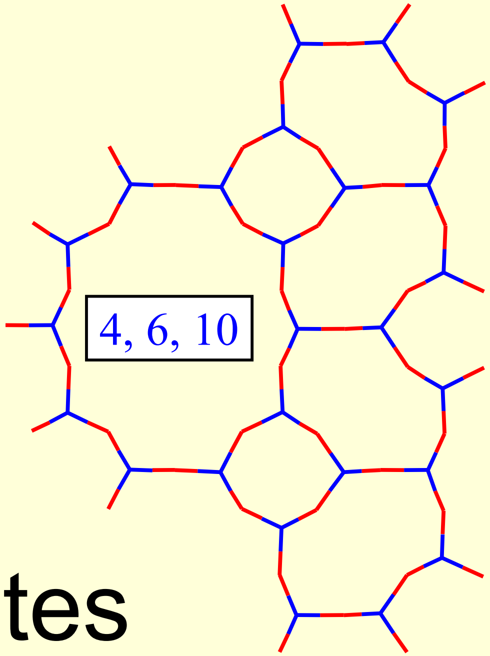
Hexagonal close-packed

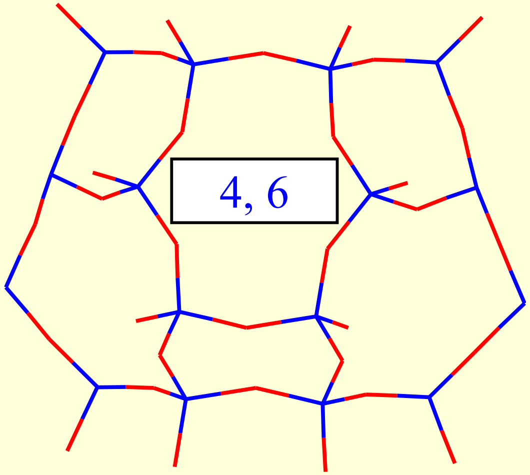
Silica polymerization

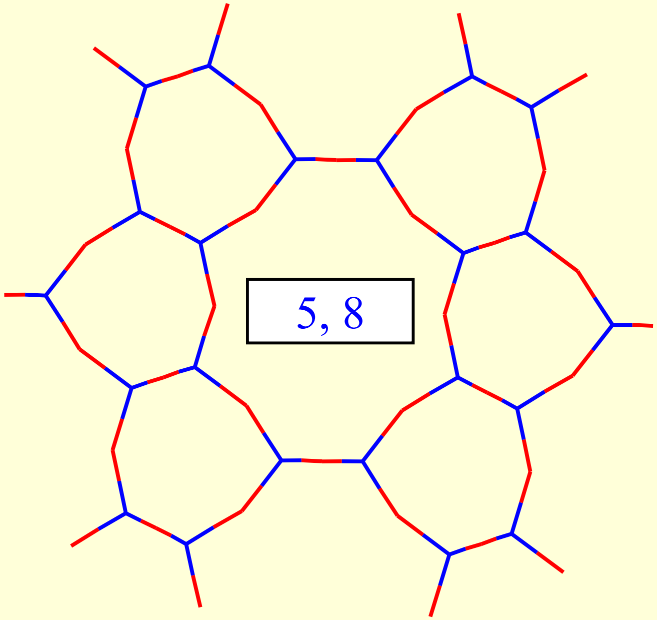


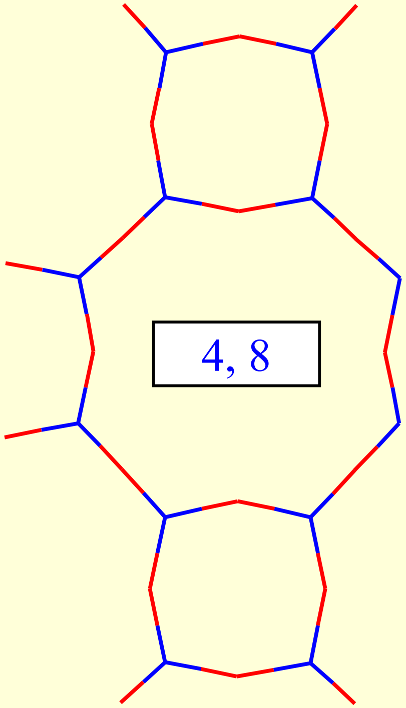
Zeolites

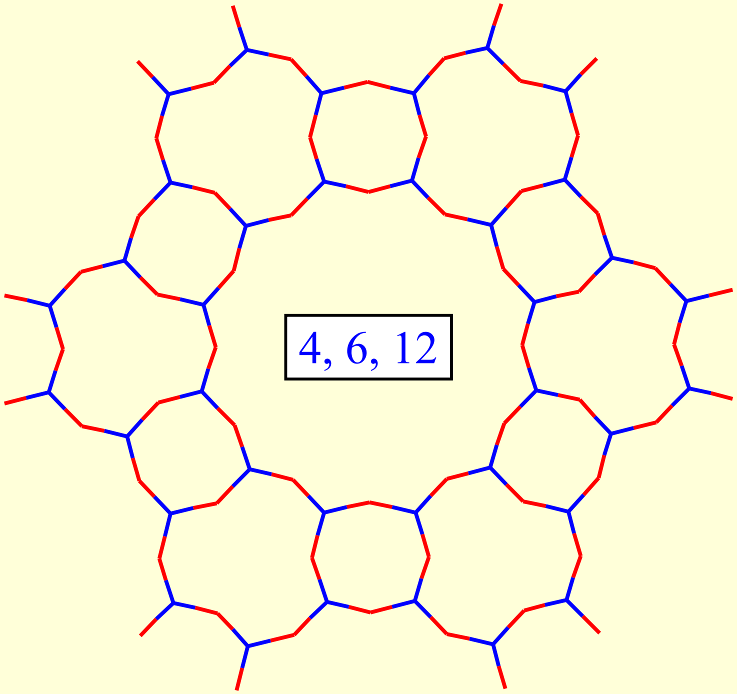






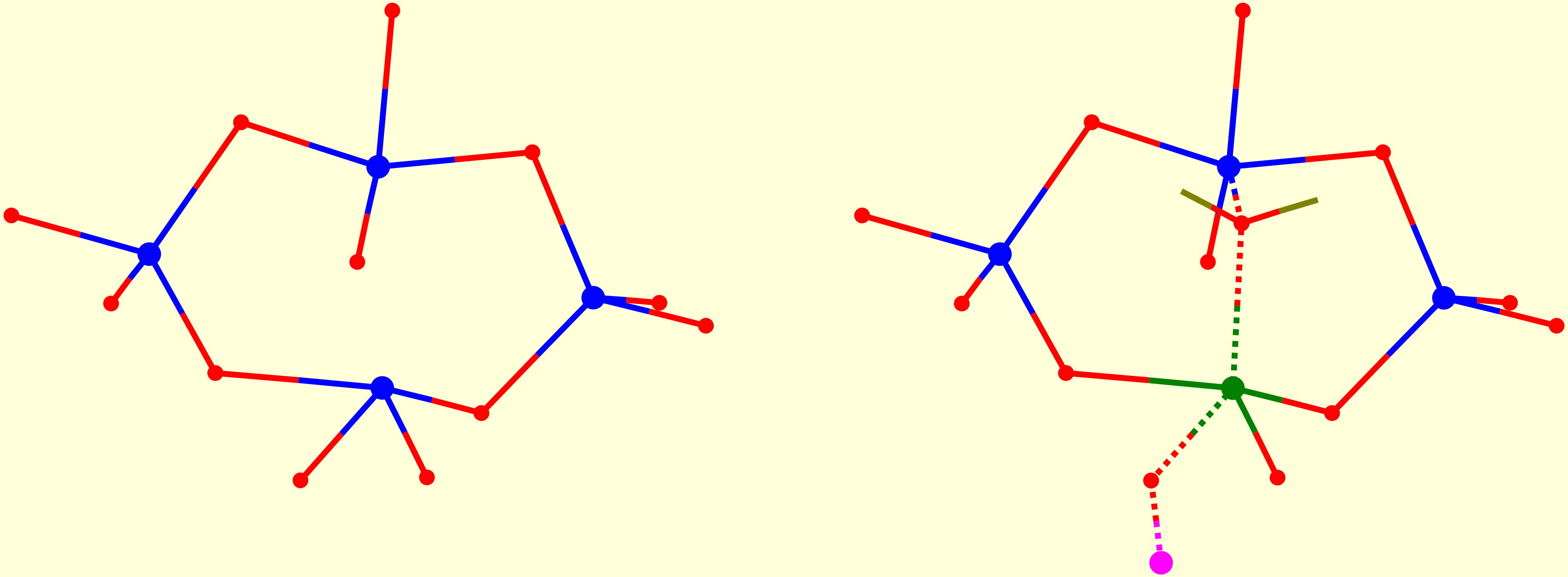






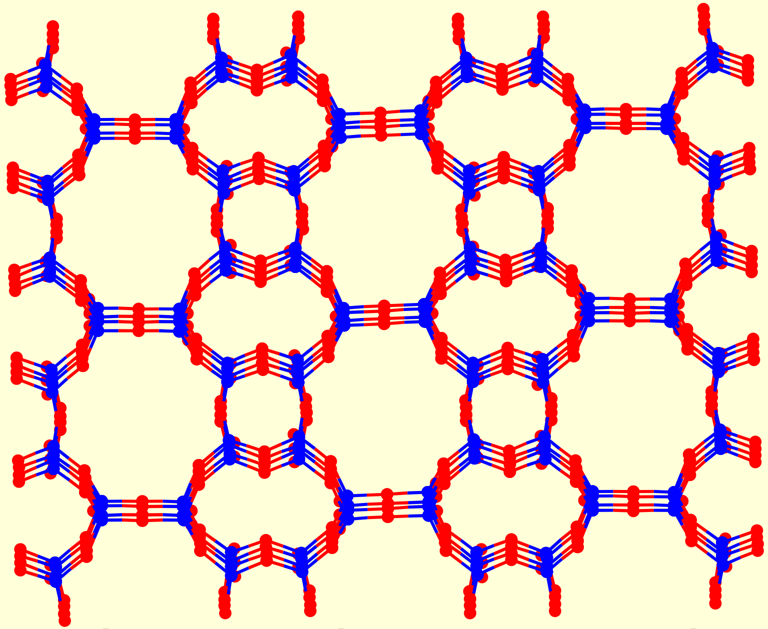
Zeolites formation

$$Si_4O_8 \longrightarrow NaAlSi_3O_8 \cdot H_2O$$



Zeolites uses

Zeolites have the ability to act as **catalysts** for chemical reactions which take place within the internal cavities. An important class of reactions is that catalysed by hydrogen-exchanged zeolites, whose framework-bound protons give rise to very high acidity. This is exploited in many organic reactions, including crude oil cracking, isomerisation and fuel synthesis.



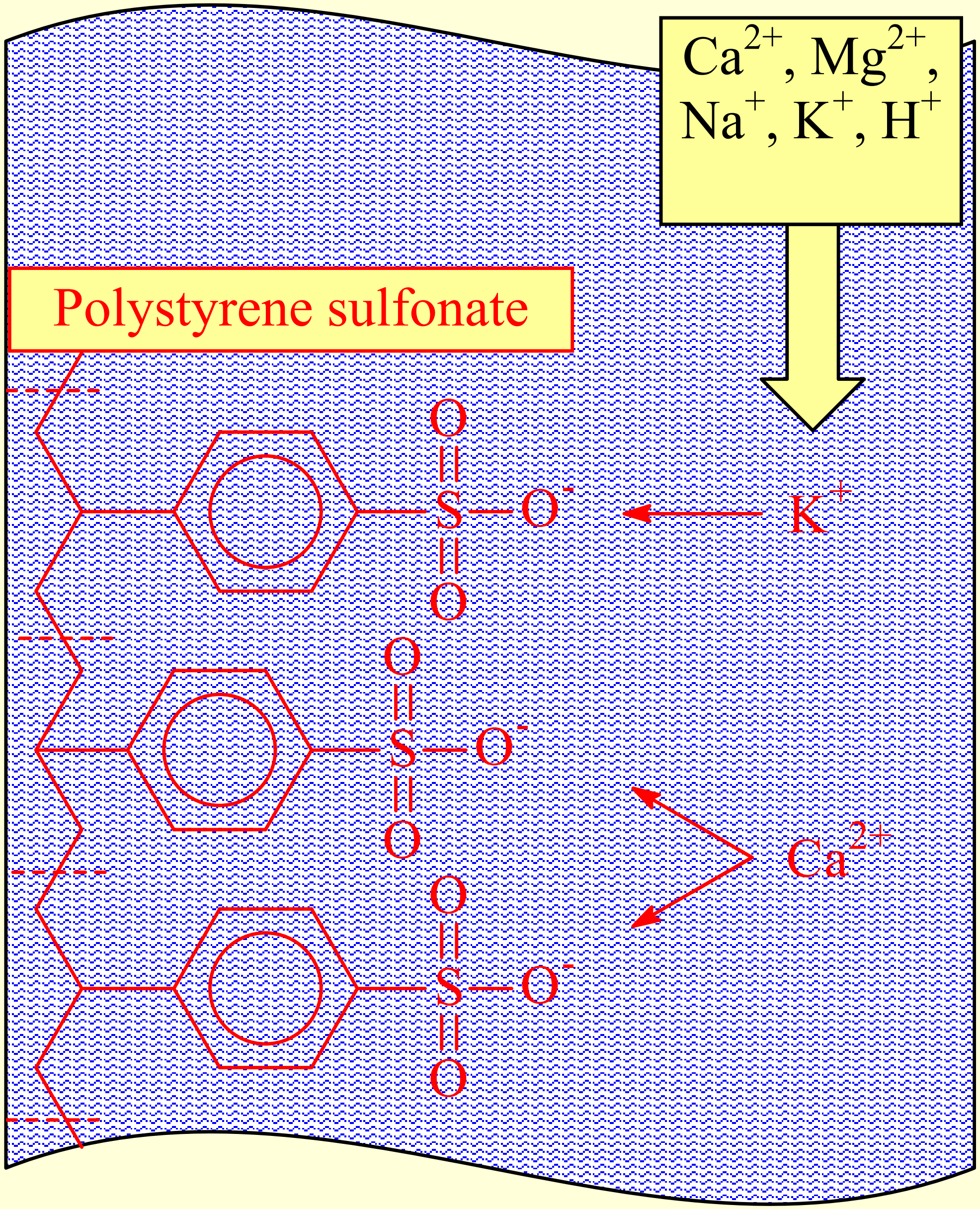
Because of their unique porous properties, zeolites are used in a variety of applications with a global market of several milliion tonnes per annum. In the western world, major uses are in petrochemical cracking, ion-exchange (water softening and purification), and in the separation and removal of gases and solvents. Other applications are in agriculture, animal husbandry and construction. They are often also referred to as *molecular sieves*.

Zeolites – Adsorption & Separation

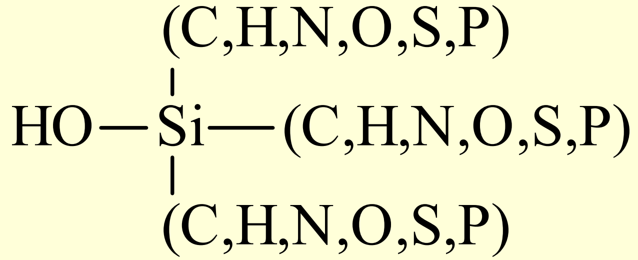
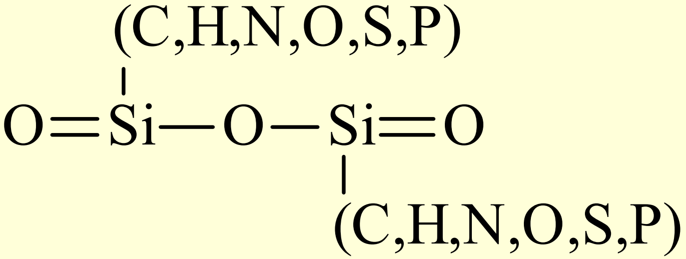
- The shape-selective properties of zeolites are also the basis for their use in molecular adsorption. The ability preferentially to adsorb certain molecules, while excluding others, has opened up a wide range of molecular sieving applications. Sometimes it is simply a matter of the size and shape of pores controlling access into the zeolite. In other cases different types of molecule enter the zeolite, but some diffuse through the channels more quickly, leaving others stuck behind, as in the purification of *para*-xylene by silicalite.
- This is exploited in a major way in water softening, where alkali metals such as sodium or potassium prefer to exchange out of the zeolite, being replaced by the "hard" calcium and magnesium ions from the water. Many commercial washing powders thus contain substantial amounts of zeolite. Commercial waste water containing heavy metals, and nuclear effluents containing radioactive isotopes can also be cleaned up using such zeolites.

Ion exchangers

Zeolites can also serve as oxidation or reduction catalysts, often after metals have been introduced into the framework. Examples are the use of titanium ZSM-5 in the production of caprolactam, and copper zeolites in NOx decomposition.



Silica copolymerization

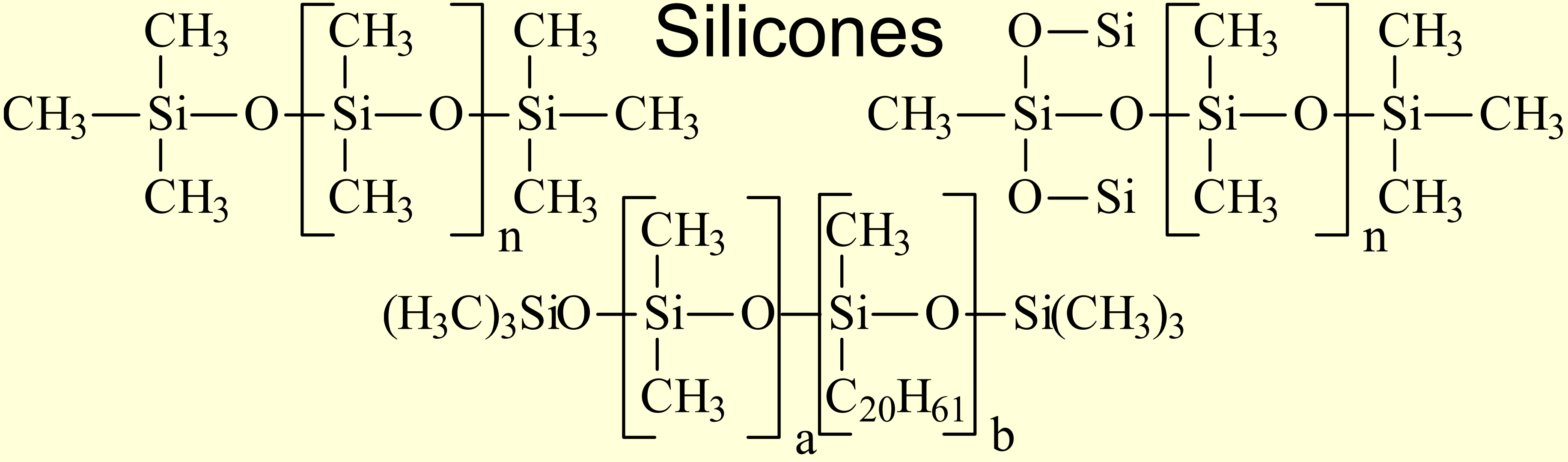
$O{=}Si{=}O$	+	$3H-(C,H,N,O,S,P)$	→	 $HO-\overset{(C,H,N,O,S,P)}{\underset{(C,H,N,O,S,P)}{Si}}-(C,H,N,O,S,P)$	+	OH_2
Silica powder (SiO_2)		Organics (possibly polymer)		Organic-silica compounds		Water
$2O{=}Si{=}O$	+	$2H-(C,H,N,O,S,P)$	→	 $O{=}\overset{(C,H,N,O,S,P)}{Si}-O-\underset{(C,H,N,O,S,P)}{Si}{=}O$	+	OH_2

Organic-silica compounds contains Si-C bonds. In well controlled conditions, are obtained cyclosiloxanes (rings with 3-6 Si atoms, which oxidants used in waterproofing of buildings, cars, and shoes).

Silicones are compounds with special properties, well valuable in technique and include silicone oil, grease, rubber, resin, and caulk.

Comparing it with organic polymers the silicones have better thermal stability – it can be used in warm environments. It have chemical inertia – resisting to oxidation, to water and wide range of chemical agents.

Silicones



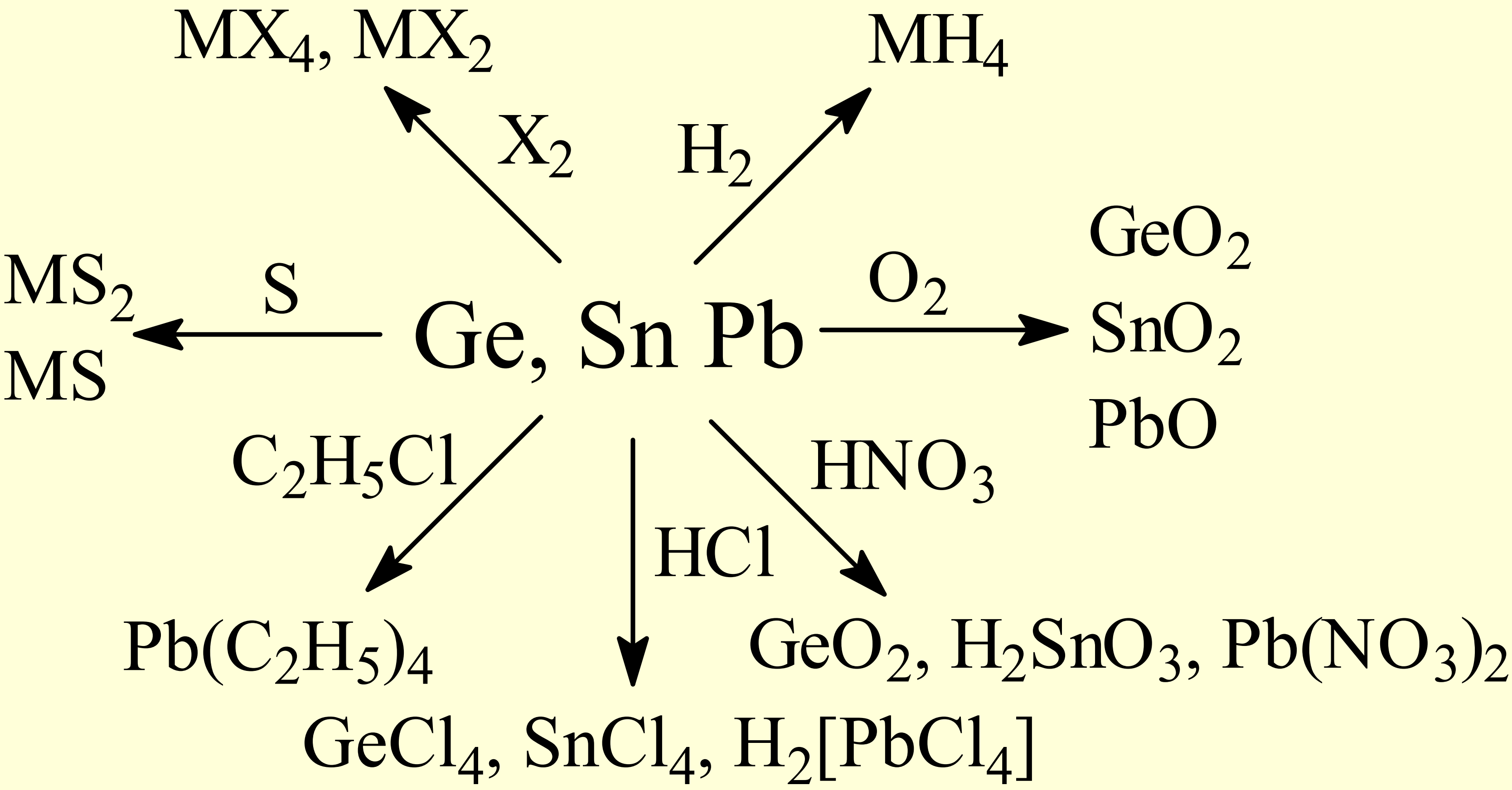
$$CH_3-Si(CH_3)_2-O-[Si(CH_3)_2-O]_n-Si(CH_3)_2-CH_3$$

$$CH_3-Si(O-Si)_2-O-[Si(CH_3)_2-O]_n-Si(CH_3)_2-CH_3$$

$$(H_3C)_3SiO-[Si(CH_3)_2-O]_a-[Si(CH_3)(C_{20}H_{61})-O]_b-Si(CH_3)_3$$

- With 20≤n≤500 & C/Si>2 are ***silicone oils***. Apps include lubricants, dielectrics, hydraulic liquids. See for instance US Patent no. 8355209 / Jan. 15, 2013.
- With 900≤n≤2000 & C/Si>2 are ***silicone greases***, used as lubricants too. See for instance US Patent no. 8017684 / Sept. 13, 2011.
- With 6000≤n≤60000 & C/Si~2 are ***silicone rubbers***. See for instance US Patent no. 8344067 B2 / Jan. 1, 2013.
- With C/Si<2 are ***silicone resins*** (bakelite-like). See for instance US Patent no. 8334022 / Dec. 18, 2012.
- Copolymers with about 1% long organic chains are ***silicone caulks***. See for instance US Patent no. 5783719 / Jul. 21, 1998.

Ge, Sn, Pb – chemical properties



MX_4, MX_2

MH_4

X_2

H_2

GeO_2

MS_2

S

O_2

Ge, Sn Pb

SnO_2

MS

PbO

C_2H_5Cl

HNO_3

HCl

$Pb(C_2H_5)_4$

GeO_2, H_2SnO_3, $Pb(NO_3)_2$

$GeCl_4$, $SnCl_4$, $H_2[PbCl_4]$

Q & R

	In connection with the elements of group 13 (B, Al, Ga, In, Tl) and 14 (C, Si, Ge, Sn, Pb):
0	Silicone has the skeleton of carbon oxide and silicyl groups (-SiH_3) endings
1	Silicone has the skeleton of silicon oxide (-(>)Si-O-(>)Si-O-(>)Si-) and methyl groups (-CH_3) endings
0	Silicium tends to polymerize (...-Si-Si-Si-...)
0	Carbon dioxide tends to polymerize (...-O-$C(O-)_2$-O-...)
1	Silicium dioxide tends to polymerize (...-O-$Si(O-)_2$-O-...)
1	The carbon tends to polymerize (...-C-C-C-...)
0	The carbon tends to form cycles of 3, 4 and 5 atoms
1	The carbon tends to form cycles of 5, 6 and 7 atoms

Course 11

Organic chemistry
Hardness & hard materials

Alkanes

General structure

R—H

Functional group

None

Example

$CH_3CH_2CH_2CH_3$

Name

n-Butane

n-Butane isomers →

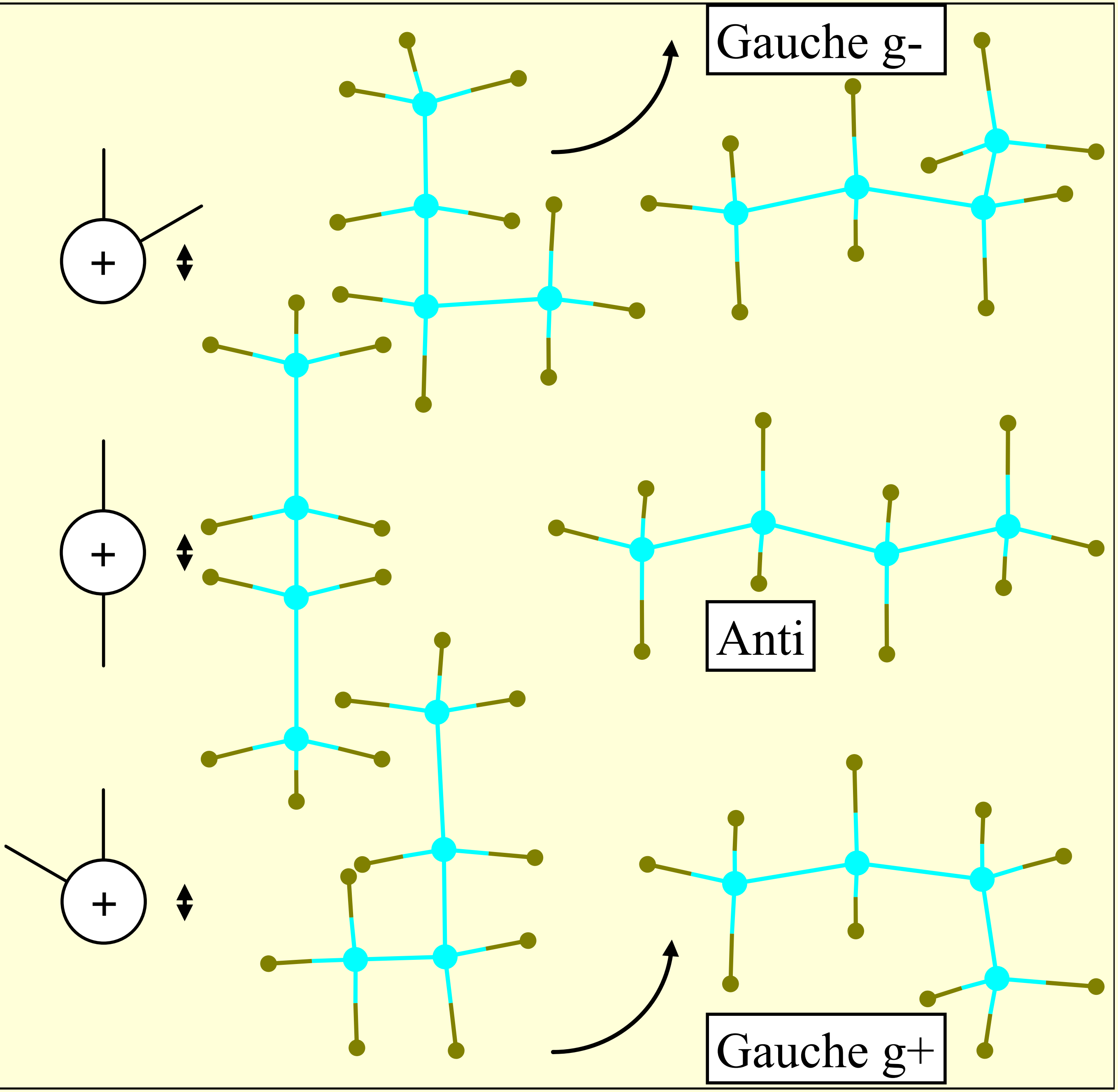
Rotamers:

"Gauche g-"

"Gauche g+"

Conformer:

"Anti"



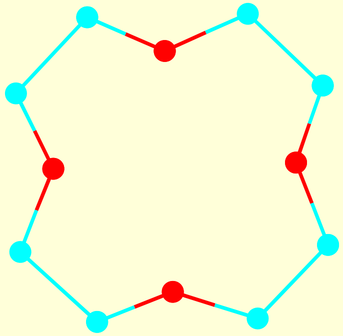
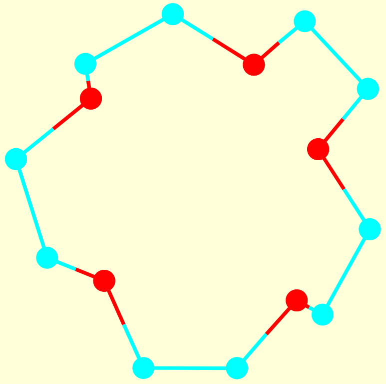
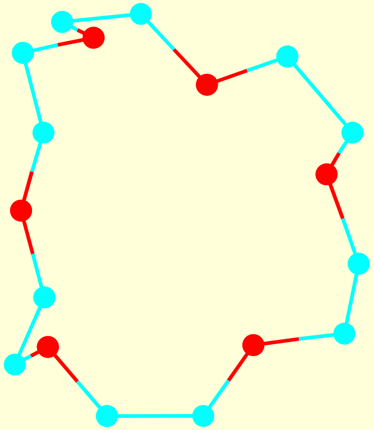
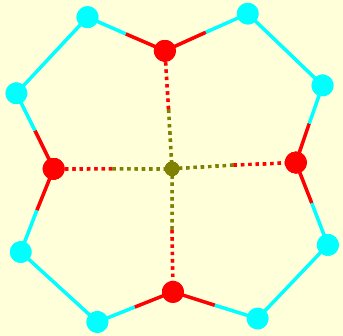
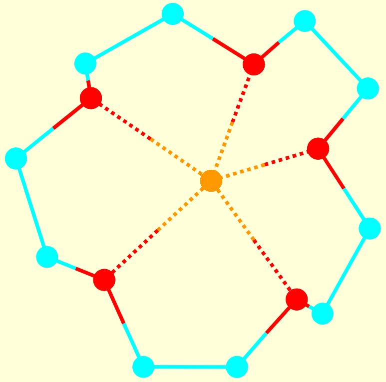
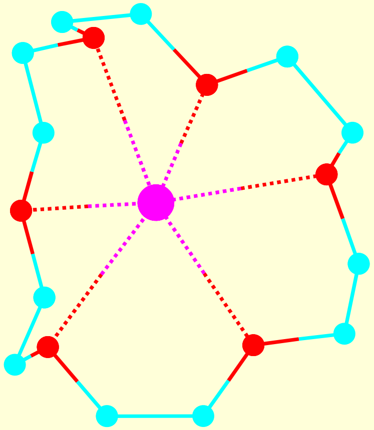
Alkanes structural formula isomers

n = 1; CH_4	1 (CH_4)
n=2; C_2H_6	1 (CH_3-CH_3)
n=3; C_3H_8	1 (CH_3-CH_2-CH_3)
n=4; C_4H_{10}	2 (butane (3 geometry isomers) & 2-methyl-propane)
n=5; C_5H_{12}	3
n=6; C_6H_{14}	5
n=7; C_7H_{16}	9
n=8; C_8H_{18}	18
n=9; C_9H_{20}	35
…	
In general?	Hard problem – see Open Encyclopedia of Integer Sequences
	http://oeis.org
n	OEIS: A000602 (http://oeis.org/A000602)
	A000602=A000022+A000200 (n>0)
	A000602, A000022, A000200: No explicit formula!
	A000602, A000022, A000200: No explicit recurrence formula!

Substituted alkanes	
General structure R—G	Example CH_3HgCH_3; CH_3CdCH_3
Functional group G	Name dimethylmercury; dimethylcadmium;
Example CH_3HgA; CH_3CdA; A=anion	Remarks: CH_3HgCH_3 is one of the strongest known neurotoxins; CH_3CdCH_3 is toxic too
Name "A"-methylmercury; "A"-methylcadmium;	Example CH_3ZnCH_3
Remarks: $[CH_3Hg]^+$ is a bioaccumulative environmental toxicant; $[CH_3Cd]^+$ is toxic too	Remarks: CH_3ZnCH_3 is spontaneously combustible

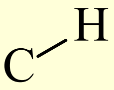
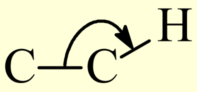
Haloalkanes	
General structure: R-X	Functional group: X
Example: CH_3Cl	Name: Methyl chloride; chloromethane
Remarks: It is toxic and extremely flammable. It is an intermediate in the production of silicone polymers. CH_3CH_2I uses in alkylation: $RH + ICH_2CH_3 \rightarrow R\text{-}CH_2\text{-}CH_3 + HI$	
Example: CH_2Cl_2	Name: Methylene chloride
Remarks: It is widely used as a solvent. It is not miscible with water, and is miscible with many organic solvents. It is widely used as a paint stripper and a degreaser.	
Example: $CHCl_3$	Name: Chloroform
Remarks: Chloroform is a solvent (relatively unreactive, miscible with most organic liquids, conveniently volatile)	
Example: CCl_4	Name: Carbon tetrachloride
Remarks: Carbon tetrachloride uses as a dry cleaning solvent, and as a refrigerant. Carbon tetrachloride is one of the most potent hepatotoxins (toxic to the liver, it causes fulminant necrosis).	

Alcohols	
General structure: R-OH	Functional group: OH
Example: CH_3-OH	Name: Methanol; methyl alcohol
Remarks: Methanol is produced naturally in the anaerobic metabolism of many varieties of bacteria. Methanol is a common laboratory solvent. Methanol uses to obtain formaldehyde, and from there into products as diverse as plastics, plywood, paints, explosives, and permanent press textiles. In addition to direct use as a fuel (alternative to gasoline), methanol is used as a component in the transesterification of triglycerides to yield a form of biodiesel.	
Example: CH_3-CH_2-OH	Name: Ethanol; ethyl alcohol
The largest single use of ethanol is as a motor fuel (alternative to gasoline) and fuel additive. Ethanol is the principal psychoactive constituent in alcoholic beverages, with depressant effects on the central nervous system. Long-term use by ingestion can result in serious liver damage. Ethanol is used in medical wipes and antibacterial hand sanitizer gels. Ethanol kills most bacteria and fungi, and many viruses by denaturing their proteins and dissolving their lipids, but is ineffective against bacterial spores.	

<table>
<tr><td colspan="2">Ethers</td><td>Example: crown ethers</td></tr>
<tr><td colspan="2">General structure: R-O-R'</td><td>Functional group: O</td></tr>
<tr><td colspan="2">Example: $CH_3-CH_2-O-CH_2-CH_3$</td><td>Name: Diethyl ether</td></tr>
<tr><td colspan="3">Remarks: It is solvent and anesthetic.</td></tr>
<tr><td colspan="3">Polyethers: compounds with more than one ether group</td></tr>
<tr><td>"12-crown-4"</td><td>"15-crown-5"</td><td>"18-crown-6"</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td>Affinity for Li^+</td><td>Affinity for Na^+</td><td>Affinity for K^+</td></tr>
<tr><td></td><td></td><td></td></tr>
</table>

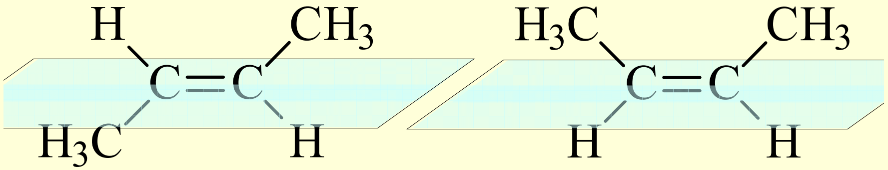
Thiols	General structure: R-SH	Functional group: SH
Example: CH_3-SH	Example: CH_3-S-CH_3	Example: CH_3-S-S-S-CH_3
Name: Methanethiol	Name: Dimethyl sulfide	Name: Dimethyl trisulfide
Remarks: Methanethiol is found in the blood and brain of humans and animals as well as in plant tissues. Methanethiol is disposed of through animal feces and it has an extremely strong and repulsive smell; it is toxic, having as points of attack the respiratory system, lung, and central nervous system.	Remarks: Dimethyl sulfide has a characteristic cabbage-like smell; is available (in low concentration) as a food additive to impart a savory flavor; Beetroot, asparagus, cabbage, corn and seafoods produce dimethyl sulfide when cooked.	Remarks: Dimethyl trisulfide is found in volatiles from cooked onion, leek, broccoli, and cabbage, and is the unpalatable aroma of aged beer and stale Japanese sake.

Alkynes	General structure: RC≡CR	Functional group: C≡C
Example: HC≡CH	Name: acetylene; ethyne	Remarks: About 20% of acetylene is consumed for oxyacetylene gas welding and cutting.

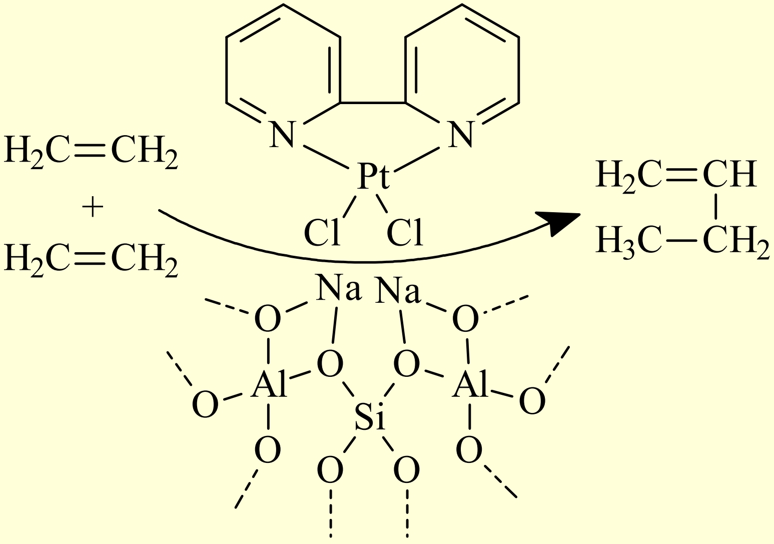
C—C		[Å]			[Å]			[°]
1	$(CH)_2$	1.205	1	$(CH)_2$	1.067	5	$(CH)_2$	180
2	$(CH_2)_2$	1.331	4	$(CH_2)_2$	1.088	4	$(CH_2)_2$	121.9
3	$(CH)_6$	1.385	2	$(CH)_6$	1.072	3	$(CH)_6$	120
4	$(CH_3)_2$	1.531	5	$(CH_3)_2$	1.096	2	$(CH_3)_2$	111.4
5	$C(CH_3)_4$	1.540	3	$C(CH_3)_4$	1.085	1	$C(CH_3)_4$	110.6
bonds lengths and angles from simple to triple bond								

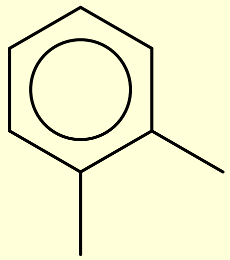
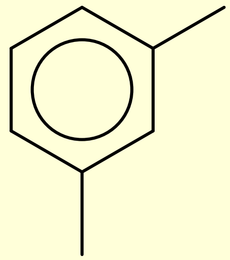
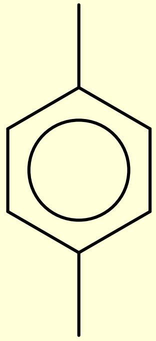
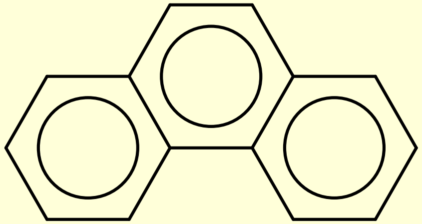
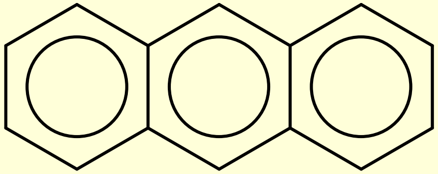
pKa ranges ($RH \leftrightarrow R^- + H^+$)		
Alkynes	Alkenes	Alkanes
pKa≤24	24≤pKa≤48	48≤pKa
H_2O	Arenes	H_2
pKa=15.7	30≤pKa≤43	pKa=35

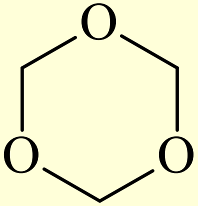
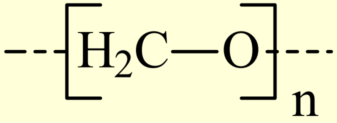
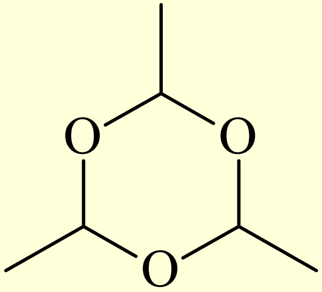
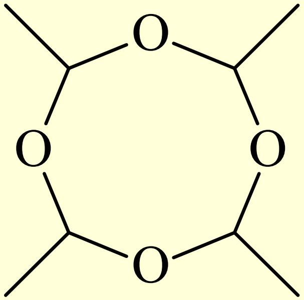
Alkenes	General structure: RC=CR	Functional group: C=C
Example: CH_3-CH=CH-CH_3	Name: 2-butene	Isomers: "cis-" & "trans-"

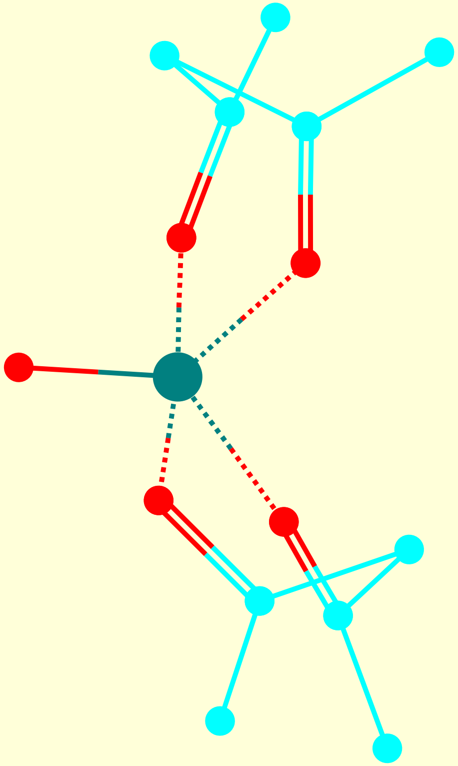
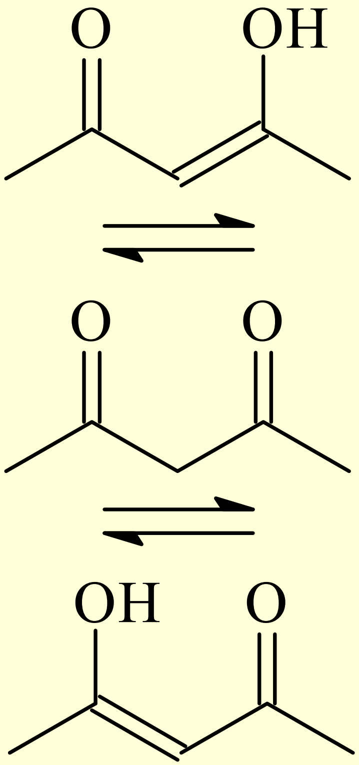
trans-2-butene: 

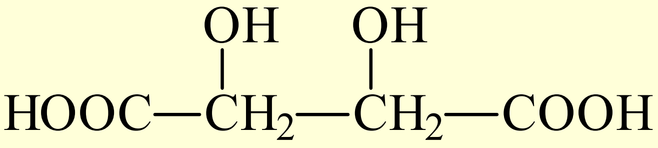
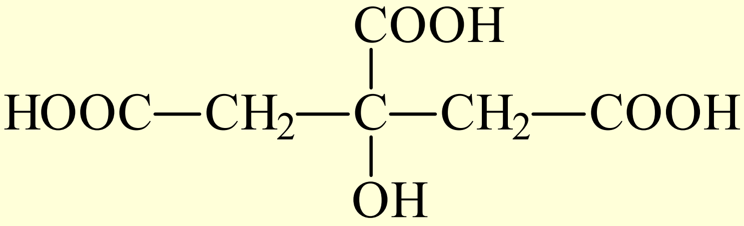
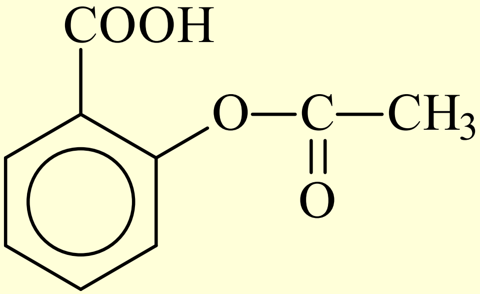
:cis-2-butene

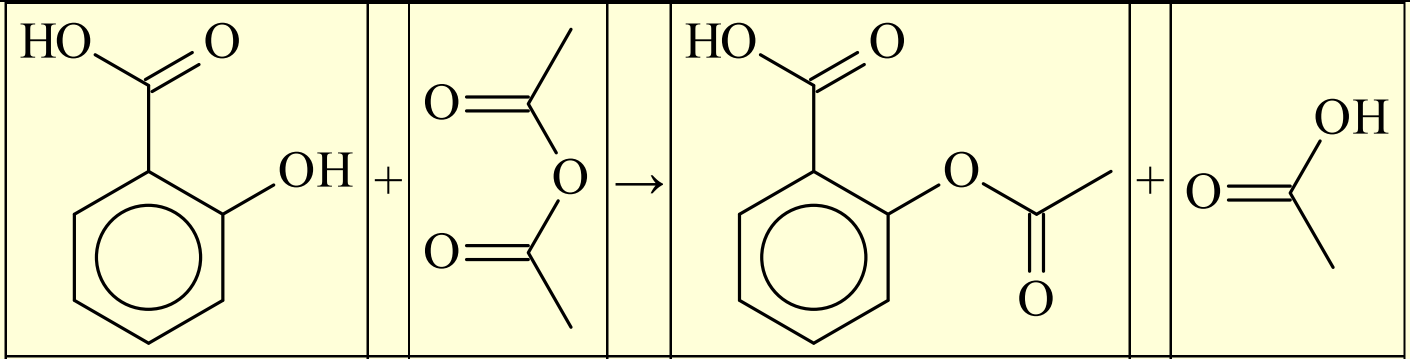
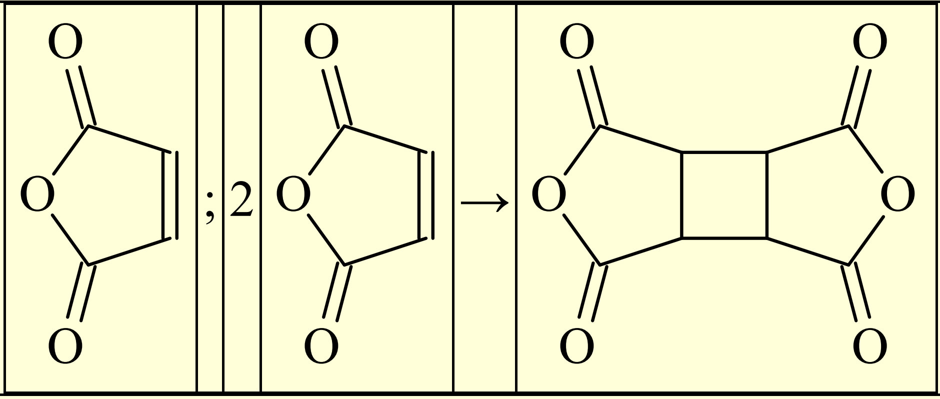
Example: H_2C=CH-CH_3	Example: H_2C=CH_2	Example: CH_2=CH-CH_2-CH_3
Name: Propene	Name: Ethene; Ethylene	Name: 1-Butene
Remarks: Propene is produced naturally by vegetation, particularly certain tree species. It is a product of combustion, from forest fires and cigarette smoke to motor vehicle and aircraft exhaust. With a relatively short half-life, it is not bioaccumulate, therefore with low acute toxicity from inhalation.	Remarks: It is a colorless flammable gas with a faint sweet and musky odor and is an important natural plant hormone, used in agriculture to force the ripening of fruits with a niche use as anesthetic.	Remarks: It is highly flammable and readily forms explosive mixtures with air. 

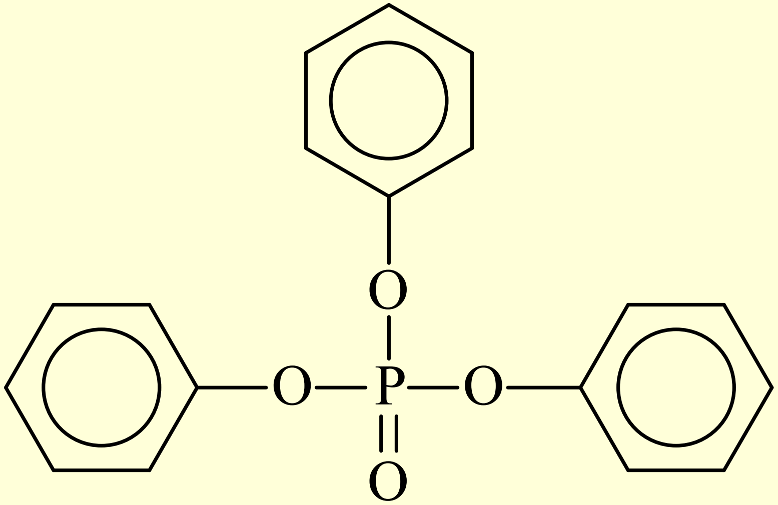
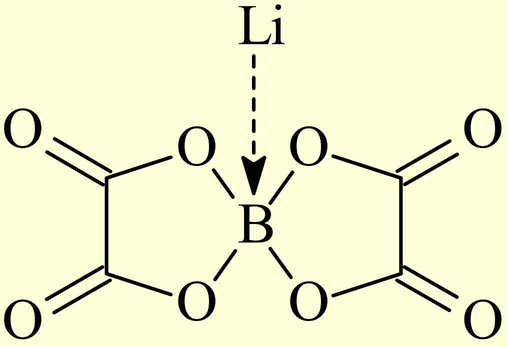
Arenes (Aromatic compounds)	General structure: Aryl-H	Functional group: Aryl
Example: Ph-H (C_6H_6)	Example: C_6H_5-CH_3	Example: $(CH_3)C_6H_4(CH_3)$
Name: Benzene	Name: Toluene	Name: Xylene (dimethylbenzene)
Remarks: Natural constituent of crude oil; is highly flammable liquid with a sweet smell with carcinogen potency; about 80% is used for production of ethylbenzene, cumene, and cyclohexane.	Remarks: A common solvent; can be used as an octane booster in gasoline fuels used in internal combustion engines and for removing the cocaine from coca leaves in the production of Cola syrup.	Structures: (3 Isomers)  o-(ortho-)  m-(meta-)  p-(para-)
Polycyclic aromatic hydrocarbons (PAH's)		Example: $C_{14}H_{10}$
Remarks: Phenanthrene is found in cigarette smoke. Anthracene is a component of coal tar. Phenanthrene is more stable than anthracene.		
	Name: Phenanthrene	Name: Anthracene

<table>
<tr><td colspan="2">Aldehydes</td><td>General structure: R-COH</td><td>Functional group: COH</td></tr>
<tr><td colspan="2">Example: H_2CO</td><td>Example: CH_3CHO</td><td>Name: Acetaldehyde</td></tr>
<tr><td colspan="2">Name: Formaldehyde</td><td colspan="2" rowspan="3">Remarks: Acetaldehyde occurs widely in nature (coffee, bread, ripe fruit, and is produced by plants as part of their normal metabolism) and is produced on large scale industrially.</td></tr>
<tr><td colspan="2">Remarks: It has an important series of polymers.</td></tr>
<tr><td>1,3,5-trioxane</td><td>polyoxymethylene</td></tr>
<tr><td></td><td></td><td></td><td>Remarks: paraldehyde is an anticonvulsant, hypnotic and sedative. In resin manufacture, serves as preservative.</td></tr>
<tr><td colspan="2">Remarks: polyformaldehyde is a thermoplastic used in precision parts that require high stiffness, low friction, and dimensional stability.</td><td></td><td>Remarks: metaldehyde is used as a pesticide against slugs, snails, and other gastropods.</td></tr>
</table>

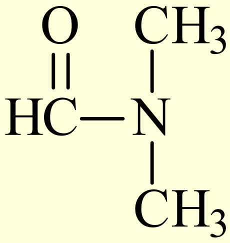
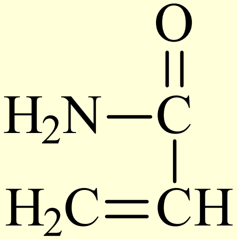
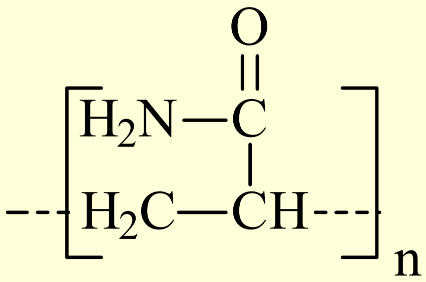
Ketones	General structure: R-COR'	Functional group: CO
Example: $(CH_3)_2CO$	Example: $(CH_3)(CO)(CH_2)(CO)(CH_3)$	
Name: Acetone; propanone	Name: Acetylacetone	
Remarks: Acetone is produced and disposed of in the human body through normal metabolic processes; is normally present in blood and urine; serves as solvent (of polystyrene, polycarbonate, and some polypropylenes)	Remarks: Acetylacetone exists in two tautomeric forms that rapidly interconvert. It is useful for synthesis of metal complexes.	
	 $OV(CH_3COCH_2COCH_3)_2$	

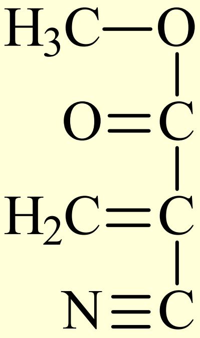
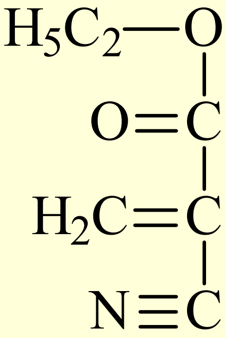
Carboxylic acids	General structure: R-COOH	Functional group: COOH
Example: HCOOH	Remarks: Formic acid occurs naturally, most notably in the venom of bee and ant stings.	
Name: Formic acid		
Example: CH_3COOH	Remarks: Acetic acid is the main component of vinegar.	
Name: Acetic acid		
Example: HOOCCOOH	Remarks: It is used as a mordant in dyeing processes, and in bleaches, especially for pulpwood.	
Name: Oxalic acid		
Example: $C_4H_6O_6$	 $\mathrm{HOOC-\overset{\overset{OH}{\vert}}{C}H_2-\overset{\overset{OH}{\vert}}{C}H_2-COOH}$	
Name: Tartaric acid		
Found in grapes, bananas		
Example: $C_6H_8O_7$	 $\mathrm{HOOC-CH_2-\underset{\underset{OH}{\vert}}{\overset{\overset{COOH}{\vert}}{C}}-CH_2-COOH}$	
Name: Citric acid		
Found in lemons, oranges, limes		
Example: $C_9H_8O_4$		
Name: Acetylsalicylic acid		
Aspirin is used in the treatment of a number of conditions, including fever, pain, and inflammatory diseases		

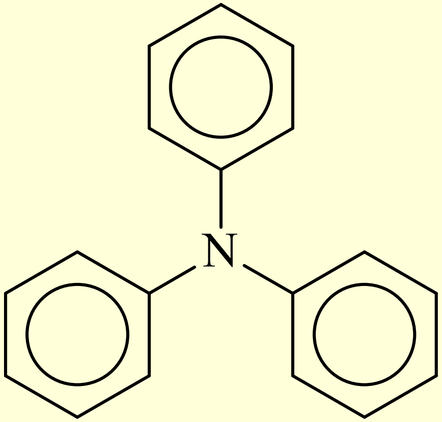
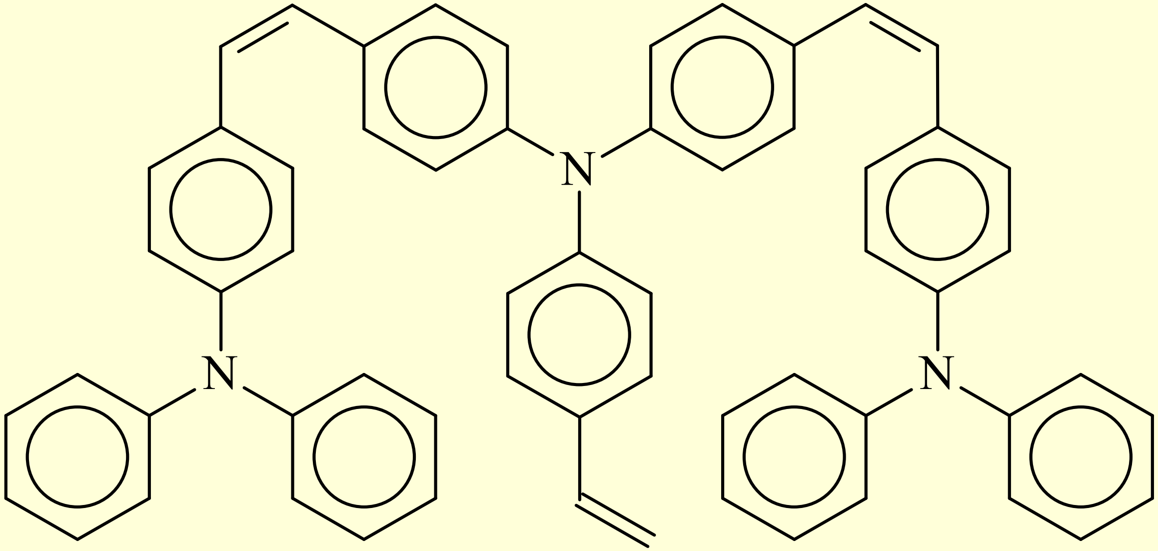
Anhydrides	General structure: R(CO)O(CO)R'	Functional group: OC-O-CO
	Example: $(CH_3CO)_2O$; Ac_2O, Ac=(CH_3CO)	Name: Acetic anhydride
	Remarks: Is a widely used reagent in organic synthesis.	
	 Salicylic acid + Ac_2O → Acetylsalicylic acid + HAc	
	Example: $C_4H_2O_3$ and its dimmer	Name: Maleic anhydride
		Remarks: cyclobutane tetracarboxylic dianhydride (maleic anhydride dimer) is used in the production of polyimides and as an alignment film for liquid crystal displays.
Poly-anhydrides	Remarks: Anhydride bonds in aromatic polyanhydrides are water-labile - the polymer chain breaks apart at different reaction rates at the anhydride bond. Resulted carboxylic acid groups are easily metabolized and therefore biocompatible. Applications include releasing of physically entrapped or encapsulated drugs by well-defined kinetics.	

<table>
<tr><td>Esters</td><td>General structure: R(COO)R'</td><td>Functional group: COO</td></tr>
<tr><td colspan="3">Remarks: Naturally occurring fats and oils are the fatty acid esters.</td></tr>
<tr><td></td><td>Example: EtOAc; Et=CH_2CH_3; Ac=CH_3CO</td><td>Name: Ethyl acetate</td></tr>
<tr><td colspan="3">Remarks: Ethyl acetate, with a characteristic sweet smell (like pear drops) and is used in glues, and decaffeinating tea and coffee (is manufactured for use as a solvent). Ethyl acetate is the most common ester in wine.</td></tr>
<tr><td>Inorganic esters</td><td colspan="2">General structure: compounds derived from the condensation of RCOOH and R'OH. Examples:</td></tr>
<tr><td colspan="2">
It is used as a plasticizer and a fire retardant.</td><td>
Apps include Li ion cell batteries with high temperature stability (until 302°C), high power density, and long shelf life as well as super-capacitors.</td></tr>
</table>

See http://www.arl.army.mil/www/pages/556/0933TFSPurifiedLiBOB.pdf

Amides	General structure: R(CO)NR'R"	Functional group: OCN
Remarks: Amides are used in nature and technology as structural materials.		
	Example: $(CH_3)_2NCHO$	Name: Dimethylformamide; DMF
	Remarks: DMF is a solvent with low evaporation rate; is used in the production of acrylic fibers and plastics and as a solvent in peptide coupling for pharmaceuticals, in the development and production of pesticides, and in the manufacture of adhesives, synthetic leathers, fibers, films, and surface coatings.	
	Example: $(H_2CCH)(CO)NH_2$	Remarks: Acrylamide is used to synthesize polyacrylamides
	Name: Acrylamide; Acrylic amide	Remarks: One of the properties of polyacrylamide is to flocculate solids in a liquid and find its uses in wastewater treatment, papermaking, pesticides, cosmetics, sugar manufacturing, and soil conditioning.
	Example: polyacrylamide	

<table>
<tr><td>Nitriles</td><td>General structure: RCN</td><td>Functional group: CN</td><td></td></tr>
<tr><td></td><td>Example: H_3CCN</td><td>Name: acetonitrile</td><td></td></tr>
<tr><td colspan="4">Acetonitrile is used mainly as solvent for purification of butadiene in refineries.</td></tr>
<tr><td></td><td>Example: $(CH3)_2CHCN$</td><td>Name: Isobutyronitrile</td><td></td></tr>
<tr><td colspan="4">It is used as organic solvent, for producing insecticides, and as gasoline additive.</td></tr>
<tr><td rowspan="3"> $\begin{array}{r} H_3C-O \\ | \\ O=C \\ | \\ H_2C=C \\ | \\ N\equiv C \end{array}$</td><td>Example: $C_5H_5NO_2$</td><td>Example: $C_5H_5NO_2$</td><td rowspan="3"> $\begin{array}{r} H_5C_2-O \\ | \\ O=C \\ | \\ H_2C=C \\ | \\ N\equiv C \end{array}$</td></tr>
<tr><td>Name: Methyl cyanoacrylate (MCA)</td><td>Name: Ethyl cyanoacrylate (ECA)</td></tr>
<tr><td colspan="2">Remarks: MCA and ECA are colorless liquids with low viscosity, being used as the main component of certain glues. Both polymerizes rapidly in presence of moisture.</td></tr>
<tr><td></td><td>Example: NCCCCN</td><td>Name: Dicyanoacetylene</td><td></td></tr>
<tr><td></td><td colspan="2">Dicyanoacetylene is liquid which can explode to carbon powder and nitrogen gas. It burns in oxygen with a bright blue-white flame at a temperature of 5000 °C - hottest flame of any chemical.</td><td></td></tr>
</table>

<table>
<tr><td>Amines</td><td></td><td></td></tr>
<tr><td>General structure: R_3N</td><td>Functional group: N</td><td></td></tr>
<tr><td>Example: H_2NCH_3</td><td>Example: $HN(CH_3)_2$</td><td>Example: $N(CH_3)_3$</td></tr>
<tr><td>Name: Methylamine</td><td>Name: Dimethylamine</td><td>Name: Trimethylamine</td></tr>
<tr><td colspan="3">Methylamines are gases with strong odor similar to fish; are used as building blocks for the synthesis of many compounds.</td></tr>
<tr><td rowspan="4"></td><td colspan="2">Example: $(C_6H_5)_3N$</td></tr>
<tr><td colspan="2">Name: Triphenylamine</td></tr>
<tr><td colspan="2">Remarks: Triphenylamine derivatives have useful applications in electric conductivity and electroluminescence, and they are used in organic light-emitting diodes.</td></tr>
<tr><td colspan="2">Triphenylamine derivative for solar cells</td></tr>
<tr><td colspan="3"></td></tr>
</table>

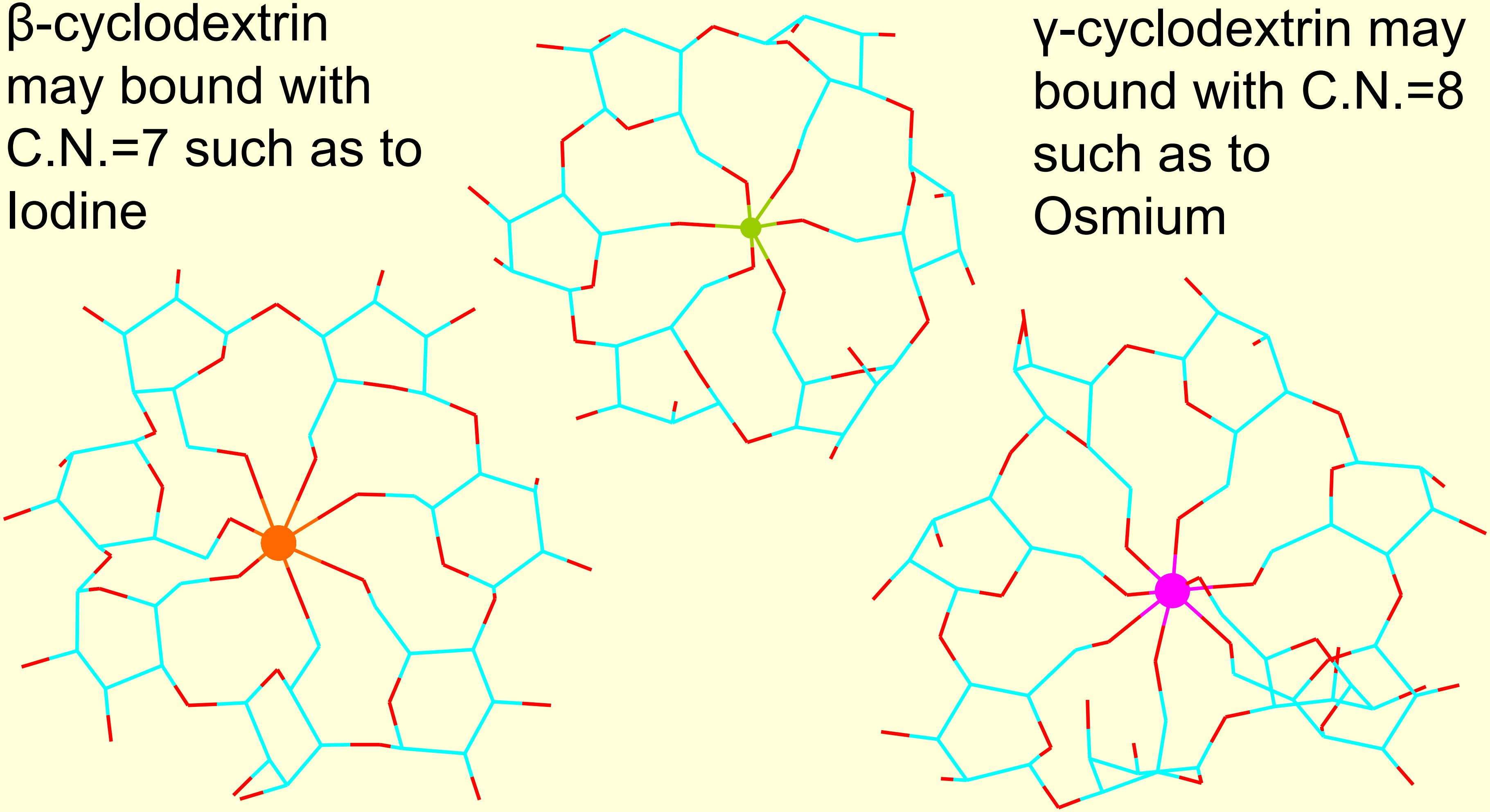
Cyclodextrins

Sugar molecules bound together in a ring.

α-cyclodextrin may bound with C.N.=6 such as to Selenium

β-cyclodextrin may bound with C.N.=7 such as to Iodine

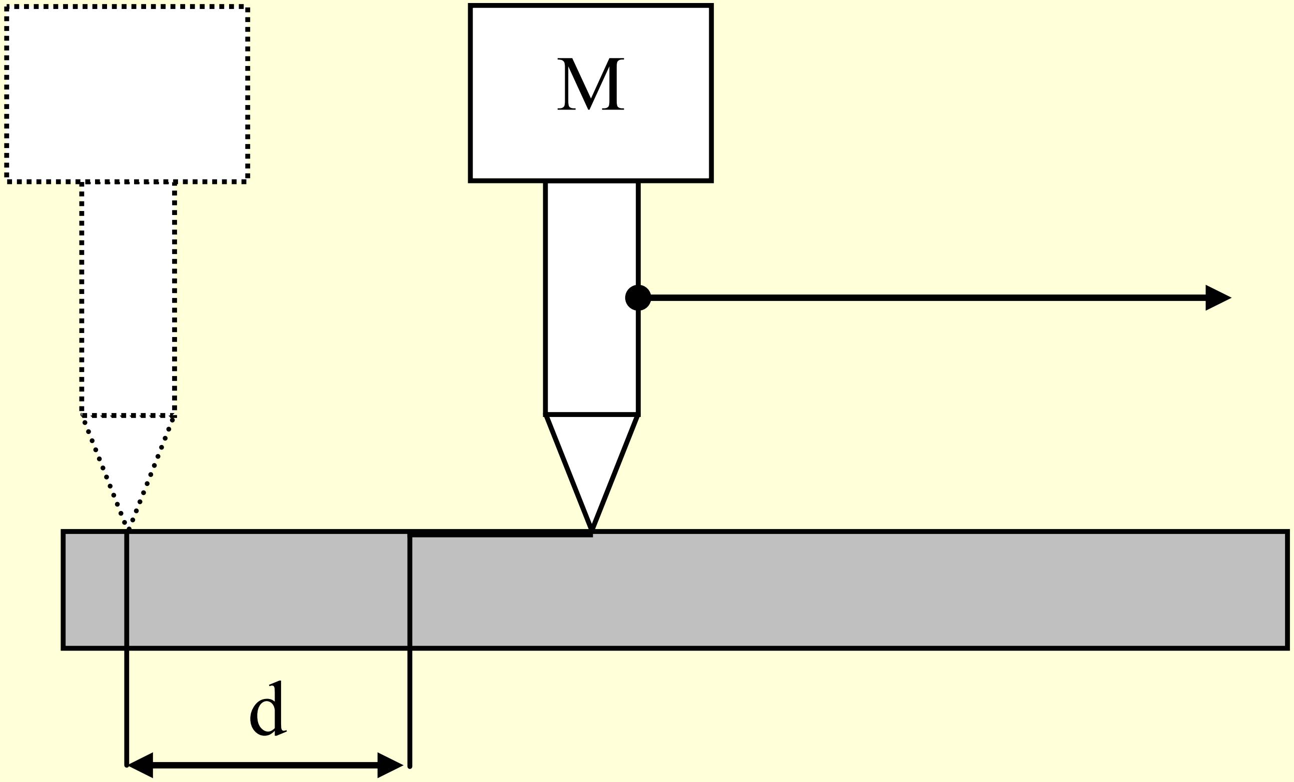
γ-cyclodextrin may bound with C.N.=8 such as to Osmium



Hardness

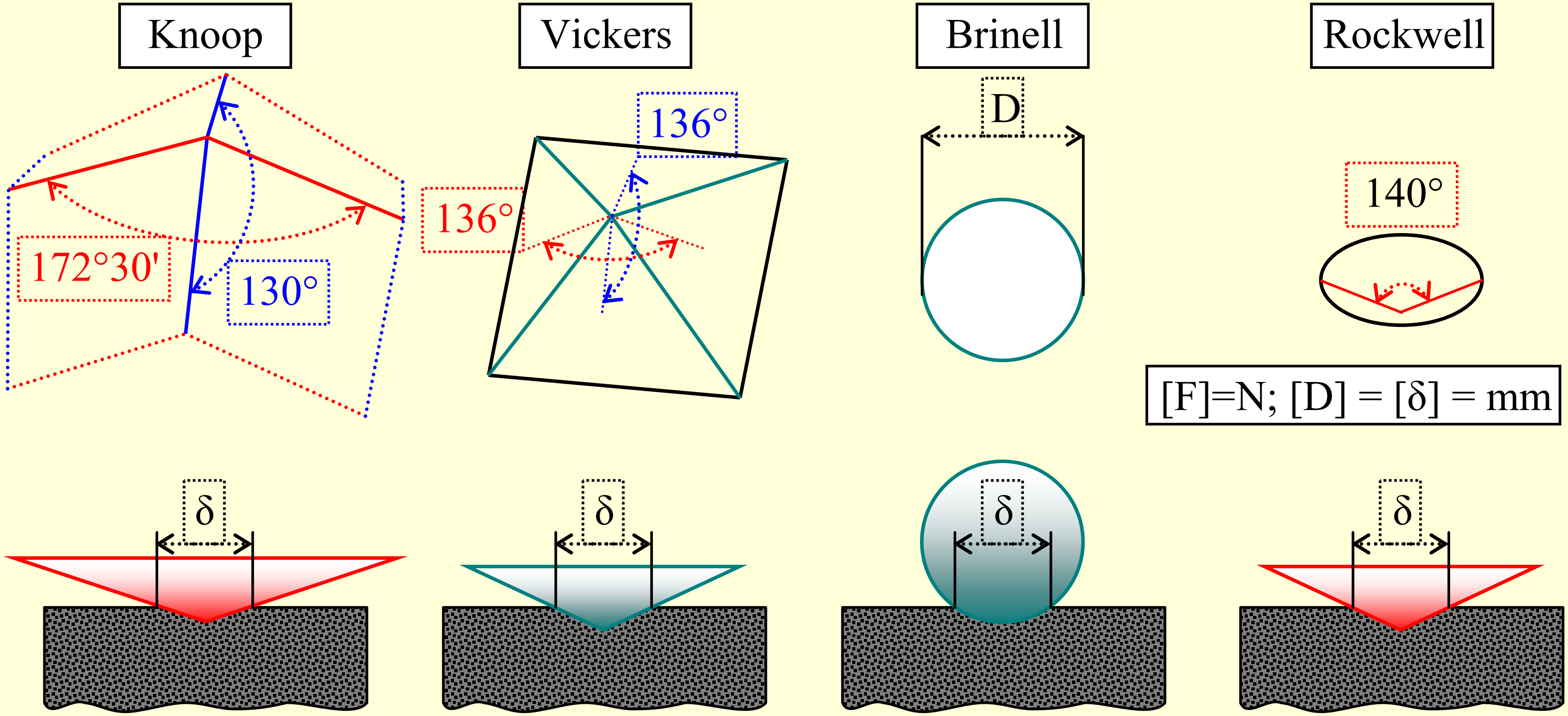
- In **mineralogy**, *hardness* commonly refers to a material's ability to penetrate softer materials. An object made of a *hard* material will scratch an object made of a *softer* material - **Scratch hardness** conducted with **sclerometer**.
- Also known as *dynamic* or *absolute hardness*, rebound hardness measures the height of rebound of an indenter dropped onto a material using an instrument known as a **scleroscope** - **Rebound, dynamic or absolute hardness**.
- In *materials science*, hardness is the characteristic of a solid material expressing its *resistance to permanent deformation*. - **Indentation hardness**.

Hardness with sclerometer



Sclerometer - a mineralogist's (usually) instrument used to measure the hardness of materials. The instrument is designed to determine the degree of hardness of a given **mineral** by applying pressure on a moving diamond point until a "scratch" has occurred.

Hardness with scleroscope (intender)



[F]=N; [D] = [δ] = mm

$$H_K = 0.01423\frac{F}{\delta^2}$$

$$H_V = 0.001854\frac{F}{\delta^2}$$

$$H_B = \frac{2F}{\pi D}\left(D - \sqrt{D^2 - \delta^2}\right)^{-1}$$

$$H_R = 100 - 182\delta$$

$$F \in \{600, 1000, 1500\}$$

Hardness scales

- **Brinell** *BS EN ISO 6506 Parts 1, 2, 3, and 4: 2005, Metallic materials - Brinell hardness test*
- **Knoop** *ISO 4545 Parts 1, 2, 3, and 4: 2005, Metallic materials - Knoop hardness test*
- **Rockwell** *BS EN ISO 6508 Parts 1, 2, and 3: 2005, Metallic materials - Rockwell hardness test (scales A, B, C, D, E, F, G, H, K, N, T)*
- **Vickers** *BS EN ISO 6507 Parts 1, 2, and 3: 2005, Metallic materials - Vickers hardness test*
- **Mohs** *A scale to measure hardness was devised by Austrian mineralogist Frederick (Friedrich) Mohs in 1822*
- **Barcol** *ASTM D2583-95 e1:2001, Standard Test Method for Indentation Hardness of Rigid Plastics by Means of a Barcol Impressor*

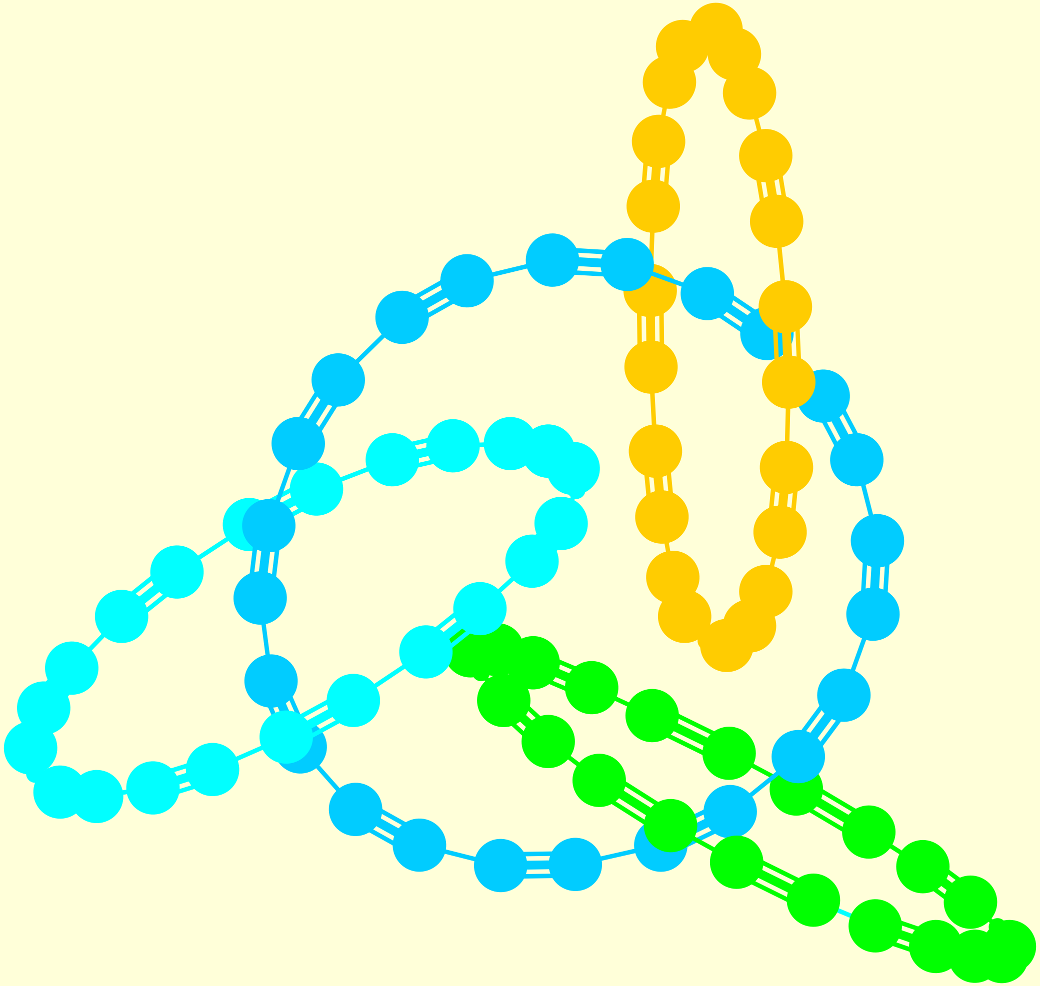
http://courses.washington.edu/me354a/chap5.pdf

Ultra-hard advanced materials – β-CN

- In 1989, Marvin Cohen and his graduate student Amy Liu (then at UC Berkeley) devised a theoretical model to predict a crystal's stiffness. Cohen's model clearly indicated that a carbon nitride crystal should be stiffer (and possibly harder) than diamond. The race was on to obtain the stuff in crystalline form and measure its properties. Some early efforts by the team of Yip-Wah Chung (Northwestern University) resulted in a layered composite of titanium nitride and carbon nitride (a so-called superlattice) which was, surprisingly, almost as hard as diamond. Estimates from proposed molecular structure indicate the hardness of ***beta carbon nitride*** should also be greater than diamond. This material has not yet been successfully synthesized.

Ultra-hard advanced materials - C≡C

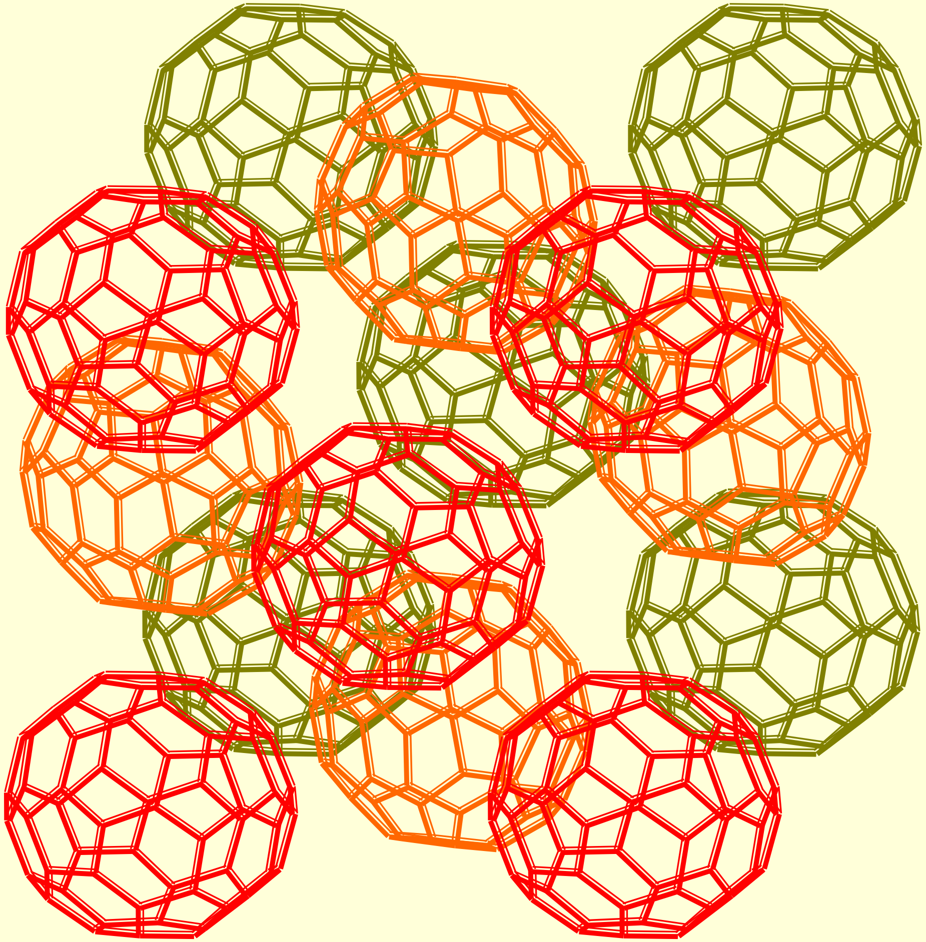
- In the December 4th, 2005 issue of The Jerusalem Post, Professors Eli Altus, Harold Basch and Shmaryahu Hoz, with doctoral student Lior Itzhaki report the discovery of **Polyyne**, a material 40 times harder than diamond. It is a superhard molecular rod, comprised of acetylene units.



Ultra-hard advanced materials – ‘centered faces cubes’ crystallized C_{60}

“C_{60}-Fullerene at 153 K, C_{60} crystallizes in a face centered cubic arrangement” -

H-B Burgi, E Blanc, D Schwarzenbach, Shengzhong Liu, Ying-jie Lu, M M Kappes, J A Ibers, Angew Chem Int Ed Engl 1992;31:640



Ultrahard fullerite

Ultra-hard advanced materials - ADNRs

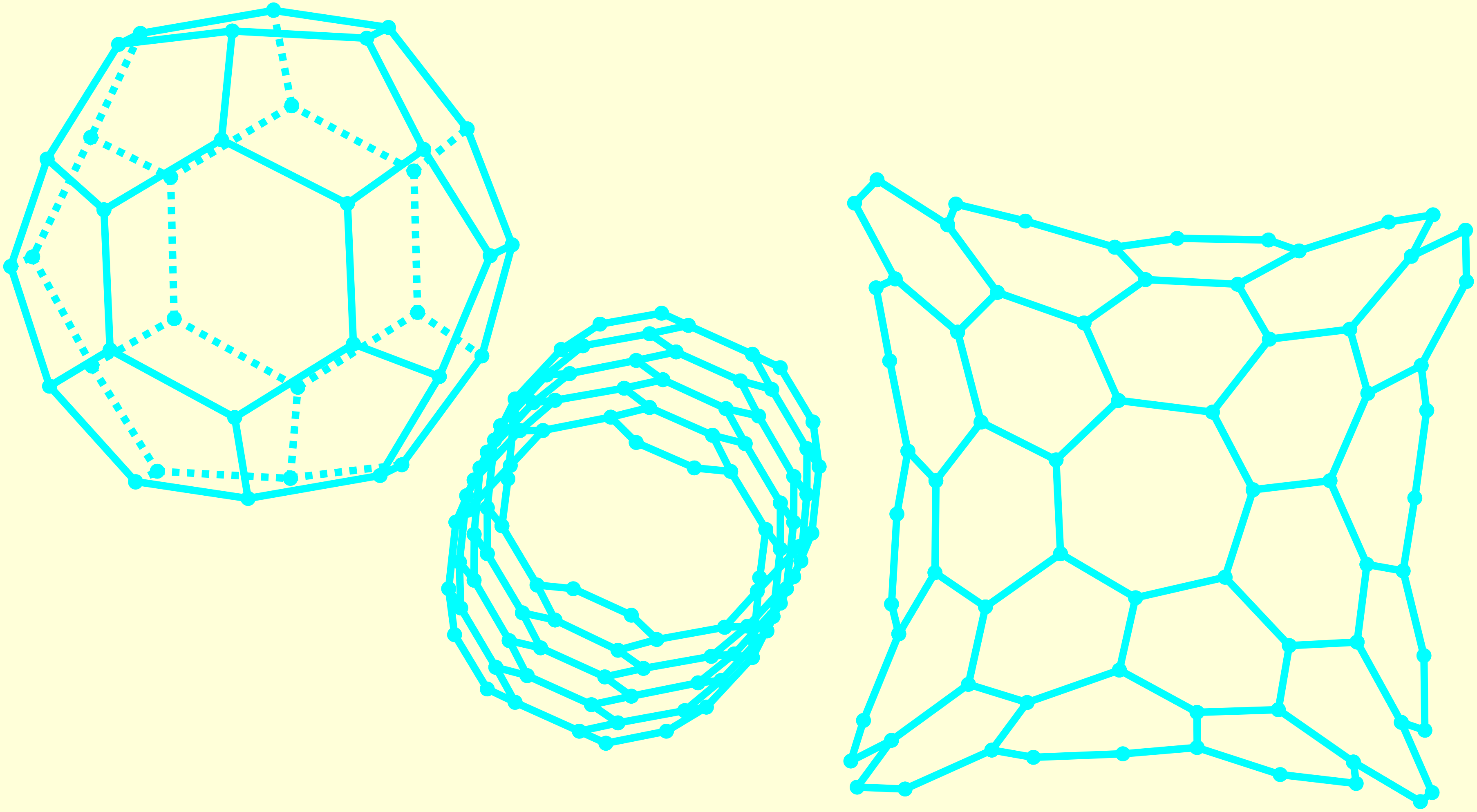
- **Synthetic diamond** (Lonsdaelite allotrope) obtained by submitting to 2400K and 5-7 GPa crystals synthesized by a chemical vapor deposition (CVD) process was found to be at least 50% harder than natural diamond.
- **Ultrahard fullerite (C60)** were found to be harder than diamond, and which can be used to create even harder materials, such as aggregated diamond nanorods.
- **Aggregated diamond nanorods**, or ADNRs, are an allotrope of carbon believed to be the least compressible material known to humankind, as measured by its isothermal bulk modulus; aggregated diamond nanorods have a modulus of 491 gigapascals (GPa), while a conventional diamond has a modulus of 442 GPa (hardness 1.11 times than diamond). ADNRs are also 0.3% denser than regular diamond. The process to produce the substance consists in compressing the C-60 molecules to 2-20 GPa, and heating to 300-2500 K. ADNRs is a series of interconnected diamond nanorods, with diameters of between 5 and 20 nanometres and lengths of around 1 micrometre each.

Hardness relativity

C allotrope	Hardness (GPa)
CCP Diamond	100±3; 167±5
HCP Diamond	152±4
Ultrahard fullerite	290±30
ADNRs	310±40
wurtzite-BC_2N	79±2

BC_2N (with same arrangement of CCP as diamond) possess an anisotropy due to the non-uniform charge distribution (B have 3 valence electrons and N have 5). Consequently, this leads to electrostatic effects at surface much higher than of diamond with other materials like iron, nickel and even silicon in a tribological environment. This seems to be a plausible reason why BC2N was found as an efficient cutting tip to machine ferrous alloys and silicon in comparison to a diamond tip. Same explanation should be given for the unexpected polyyne hardness compared with diamond.

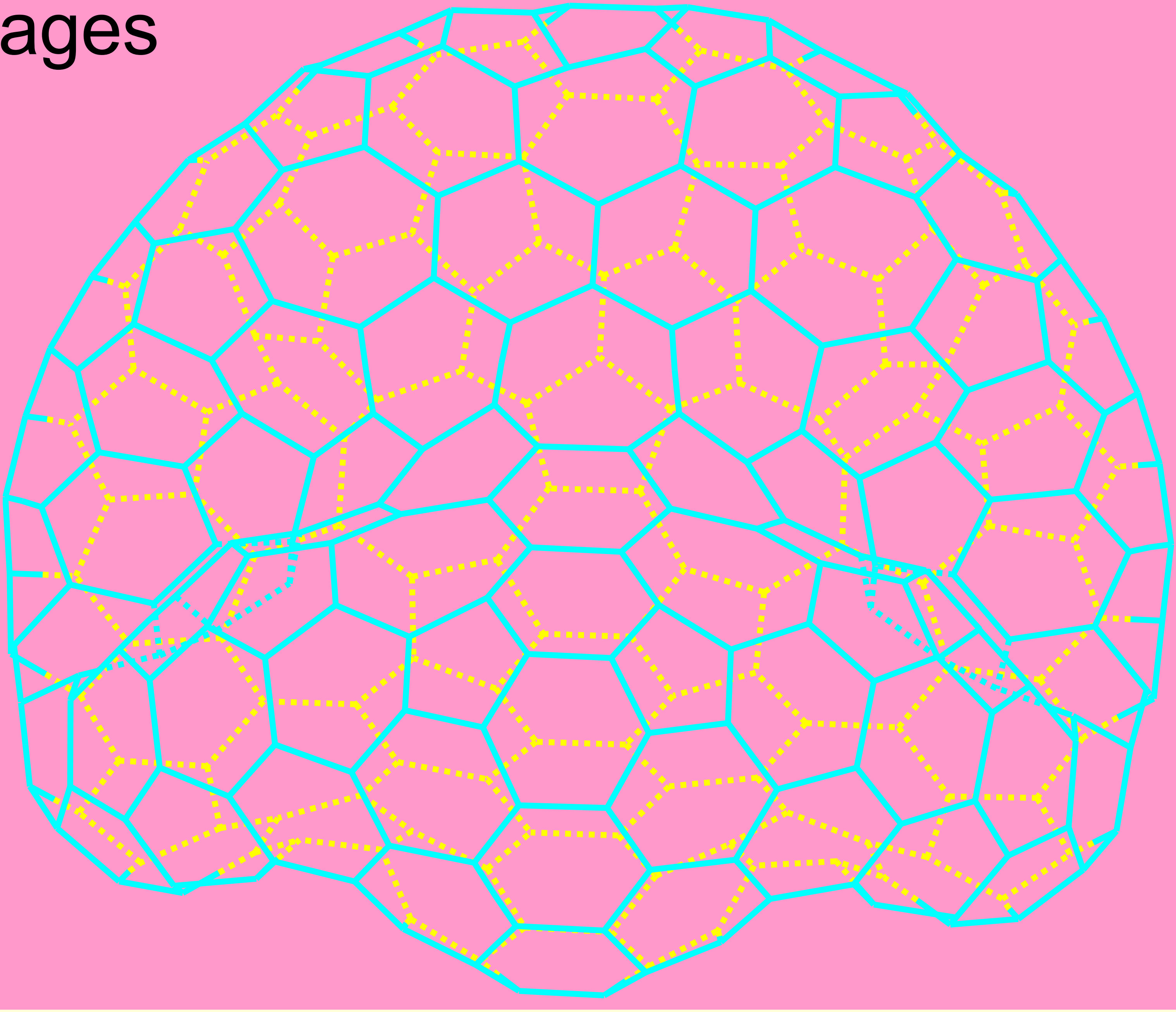
Fullerene, nanotube & nanofoam



Number of fullerenes

n	Fullerenes	n	Fullerenes
<20	0	34	6
20	1	36	15
22	0	38	17
24	1	40	40
26	1	42	45
28	2	44	89
30	3	46	116
32	6	48	199
…	…	…	…
2n	A007894 (http://oeis.org/A007894)		

Nanocages



Q & R

In connection with compounds of the carbon:		
	1	$H_3C\text{-}O\text{-}CH_3$ is an ether and $H_3C\text{-}S\text{-}CH_3$ is a thiol
	1	$HCOOH$ and CH_3COOH are acids
	0	$HCOOH$ and CH_3COOH are alcohols
	0	CH_3OH and CH_3CH_2OH are acids
	1	CH_3OH and CH_3CH_2OH are alcohols
	0	Haloalkanes have the general structure R-H, where H is hydrogen
	1	Haloalkanes have the general structure R-X, where X is halogen
	0	Alkanes have the molecular formula C_nH_{2n} (ex. CH_2)
	1	Alkanes have the molecular formula C_nH_{2n+2} (ex. CH_4)

Q & R

In connection with compounds of the carbon:		
	0	Fullerenes, nanotubes and nanofoams are allotropes of silicium
	1	Fullerenes, nanotubes and nanofoams are allotropes of carbon
	0	$H\text{-}(CO)\text{-}N(CH_3)_2$ is an amine and $N(CH_3)_3$ is an amide
	1	$H\text{-}(CO)\text{-}N(CH_3)_2$ is an amide and $N(CH_3)_3$ is an amine
	0	$HC_3\text{-}(CO)\text{-}H$ is a ketone and $HC_3\text{-}(CO)\text{-}CH_3$ is an aldehyde
	1	$HC_3\text{-}(CO)\text{-}H$ is an aldehyde and $HC_3\text{-}(CO)\text{-}CH_3$ is a ketone
	0	$H_2C{=}CH_2$ is an alkyne and an alkene is $HC{\equiv}CH$
	1	$H_2C{=}CH_2$ is an alkene and an alkyne is $HC{\equiv}CH$
	0	$H_3C\text{-}O\text{-}CH_3$ is a thiol and $H_3C\text{-}S\text{-}CH_3$ is an ether

Course 12

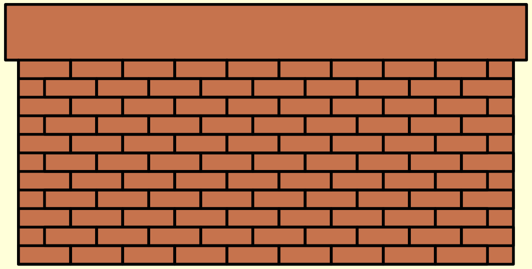
Ceramics

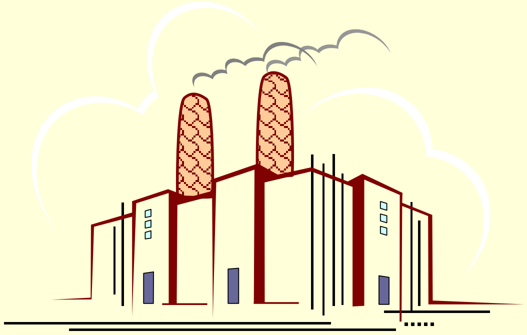
Semiconductors

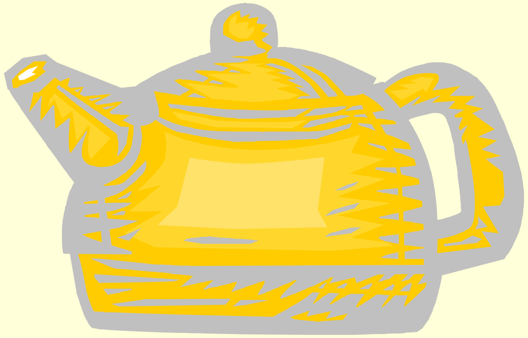
Superconductors

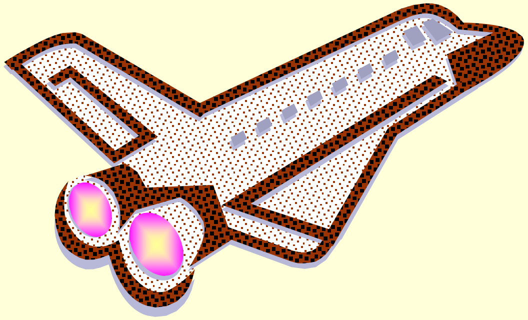
Ceramics types

- Structural (for constructions)
  - bricks, pipes, floor and roof tiles
- Refractories
  - kiln linings, gas fire radiants, steel and glass making crucibles
- Whitewares
  - tableware, cookware, wall tiles, pottery products and sanitary ware
- Technical (engineering, advanced, special)
  - tiles used in the Space Shuttle program, gas burner nozzles, ballistic protection, nuclear fuel uranium oxide pellets, biomedical implants, coatings of jet engine turbine blades, ceramic disk brake, missile nose cones



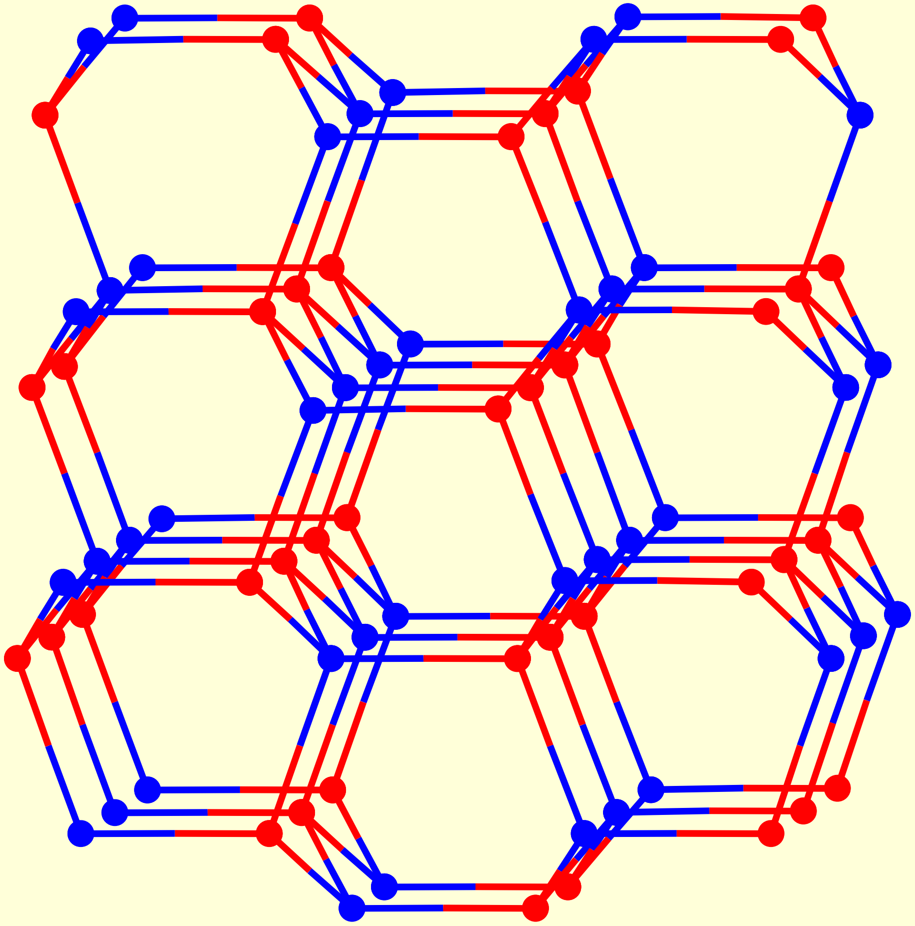






Technical ceramics

- Oxides
  - alumina, beryllia, ceria, zirconia
- Nonoxides
  - carbide, boride, nitride, silicide
- Composite materials
  - particulate reinforced, fiber reinforced, combinations of oxides and nonoxides



BeO: Formation of BeO from beryllium and oxygen releases the highest energy per mass of reactants for any chemical reaction, close to 24Mj/kg.

Technical ceramics for apps

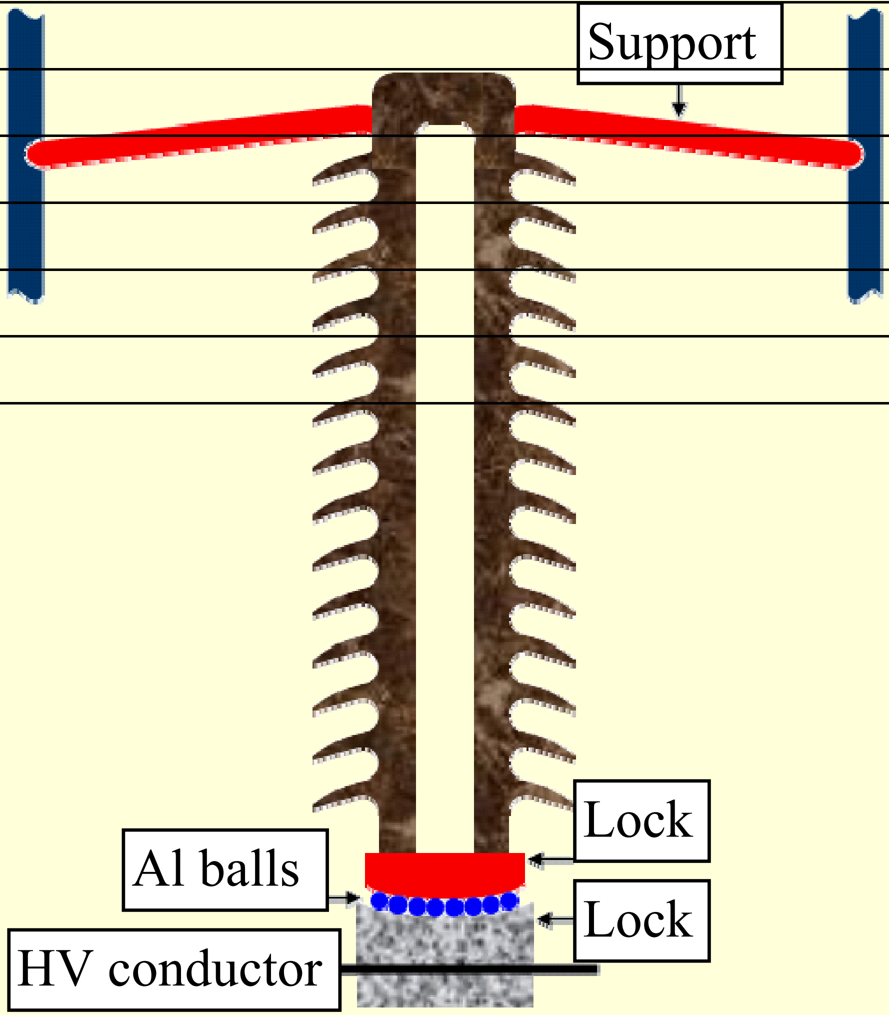
- Porcelains for high voltage
- Ceramics with special electric properties
- Ceramics with special magnetic properties
- Ceramics with special thermal properties

Porcelains for high voltage

- With increasing of long distance electricity transportation at high voltage, high voltage insulators needs increased. High voltage insulators must have very good electrical insulating properties so as to have good mechanical properties (resistance);
- Composition of porcelains for low voltage does not differ much from that of the high voltage for. They are the areas of application switches, lamp sockets, fuse blocks and handles.
- The advantage of ceramic insulators which frequently indicate their use, are superior electrical properties, absence of creep or deformation under stress at room temperature and greater resistance to environmental changes. One of the great advantages of ceramics as insulators is the fact that they are not sensitive to the minor changes in composition, fabrication, techniques, and firing temperature.

High voltage isolators

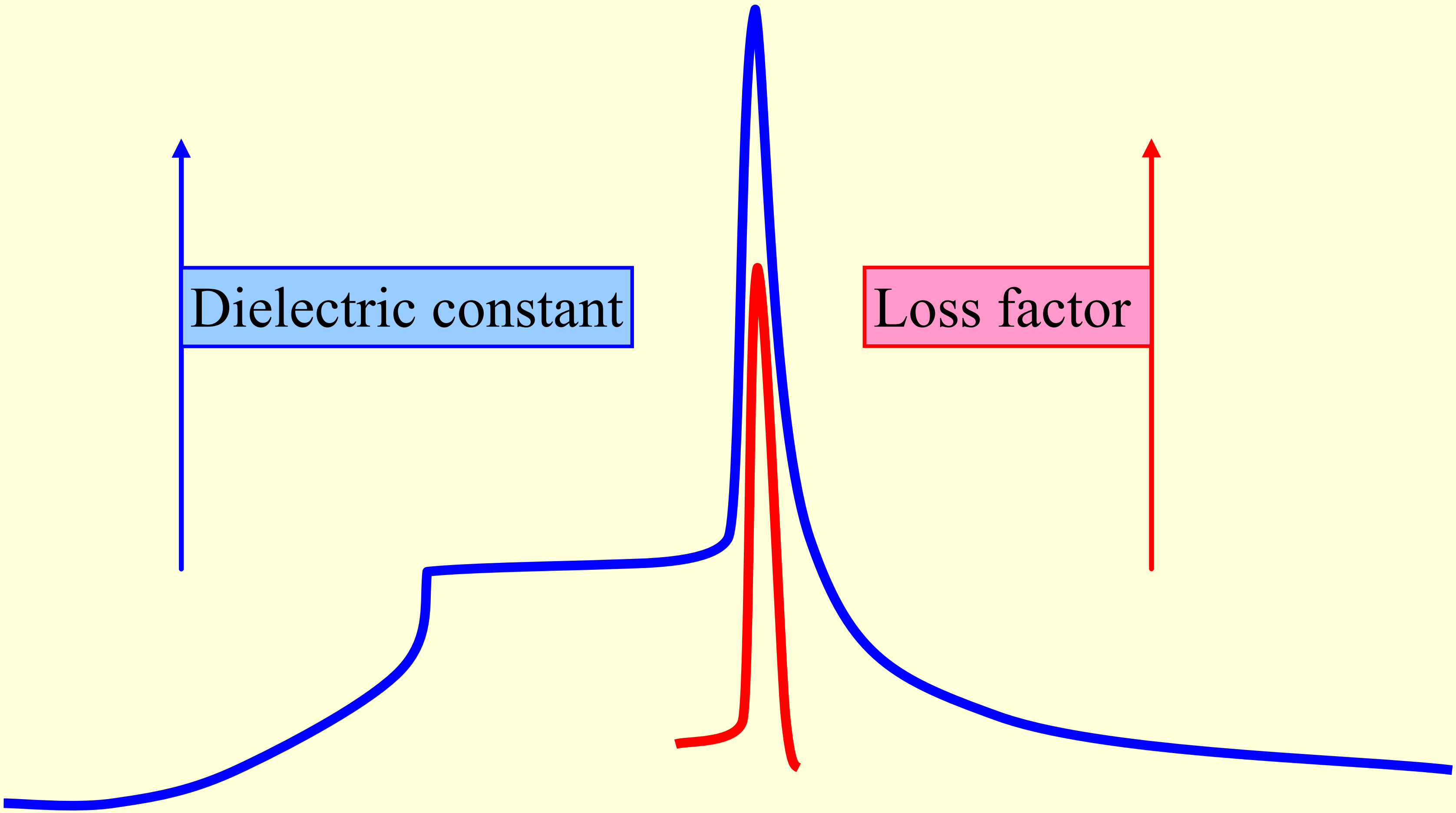
%	Feldspar ($KAlSi_3O_8 + NaAlSi_3O_8 + CaAl_2Si_2O_8$)	Quartz (SiO_2)	Clay
SiO_2	[43-69]	≥ 98	[50-70]
Al_2O_3	[18-37]	≤ 1	[20-35]
K_2O	[0-17]	≤ 1	≤ 1
CaO	[0-12]	≤ 1	≤ 1
Na_2O	[0-20]	≤ 1	≤ 1
Insulator	[20-25]	[15-20]	[55-65]



Ceramics with special electric properties

- **Electrical breakdown voltage** (in volts per millimeter of thickness) is an important factor in high stress conditions, where ceramics loss is irreversible; the values of these voltages ranges from 100 V/mm to 200 V/mm;
- **Volume resistivity** (ρ, expressed in Ω·cm), at different temperatures; most ceramics have about 10^{14} Ω·cm at room temperature; this value decreases with increasing temperature; at 900°C falls in 10^{3}-10^{7} Ω·cm range;
- **Dielectric constant κ'** (the ratio of the capacity of a condenser which has insulating material the ceramics and the capacity of the condenser having air); κ' for ceramics are from 4 to 10, but rutile (TiO_2) have 100;
  - The temperature coefficient of κ', $d\kappa'/dT$;
  - The frequency coefficient of κ', $d\kappa'/d\omega$;
- **Loss factor κ"** (the energy lost in ergs per cubic centimeter per cycle of oscillation) is important for high frequency uses;

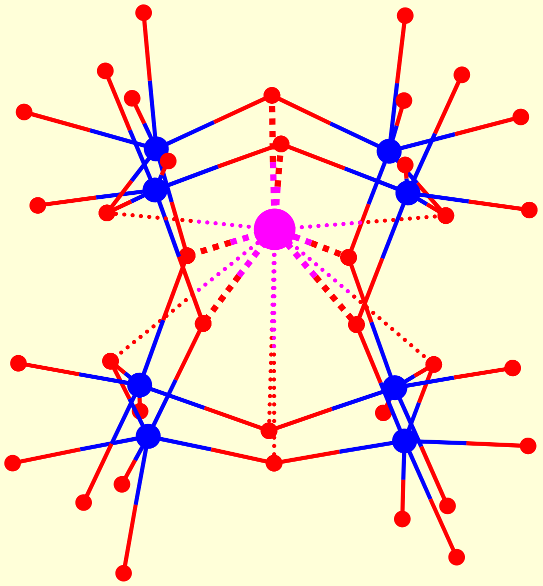
$BaTiO_3$: Dielectric constant κ' and loss factor κ''

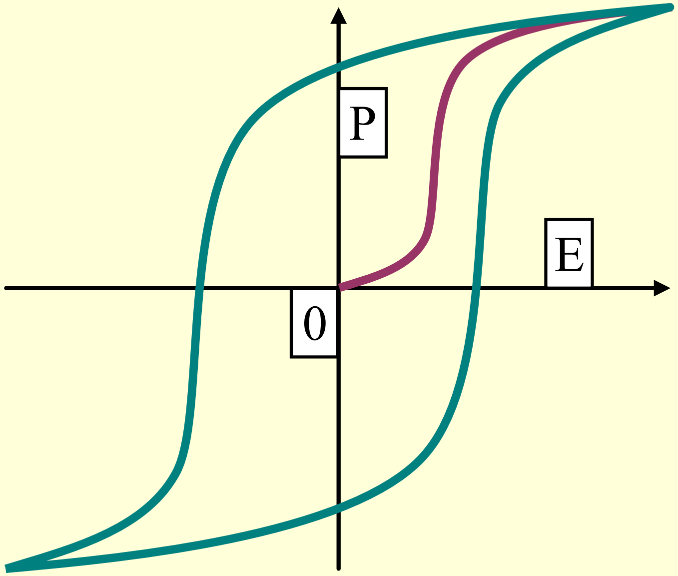


Excepting the peak at 190°C (see figure) have relatively low loss factor.

Ferroelectrics

- These materials joins good dielectric constants with low electrical loss factors.
- For example, if a ferroelectric material is placed between the plates of a capacitor, and electric field strength increases resulting charge will not be proportional as in simple dielectrics (behaves hysteresis cycles).
- Most ferroelectric materials are with perovskite-like structure.
- Elementary cell contains $3 \cdot O^{2-}$, $1 \cdot M^{2+}$ and $1 \cdot Ti^{4+}$. R is usually Ba^{2+} (Ca^{2+}, Mg^{2+}, Sr^{2+}, Rb^{2+}, Cd^{2+} can be added to provide a wide range of ferroelectric properties).



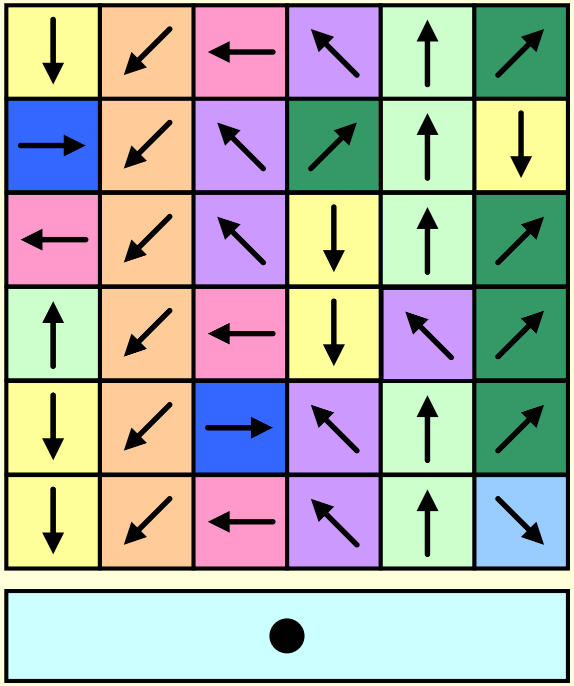


P polarization
E electric field

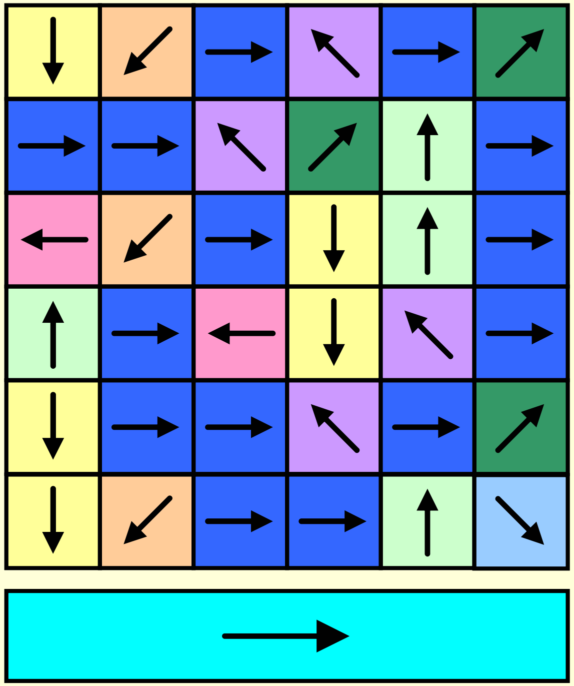
Ferromagnets

- All ferromagnetic materials possess an irreversible relationship between the applied field H and magnetization induced B. This causes hysteresis, revealed to all magnetic materials: the crystals that are formed in these magnetic materials contain entities (quantum elementary units of volume). When is not magnetized, the magnetic fields is random. When is partially magnetized, there are some alignment, but by no means all. But when it is saturated magnetic, all fields are aligned.
- It is used for surface magnetic disk drives (diskettes, hard disks). For example, floppy drives 3.5 "and 1.44 MB must be applied magnetic field of 300 Oersted to achieve a correct writing. It is therefore the saturation magnetic field. Overcoming this field is also prohibited, as it affected neighboring areas on which there is writing field.

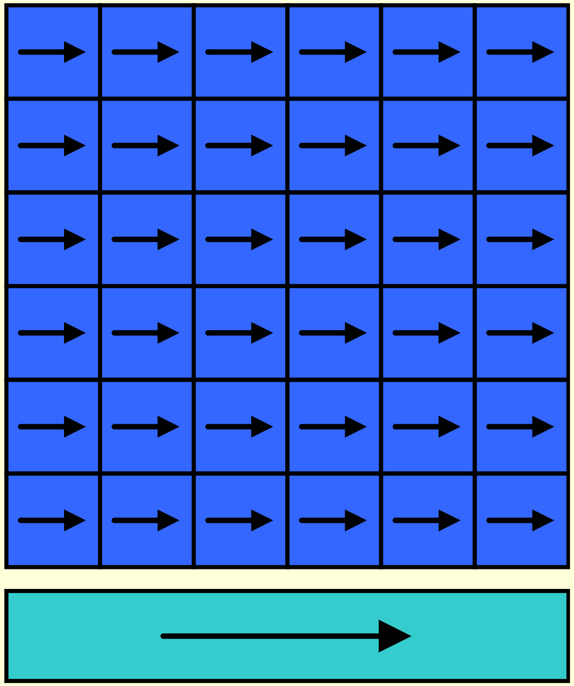
Magnetic memories



H = 0 A/m

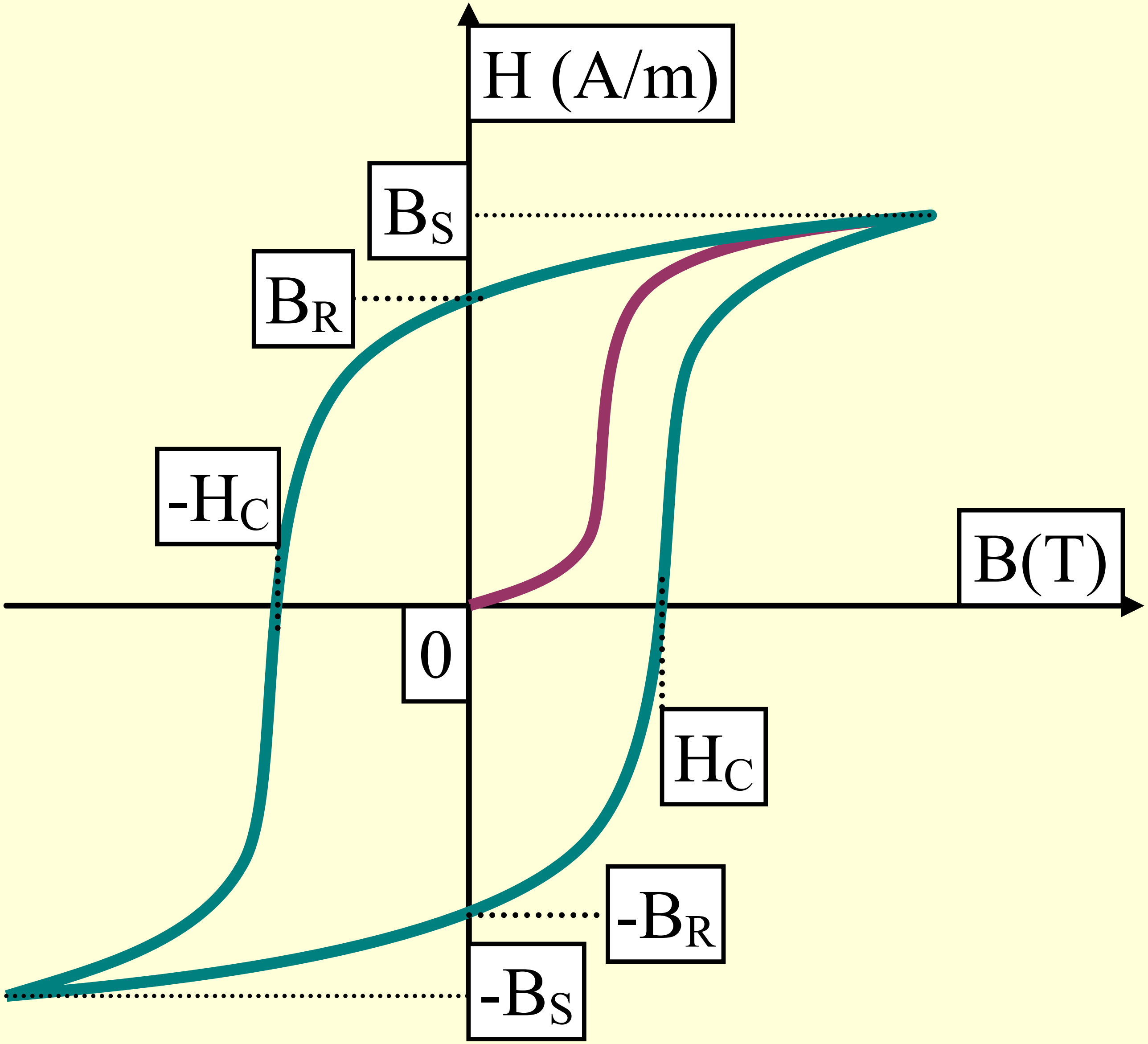


H = 12 kA/m



H = 24 kA/m

Magnetic hysteresis



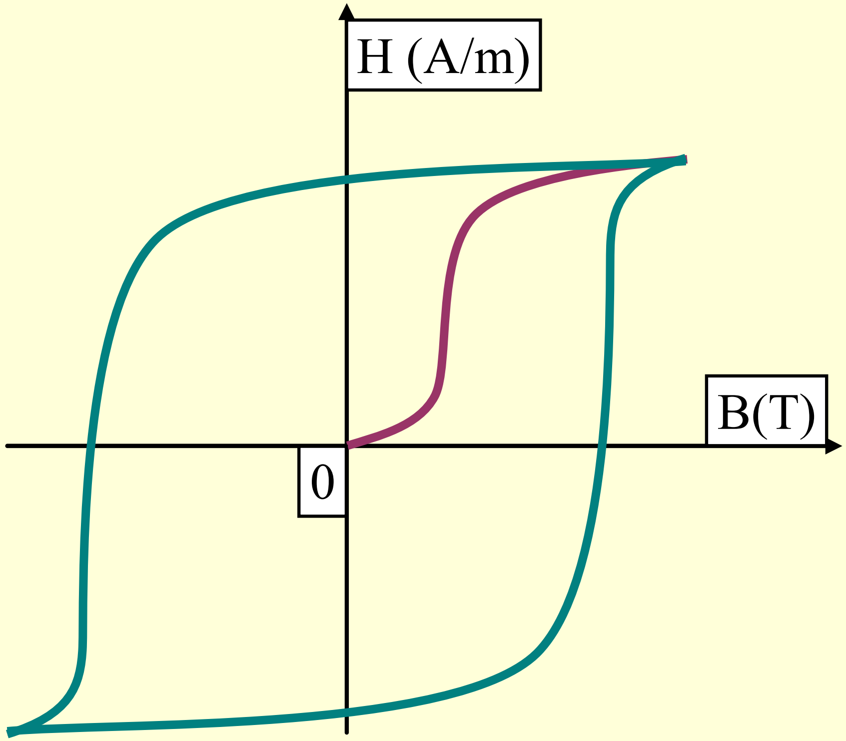
Magnetic hysteresis - explanation

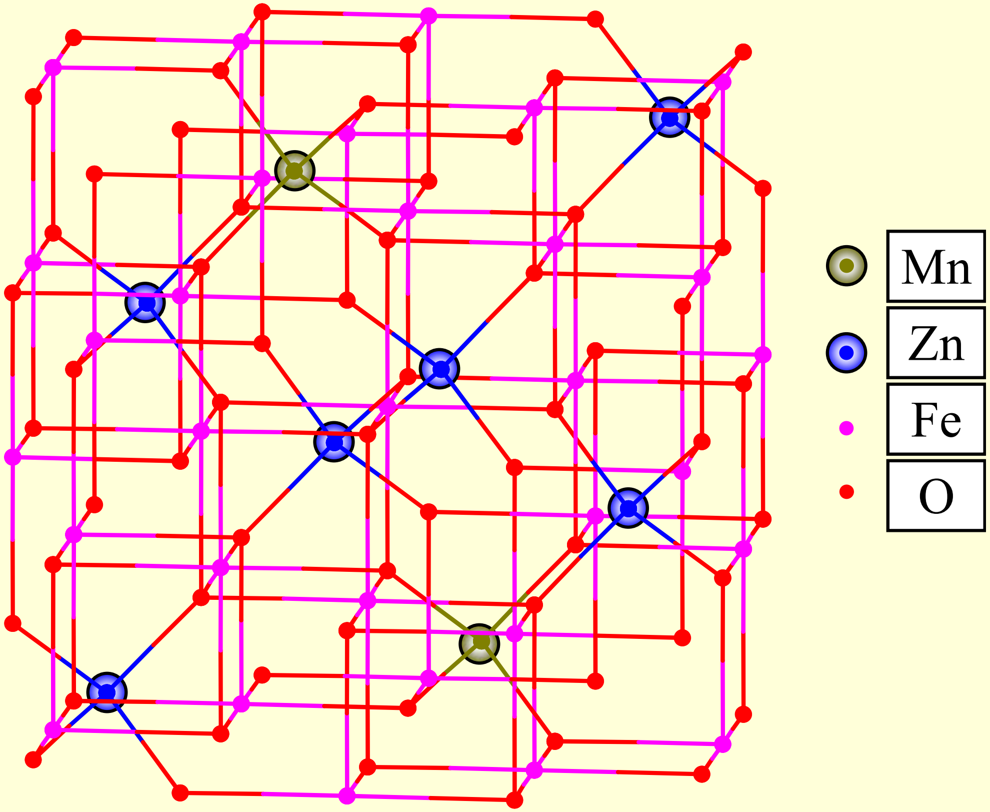
- This diagram is represented with applied field (H) on the abscissa and induced magnetization (B) on the ordinate. From the point of no magnetic conditions (0) relationship between H and B evolves as S-shaped curve (with an inflection point) to the point of maximum magnetic intensity applied H_S, the induced magnetization is $+B_S$. If now applied field decreases, the magnetization evolves curves 2, 3 and 4 intersect ordered in B_R (remanent magnetization) abscissa in $-H_C$ (field strength cancellation of residual magnetization) and if continuous $-H_S$ magnetization to magnetization will then $-B_S$. Reapply now increasing magnetic field will cause the magnetization to evolve curves 5, 6 and 7, with the same meaning for point $-B_R$, $+H_C$ and $+B_S$. Even if it stops applying the magnetic field for a long time curve from 0 to $+B_S$ will not ever be followed ceramic material unless it is previously demagnetized. This can be done for example by heating above the Curie temperature. The second quadrant, or demagnetization curve is very important for materials used in the manufacture of permanent magnets.
- Curie temperature: the temperature at which a material loses its magnetic properties

Ferrites

- These lightweight magnetic materials have a spinel structure: MFe_2O_4 where M can be Mg, Ni, Co, Cd, Zn or Mn. Antenna wires are used, magnetostrictive materials, memory cores, components of deflection cathode-ray tubes and transformers.
- Must have both good physical and electrical properties and these properties should be uniform both mass component and from one component to another. These ceramic magnets are valuable in high-frequency transformer cores due to a very low hysteresis losses. Special ferrites with square-shaped hysteresis as shown, are used as memory elements in high-speed computers.

Computer memories: hysteresis loop and structural elementary cells

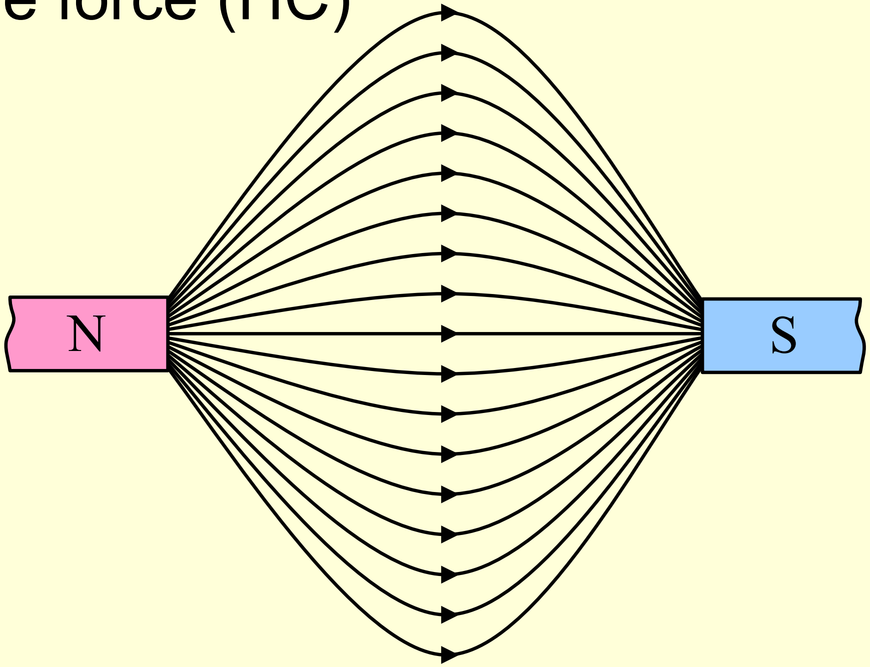




(optimized) $Mn_xZn_{1-x}Fe_{2+\delta}O_4 \leftarrow Mn_{0.25}Zn_{0.75}Fe_2O_4$

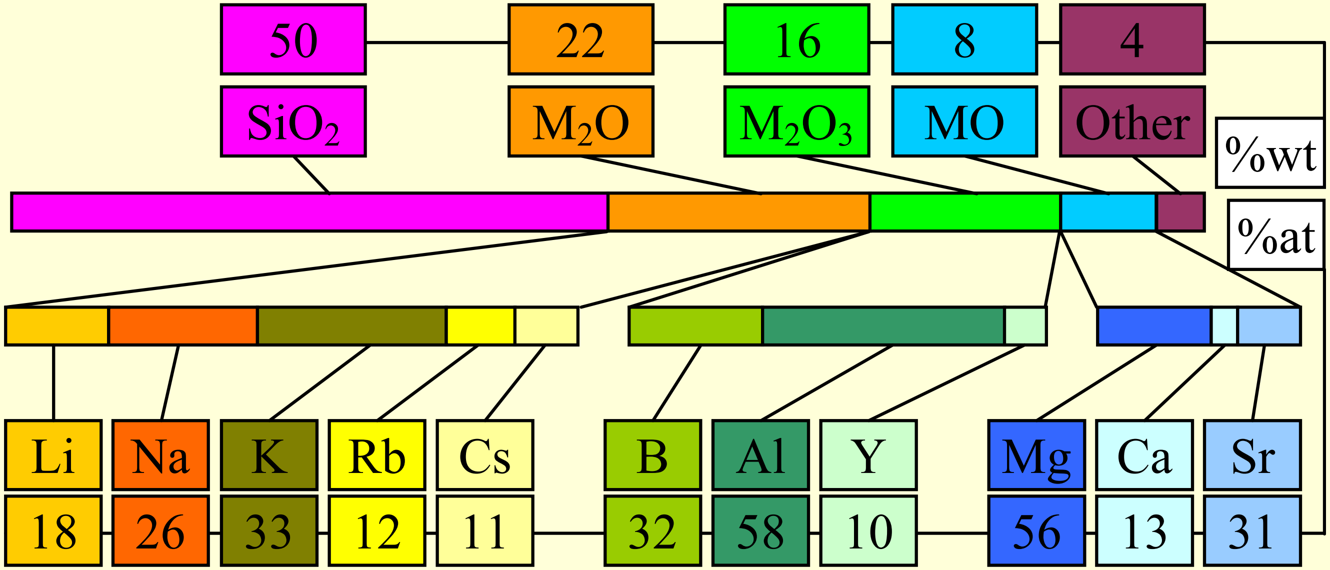
Permanent magnets

- $Pb(Fe,Mn)_{12}O_{19}$ is long known to have magnetic properties. This mineral is the basis of any permanent ceramic magnet with a few exceptions. Compounds were synthesized to replace Pb with Ba and Sr in the matrix structure. $BaFe_{12}O_{19}$ ideal structure is almost similar to the spinel structure. Ceramic permanent magnets have high levels of remanence (Br) and coercive force (HC)



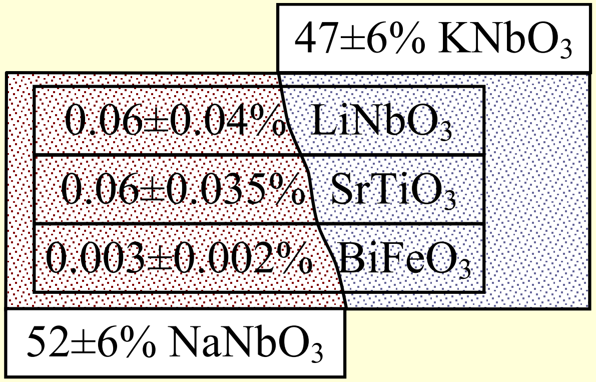
Radioceramics

- Were manufactured several types of ceramic able to deliver streams of high frequency radio waves with minimal distortion. The materials used are alumina, corrindonite and sintered glass of silicon oxide. It is essential that the porosity, if any, should be evenly distributed and therefore have very low tolerances surface. A problem that arises here is the large size required for these ceramic bodies.



Typical composition for a radioceramic

Piezoelectics, pyroelectrics and ferroelectrics



47±6% $KNbO_3$

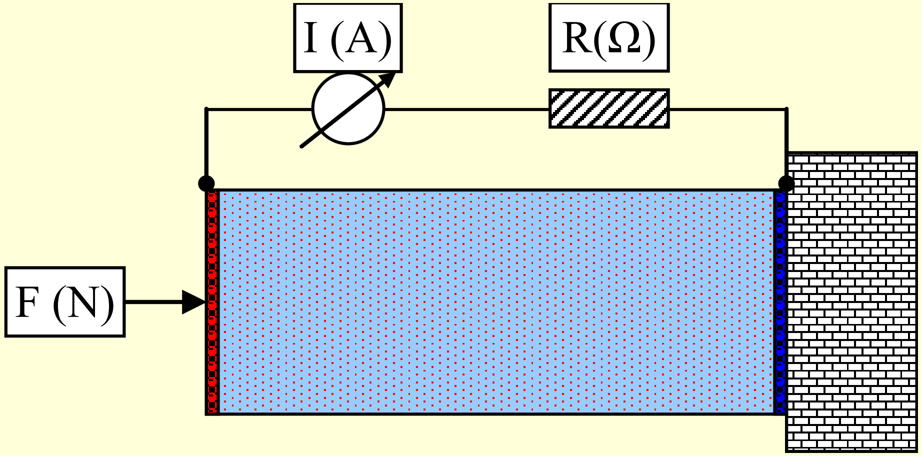
0.06±0.04% $LiNbO_3$

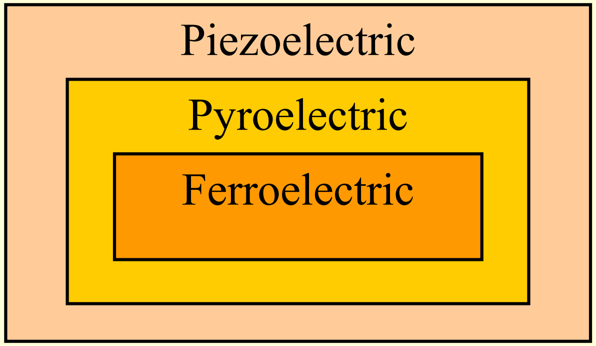
0.06±0.035% $SrTiO_3$

0.003±0.002% $BiFeO_3$

52±6% $NaNbO_3$

Piezoelectric: 100-200 pC/N

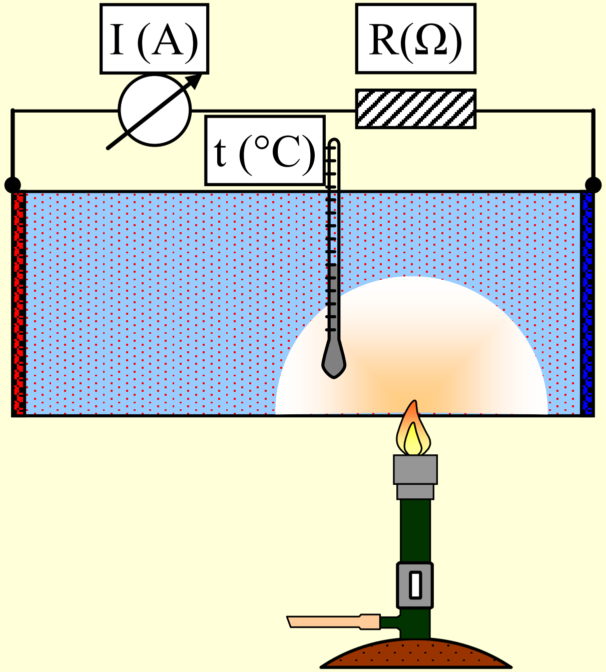


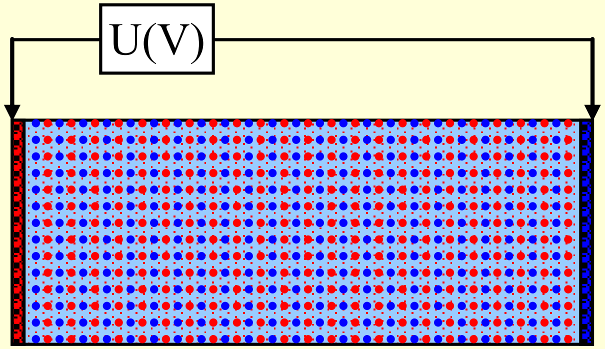


Piezoelectric

Pyroelectric

Ferroelectric

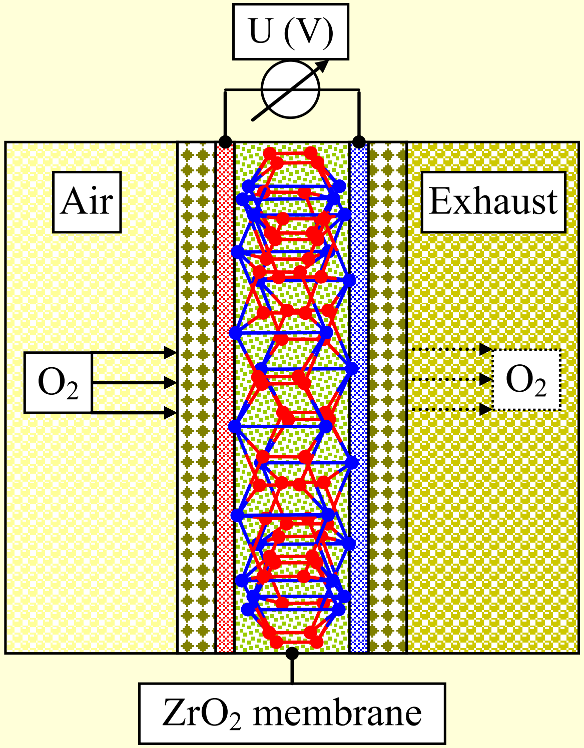


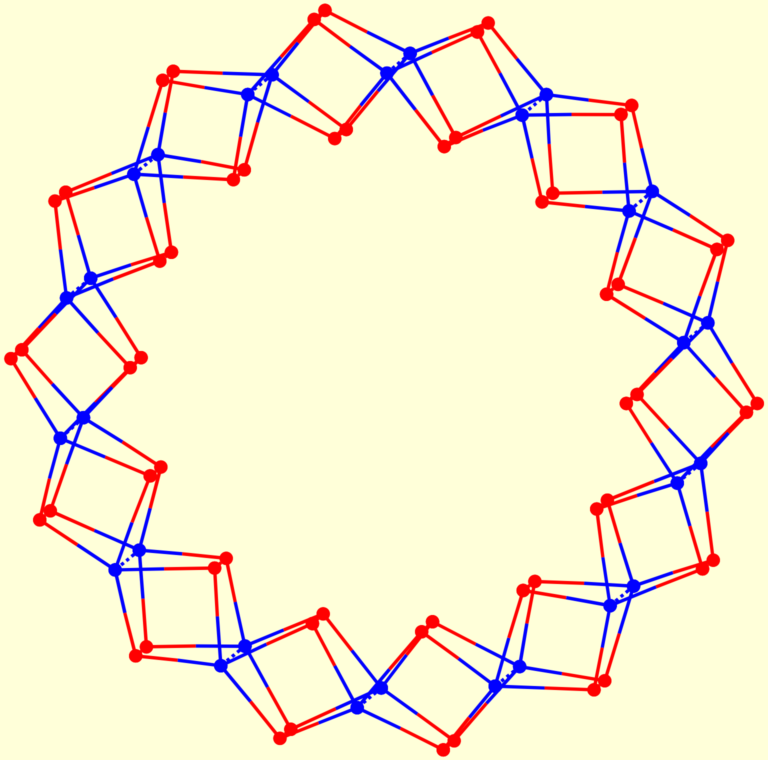


Conductor ceramics

- Some of the most guarded secrets of Corning Glass Co. was the tinning materials for the oxide electrodes used in kinescope tubes. Production patents were issued in the United States on this issue: 1952 (SnO_2, 0.5-5% As, Bi, Sn, firing at 1400 °C, $\rho = 2\Omega\cdot cm^{-3}$) 1963 (+0.5-5% V_2O_5, firing at 1300-1500 °C, $\rho = 1\Omega\cdot cm^{-3}$), 1966 (+0.1-0.5% CuO, ZnO 0.5-1%, 0.3-1.2% SnO_2, $\rho = 1\Omega\cdot cm^{-3}$). Even so, problems contact terminals is always a problem. Magnesium titanate ($MgTiO_4$) is used for resistors requiring high currents and stability.

ZrO_2 sensor used to monitor automobile exhaust gases.

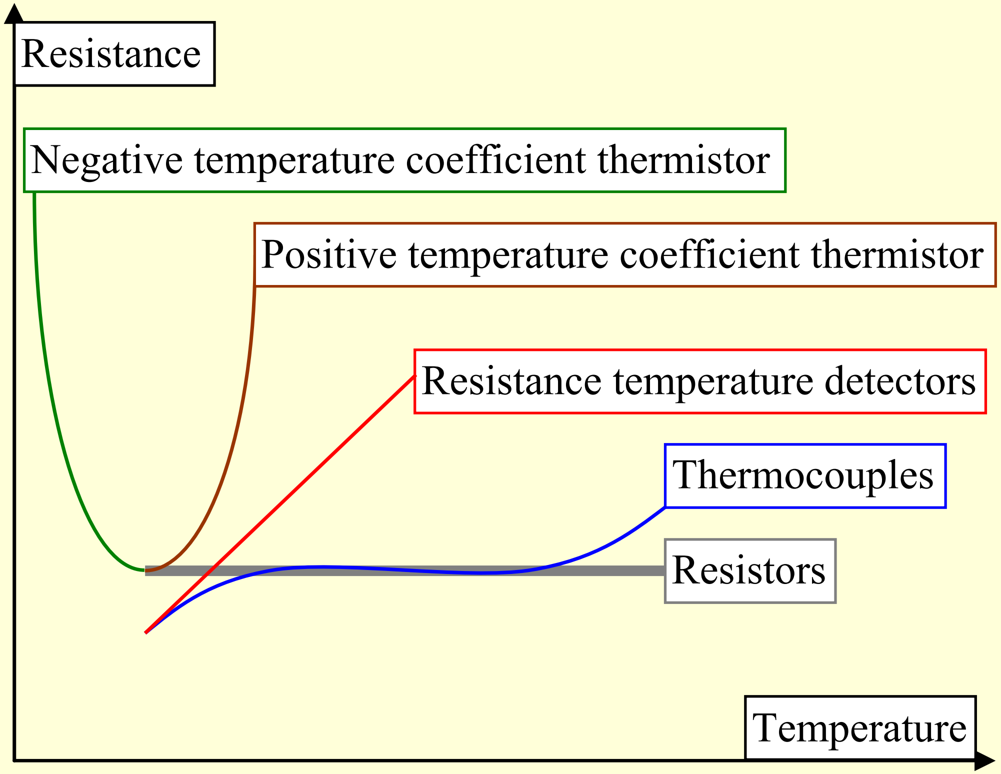




Termistors

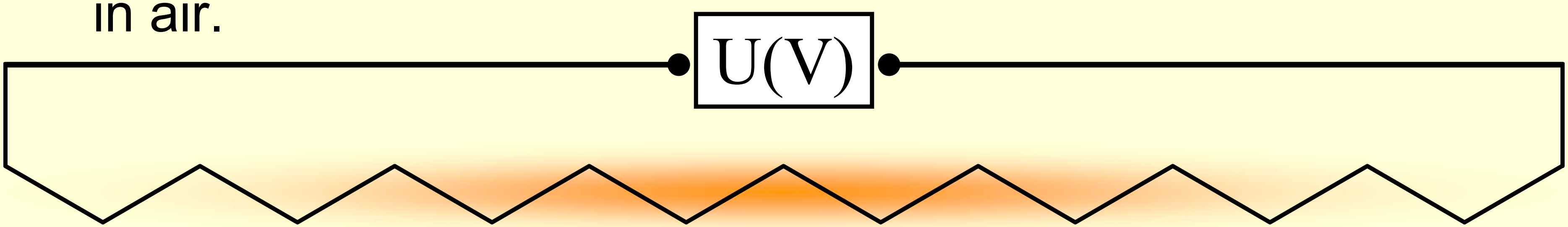
Large positive temperature coefficient thermistors finds many applications in thermostats and thermal switches. Barium titanate doped with a rare metal used in the manufacture of fine granules which are then sintered in ceramic. For this, lanthanum is folost in quantities of 0.001 to 0.005 molar percent. Barium titanate can be precipitated, then mixed with rare metal and heated in a controlled atmosphere at 1400 °C.

A thermistor is a type of resistor whose resistance varies significantly with temperature, more so than in standard resistors.



Heating ceramics

- Nonmetal electric heating elements consist of silicon carbide and molybdenum oxides. Rod-shaped or spiral tube CSi elements are widely used for electrical heating at high temperatures. They can be used at temperatures of 1600 °C for short periods and 1500 ºC under continuous working.
- $MoSi_2O_6$ heating elements can be used at temperatures of 100 ºC - 200 ºC above the limit of SiC elements and are used for elements exposed to high temperatures in furnaces.
- Heating elements as oxides of zirconium and thorium become conductors when are heated to red. Furnaces built with these elements are capable of temperatures of 2000 °C in air.



Refractory ceramics

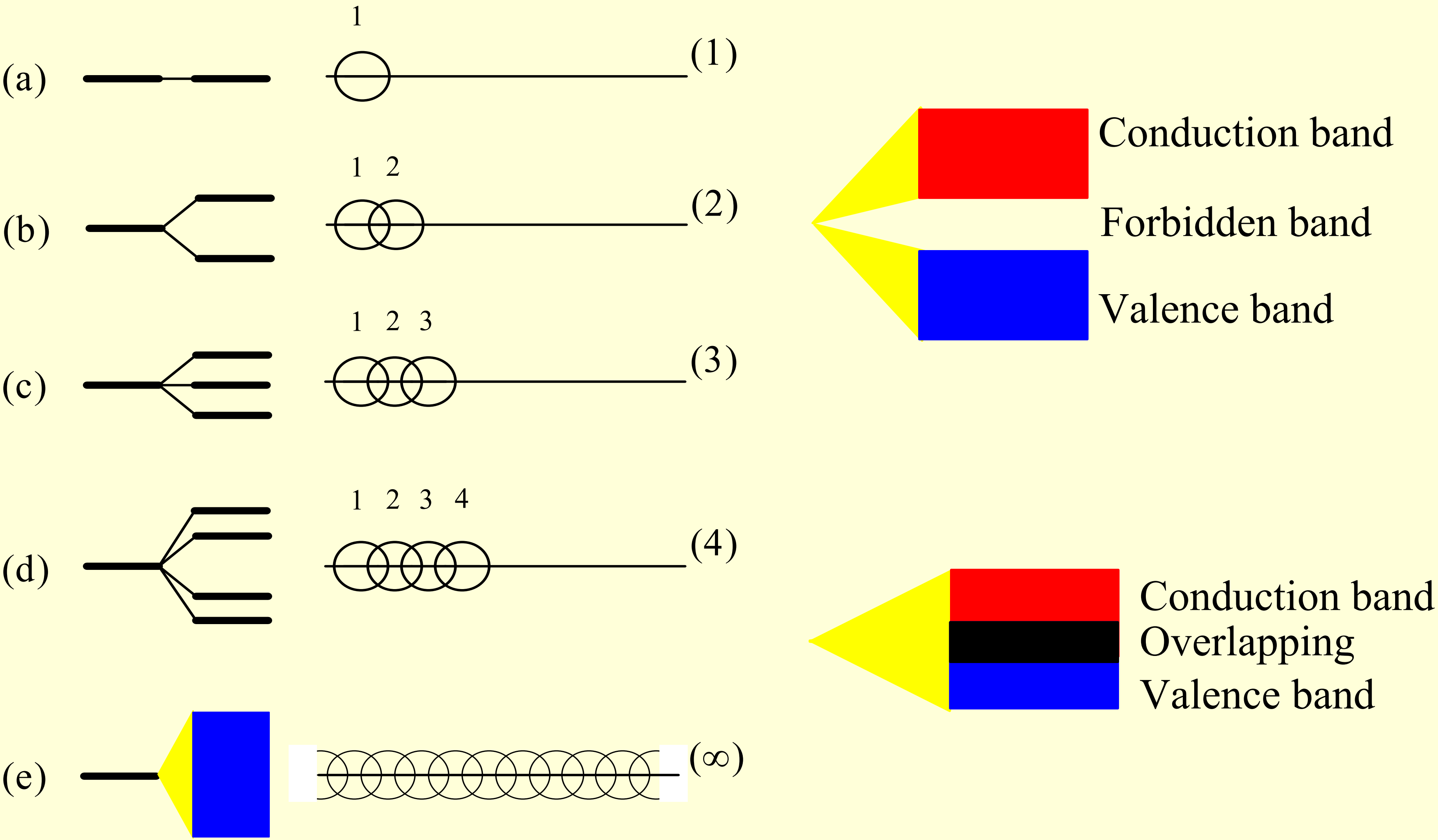
- A refractory material is one that retains its strength at high temperatures.
- Ultra high temperature ceramics are good choices for several extreme applications: thermal protection materials on hypersonic aerospace vehicles or re-usable atmospheric re-entry vehicles, specific components for propulsion, furnace elements, refractory crucibles, etc. This family of ceramic compounds is made of borides, carbides, and nitrides such as ZrB_2, HfB_2, ZrC, HfC, TaC, HfN which are characterized by high melting points.

Compound	Density (g/cm^3)	Melting (°C)
HfC	12.8	3900
TaC	14.5	3800
ZrC	6.6	3400
HfN	13.9	3385
HfB_2	11.2	3380
ZrB_2	6.1	3245
TiB_2	4.5	3225
TiC	4.9	3100
TaB_2	12.5	3040
ZrN	7.3	2950
TiN	5.4	2950
TaN	14.3	2700
SiC	3.2	2545*
* dissociates		

Q & R

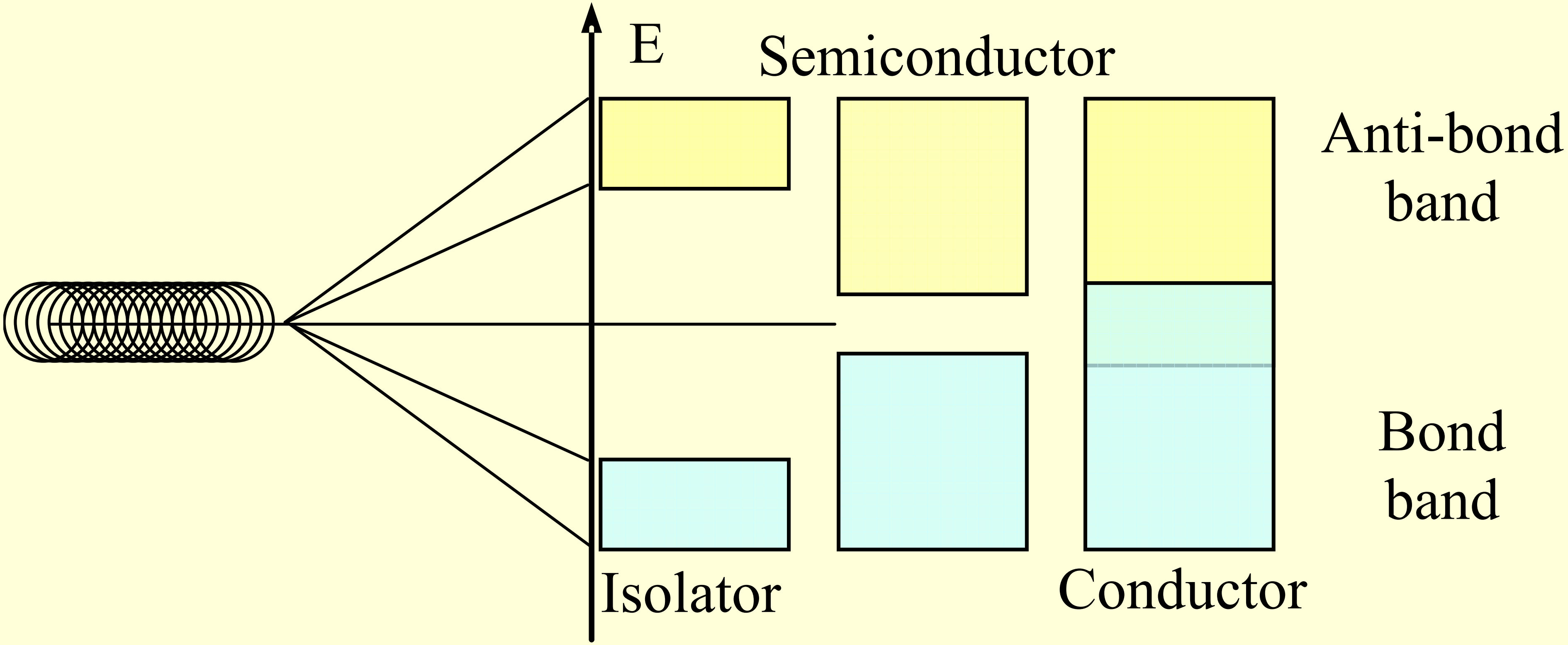
In connection with ceramics:	
0	Are designed to possess usual electrical, magnetic and thermal properties
1	Are designed to possess special electrical, magnetic and thermal properties
0	Are designed for applications of high elasticity
1	Are designed for high voltage applications
0	Contain compounds of metals with cerium
0	Contain compounds of metals with fluorine
0	Contain compounds of metals with helium
0	Contain compounds of metals with hydrogen
1	Contain compounds of metals with silicon
1	Contain compounds of metals with boron
1	Contain compounds of metals with nitrogen
1	Contain compounds of metals with oxygen

Solid state electronic bands



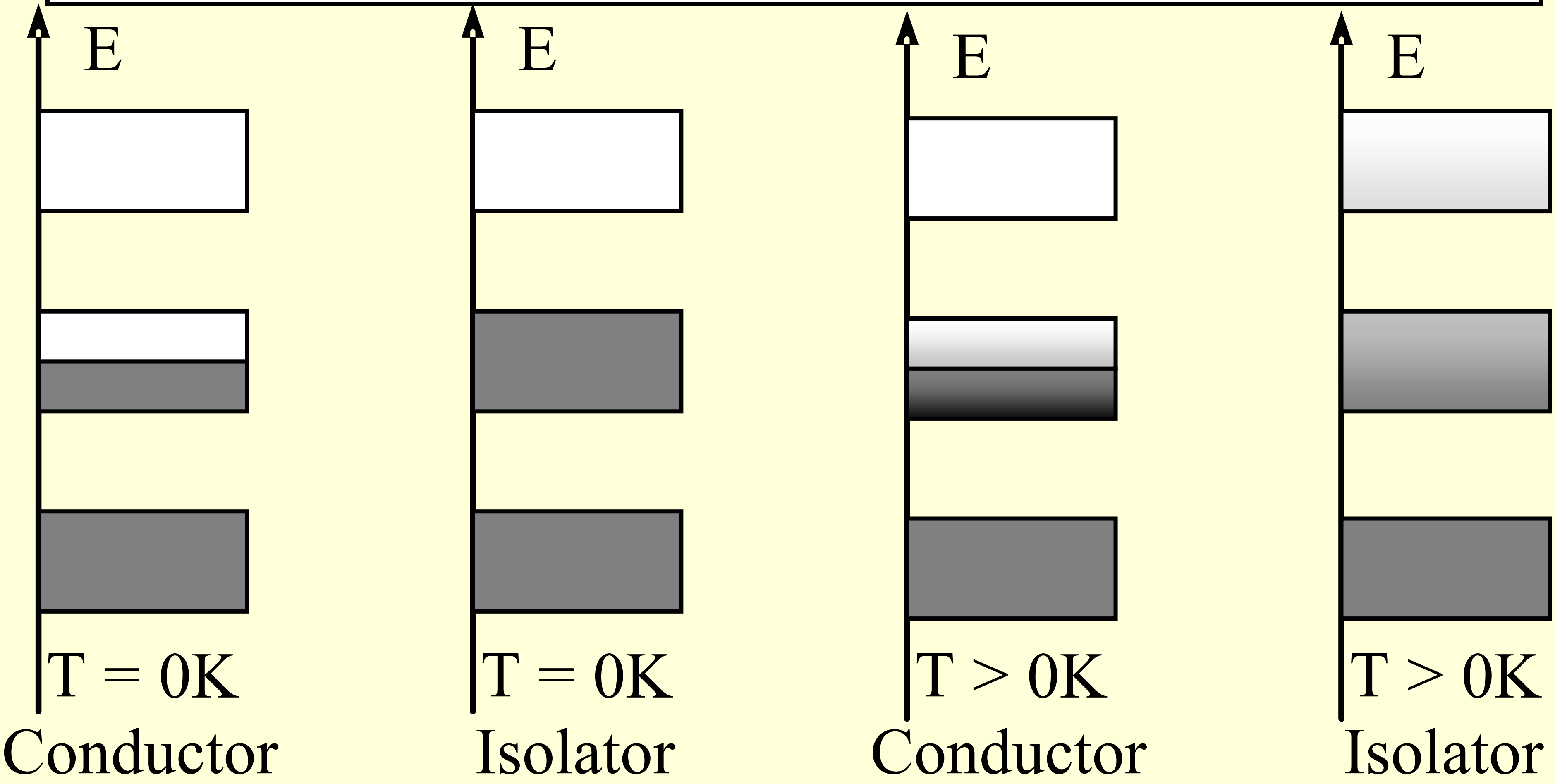
Molecular orbital formation and transformation in bands in solids

Conductors, semiconductors and isolators

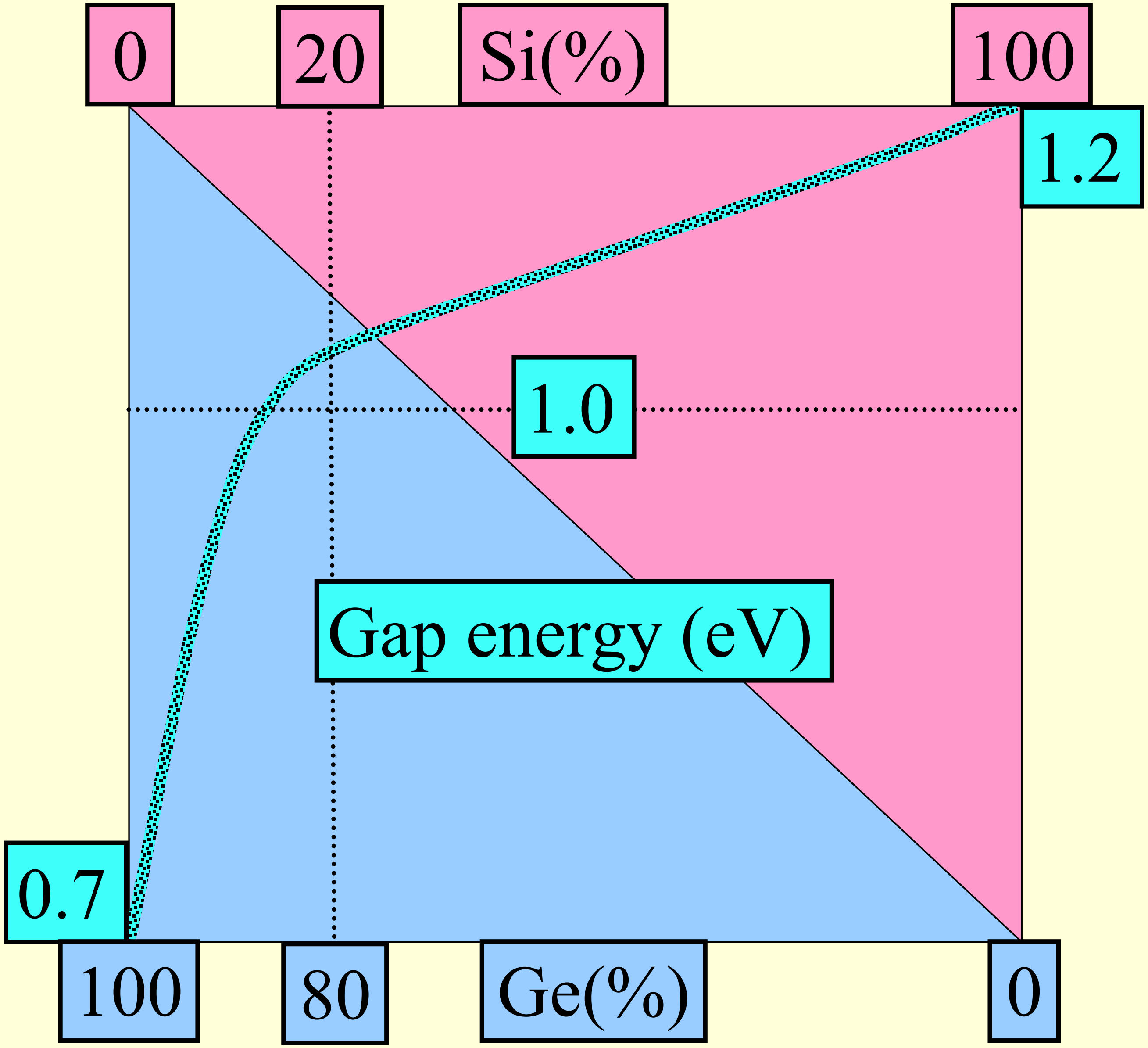


Conductors vs. semiconductors and isolators

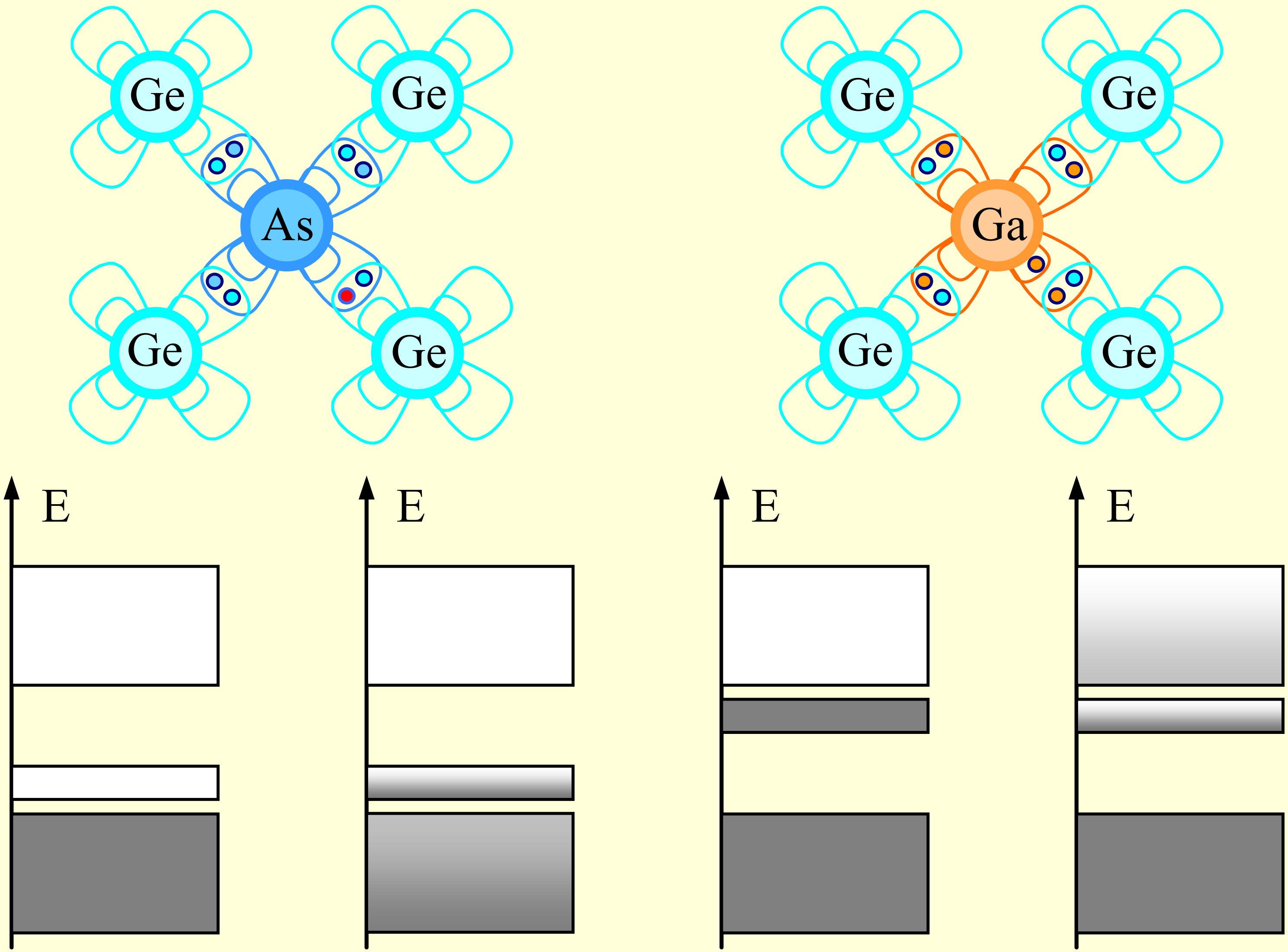
Populating the allowed bands with electrons in solids



Ge-Si alloy forbidden band



Doped semiconductors



T = 0 K
As in Ge

T > 0 K
Scond. 'p'

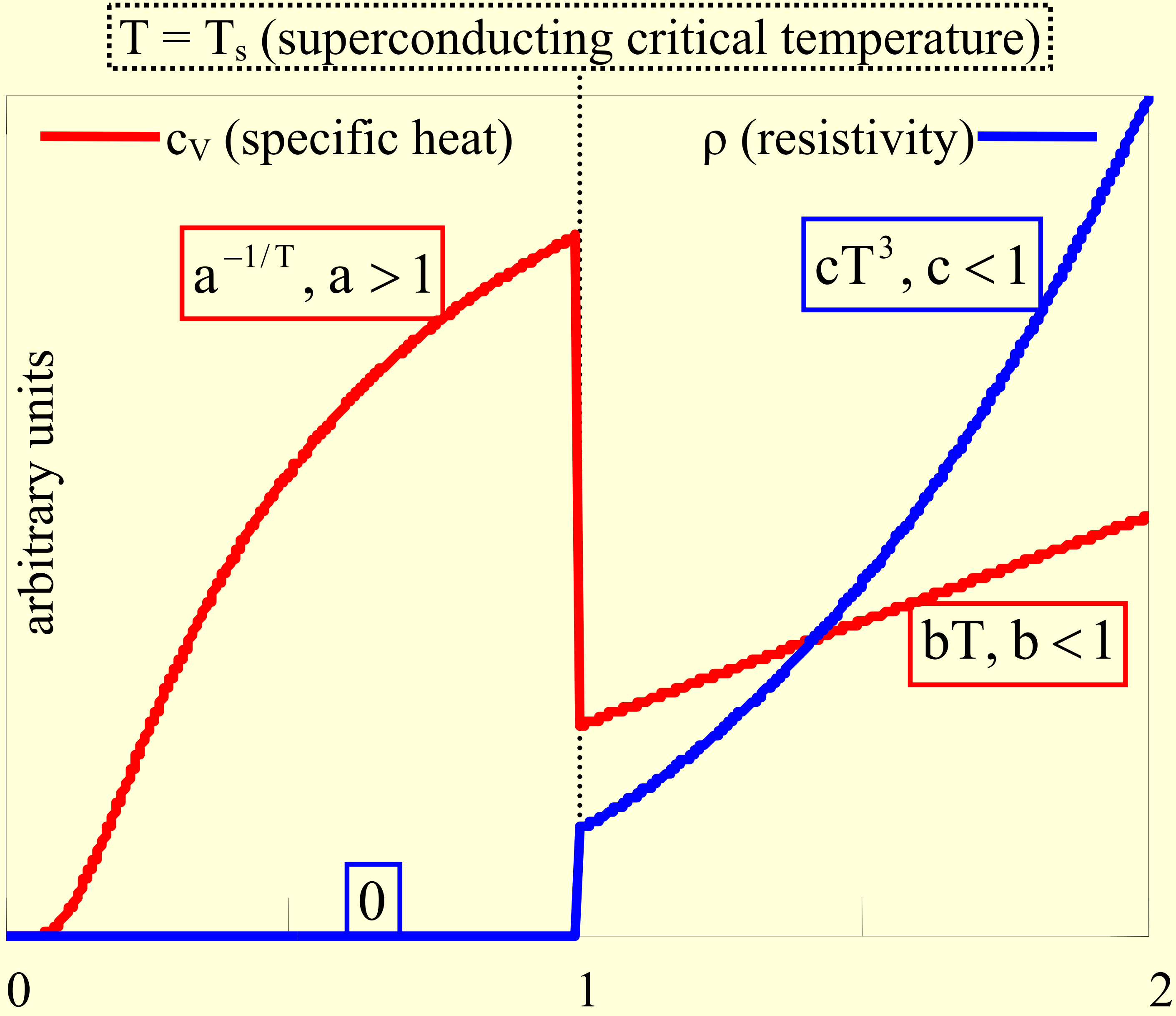
T = 0 K
Ga in Ge

T > 0 K
Scond. 'n'

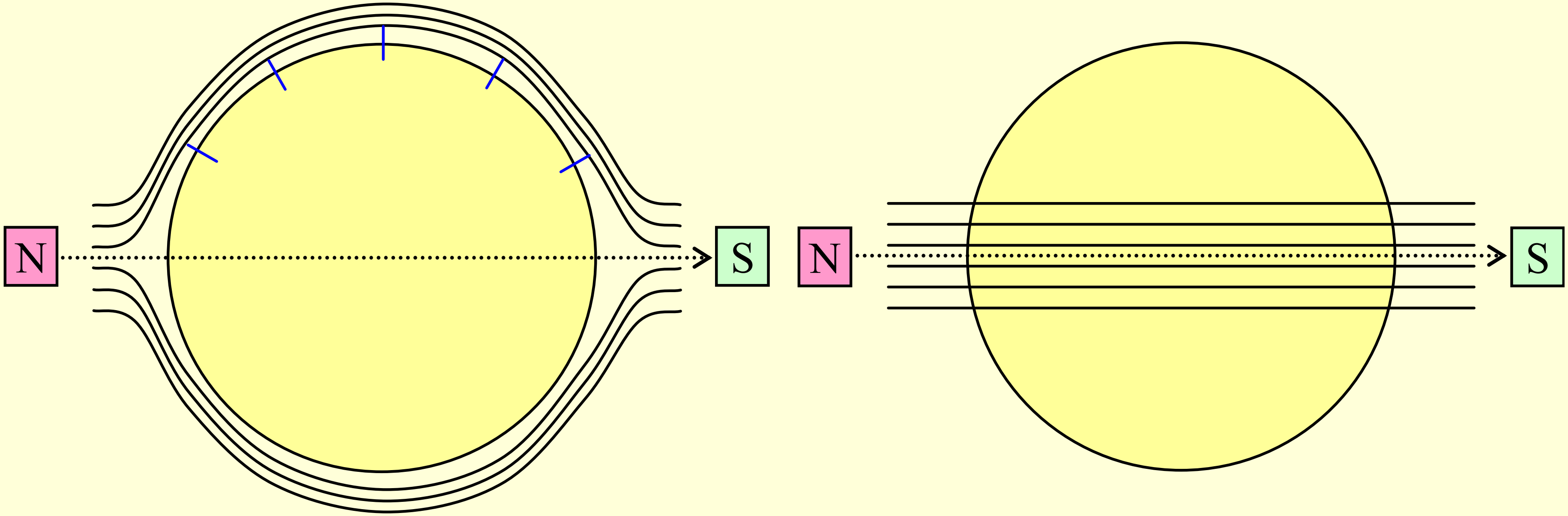
Superconductivity

- In 1908 the Dutch physicist Heike Kamerlingh Onnes was able to liquefy helium (normal boiling point 4.6 K). He reduced pressure by boiling it reached a temperature of 1.15 K. While studying properties of these temperatures from 4.1 K found that mercury undergoes a transition state in which the properties are different. The most striking change is the electrical resistance, that decreases sharply to 0. This condition is called superconductivity. Many elements are superconducting.
- The best superconducting (superconductivity occurs at a higher temperature) are: Nb (9.2 K), Tc (8.2 K), Pb (7.21 K), La (6.1 K), V (5.2 K), Ta (4.4 K) , Hg (4.15 K), Sn (3.72 K), (3.40 K).
- Metals with the highest conductivity at room temperature (Li, Be, Cu and congeners) are superconducting good (these superconductivity appears below 0.2 K).

Superconducting phase transition



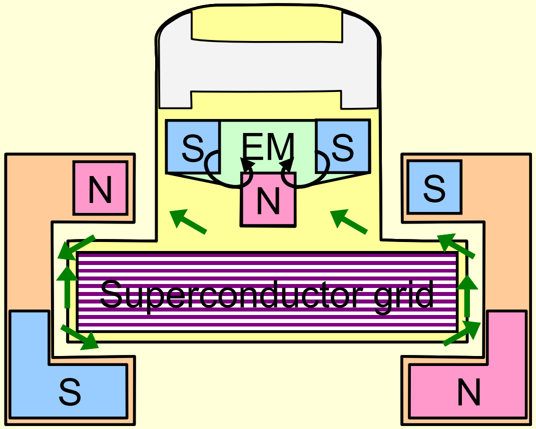
The Meissner effect

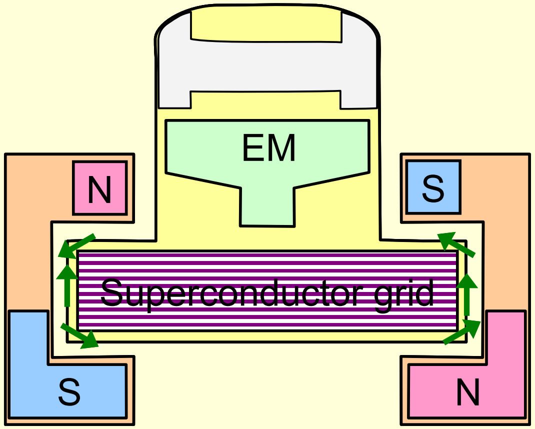


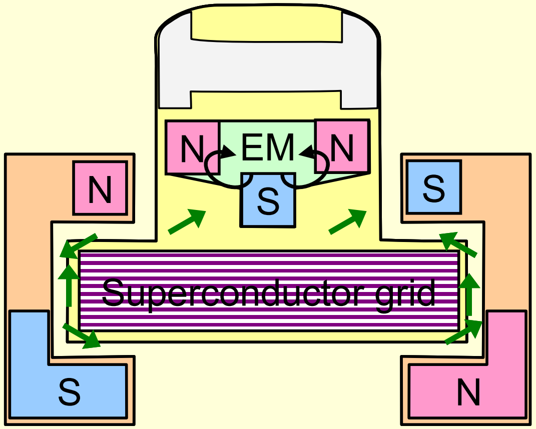
The Meissner effect is an expulsion of a magnetic field from a superconductor during its transition to the superconducting state. Walther Meissner and Robert Ochsenfeld discovered the phenomenon in 1933 by measuring the magnetic field distribution outside superconducting tin and lead samples. [Meissner W, Ochsenfeld R, 1933. Ein neuer Effekt bei Eintritt der Supraleitfähigkeit. Naturwissenschaften 21(44):787-788.]

high-temperature superconducting “MAGLEV”

Superconducting magnetically levitated vehicle



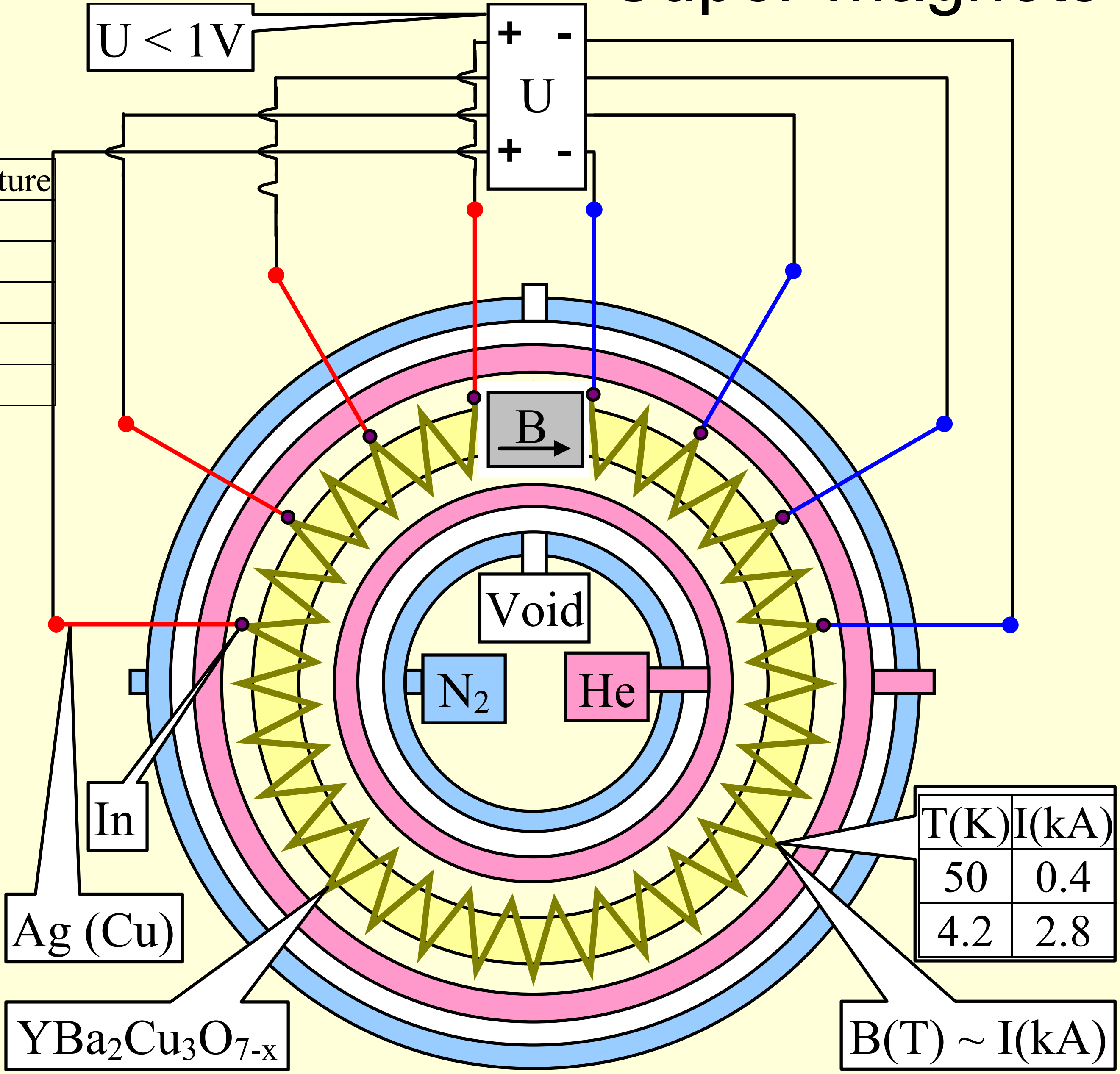




- This system is based on the Meissner effect that bulk high-temperature superconductors levitate above and below a permanent magnet. The system uses liquid helium and nitrogen to cool the superconductor.

Super-magnets

Superconductor	B_{c2}	Temperature
Nb_3Sn	22T	4K
V_3Ga	20T	4K
V_3Si	21T	4.2K
$Nb_{79}(Al_{73}Ge_{27})_{21}$	21T	14K
$YBa_2Cu_3O_{7-x}$	10T	77K



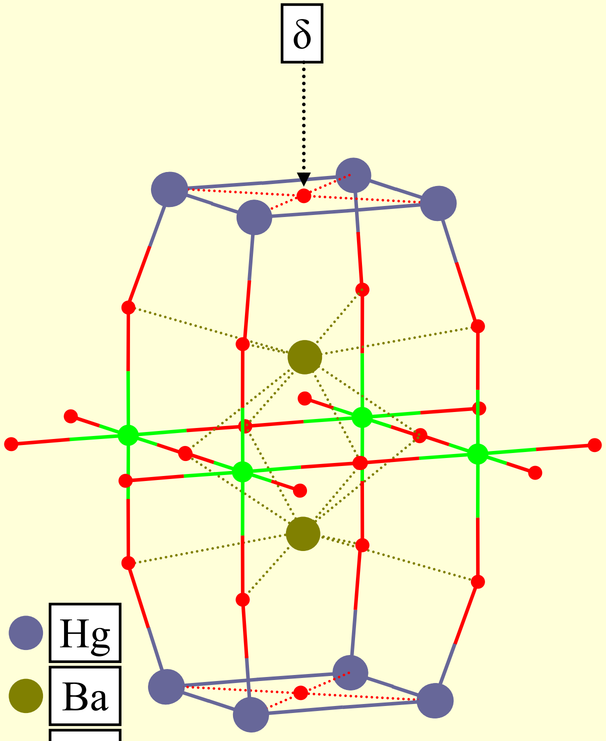
T(K)	I(kA)
50	0.4
4.2	2.8

High temperature superconductors

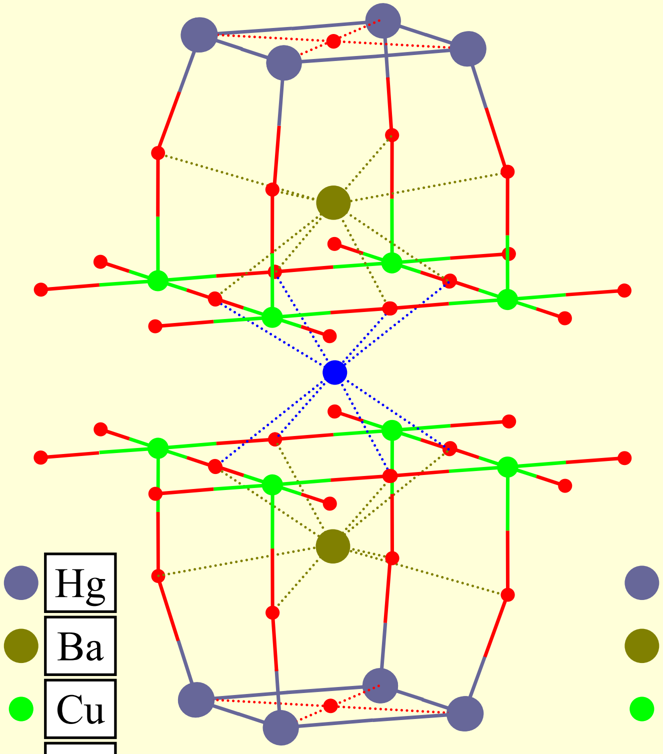
Formula	T_S (K)	Formula	T_S (K)
$YBa_2Cu_3O_7$	92	$Tl_2Ba_2CaCu_2O_8$	108
$Bi_2Sr_2CuO_6$	20	$Tl_2Ba_2Ca_2Cu_3O_{10}$	125
$Bi_2Sr_2CaCu_2O_8$	85	$TlBa_2Ca_3Cu_4O_{11}$	122
$Bi_2Sr_2Ca_2Cu_3O_6$	110	$HgBa_2CuO_4$	94
$Tl_2Ba_2CuO_6$	80	$HgBa_2CaCu_2O_6$	128
		$HgBa_2Ca_2Cu_3O_8$	134

The first superconductor found with Tc > 77 K (nitrogen boiling point) is yttrium barium copper oxide ($YBa_2Cu_3O_{7-x}$)

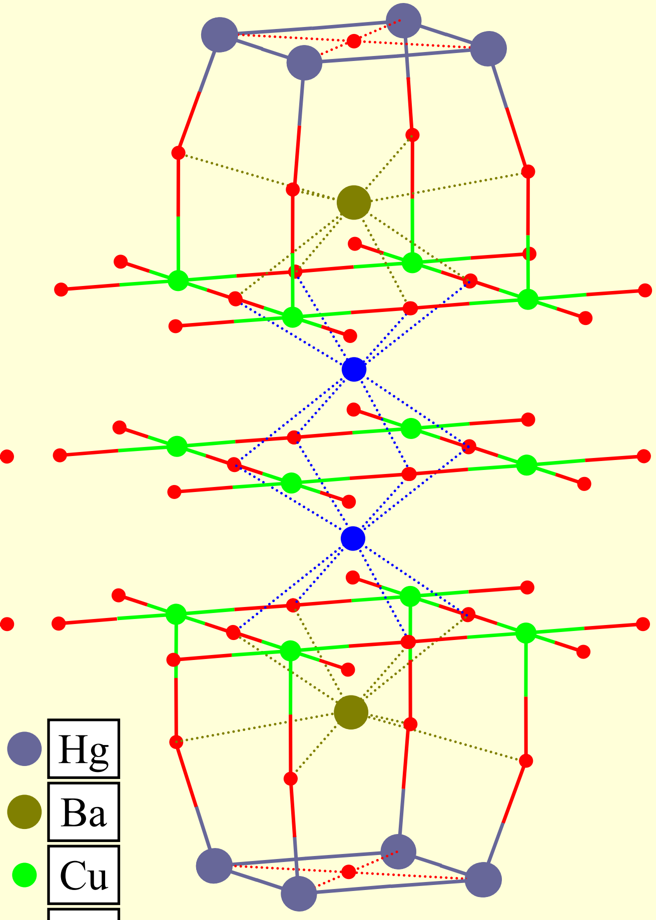
High temperature superconductors crystal structure



$HgBa_2CuO_{4+\delta}$



$HgBa_2CaCu_2O_{6+\delta}$



$HgBa_2Ca_2Cu_3O_{8+\delta}$

Q & R

In connection with insulators, semiconductors, conductors and superconductors:		
	0	Superconductor at high temperature is $HgBa_2Ca_2Cu_3O_8$ since T_S = 134 °C
	1	Superconductor at high temperature is $HgBa_2Ca_2Cu_3O_8$ since T_S = 134 K
	0	Superconductivity disappears when it falls below a certain temperature
	1	Superconductivity disappears when it exceeds a certain temperature
	0	Superconductivity appears at high temperatures
	1	Superconductivity occurs at low temperatures
	0	In conductors the conduction band and the valence band are totally stacked
	0	In semiconductors the conduction band and the valence band are apart
	0	In insulators the conduction band and the valence band are close
	1	In conductors the conduction band and the valence band are partially overlapped
	1	In semiconductor the conduction band and the valence band are close
	1	In insulators the conduction band and the valence band are apart

Course 13

Advanced materials
Polymers & plastics
Reactions & mechanisms
Biomolecules

Advanced materials

Materials:

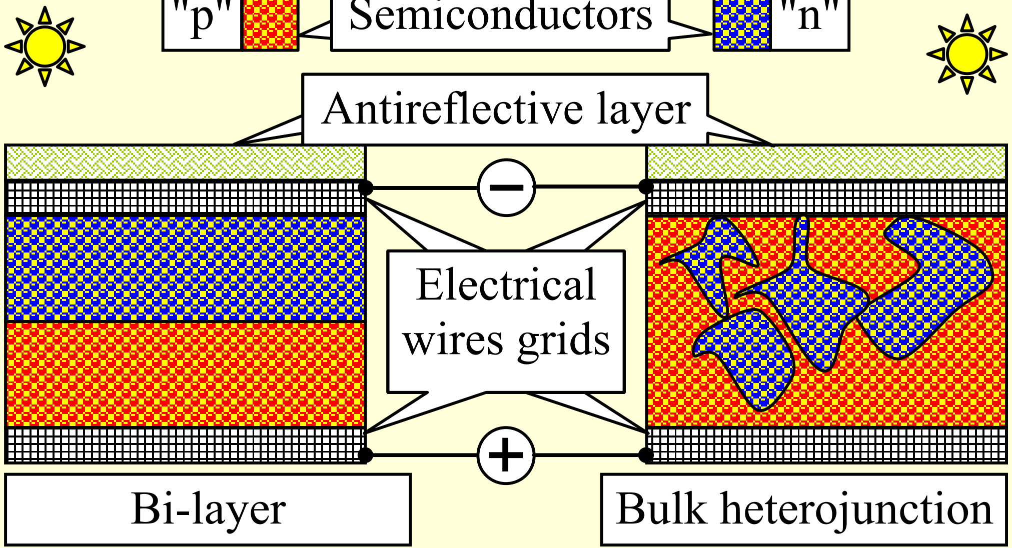
- **ZnO**
- **WO_3**
- **Fe_3Al**
- **Copper Sulfide**
- **Barium Titanate**
- **Protein Particles**
- **Peptide Nanorings**
- **Carbon Nanotubes**
- **Magnesium Diboride**
- **Fullerene Nanoparticles**

:Applications

- **Bionic Superhydrophobic Surfaces**
- **Organic Light-Emitting Diodes**
- **Thin-Film Transistors**
- **Superconductors**
- **Liquid Crystals**
- **Solar Cells**

Example from the content
of Adv Mater 2006;18(6)

Hybrid (organic-inorganic) solar



"p"

Semiconductors

"n"

Antireflective layer

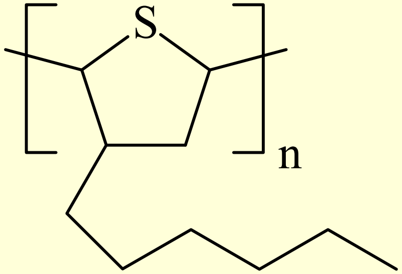
−

Electrical wires grids

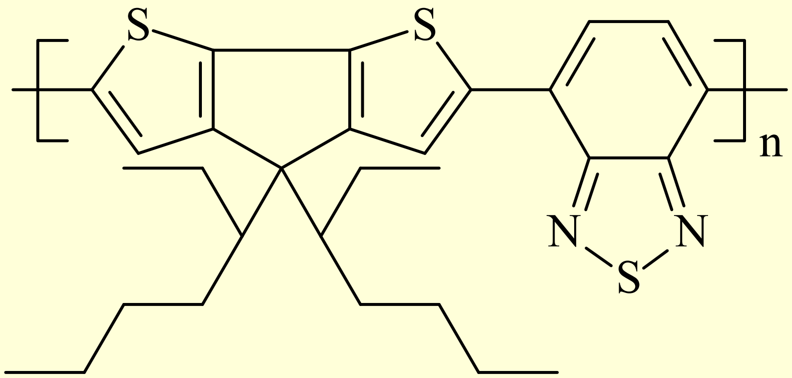
+

Bi-layer

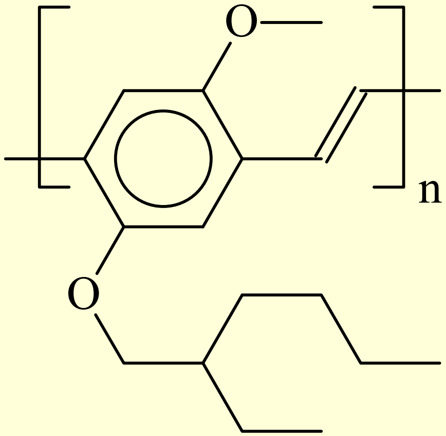
Bulk heterojunction



CdS	10.9	1.1
CdSe	5.8	0.62
Si	18.9	0.35
TiO_2	4.8	0.87
ZnO	5.2	0.75
PbS	1.0	0.42



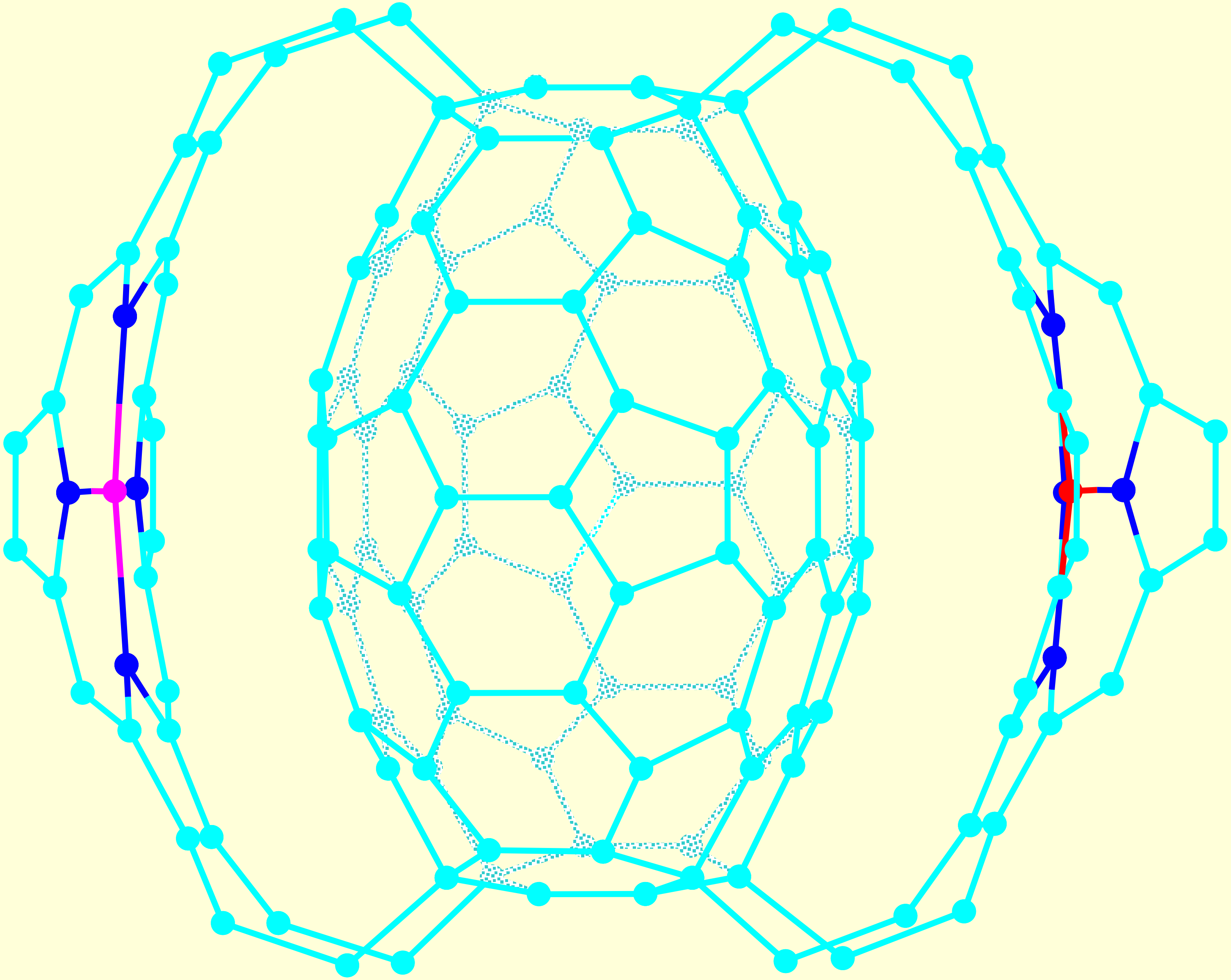
CdSe	13.9	0.48



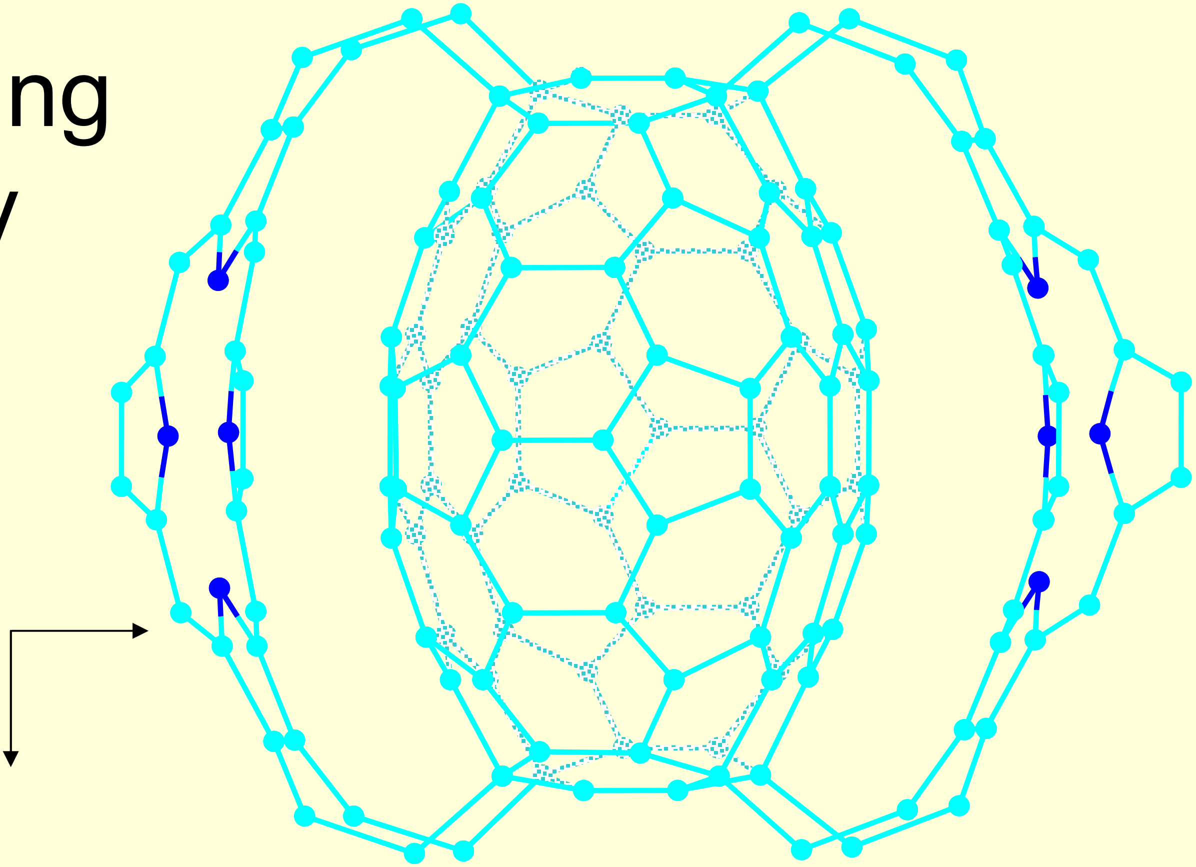
CdS	3.0	0.85
PbS	0.1	1.0

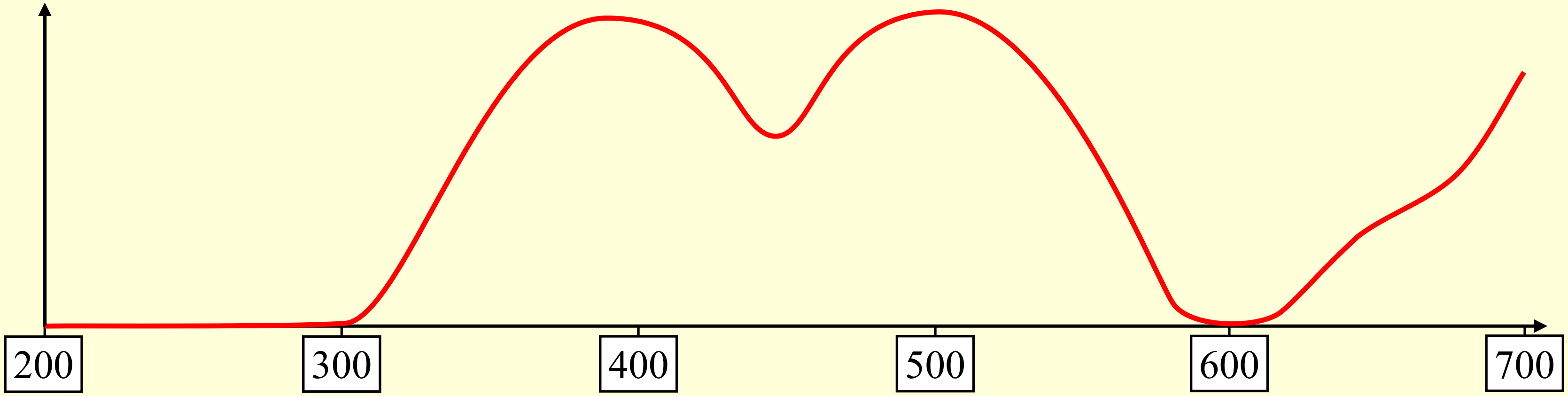
Image: Donor
Table: Acceptor, D_C [mA/cm^2], E [V]

Nanostructure design for apps



Apps: converting solar energy



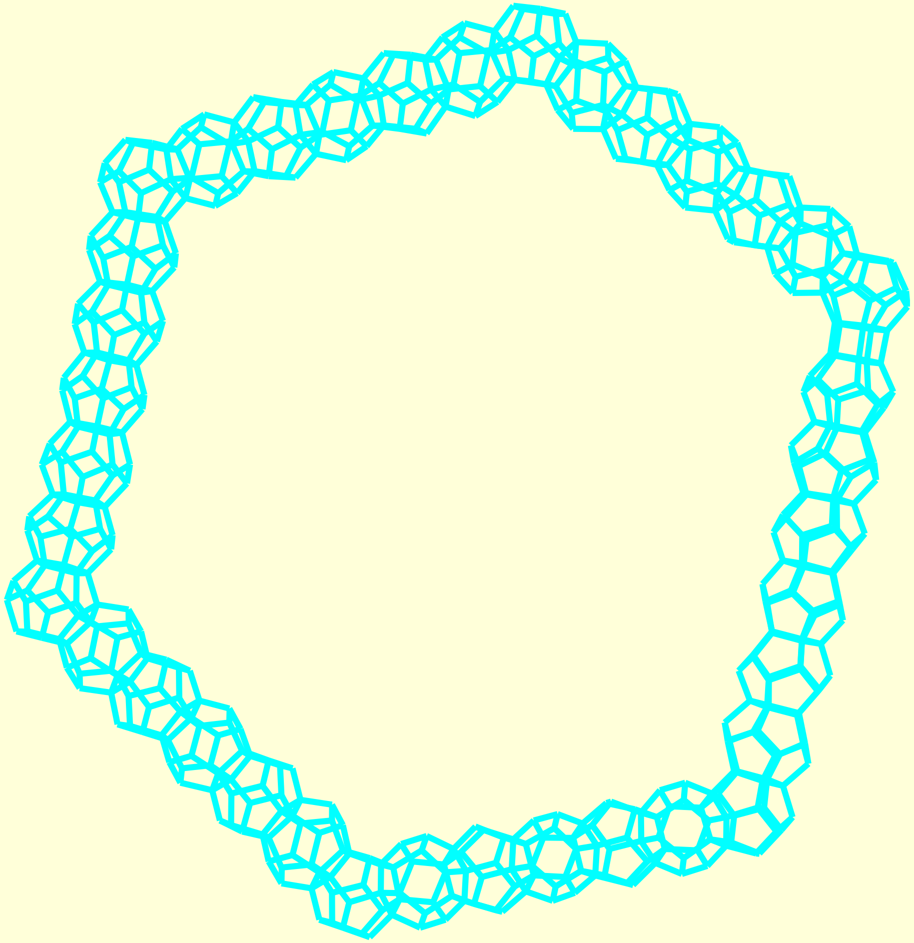


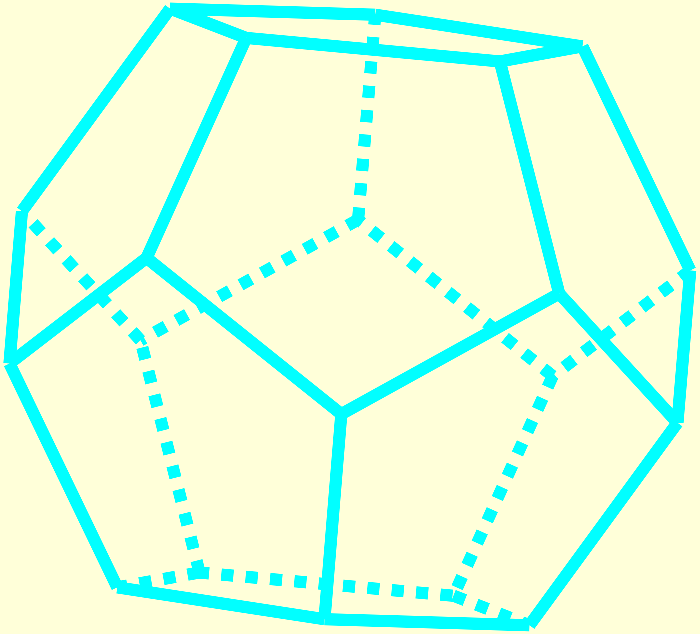
Spartan ’10 Hartree-Fock STO-G +UV-VIS (excited state)

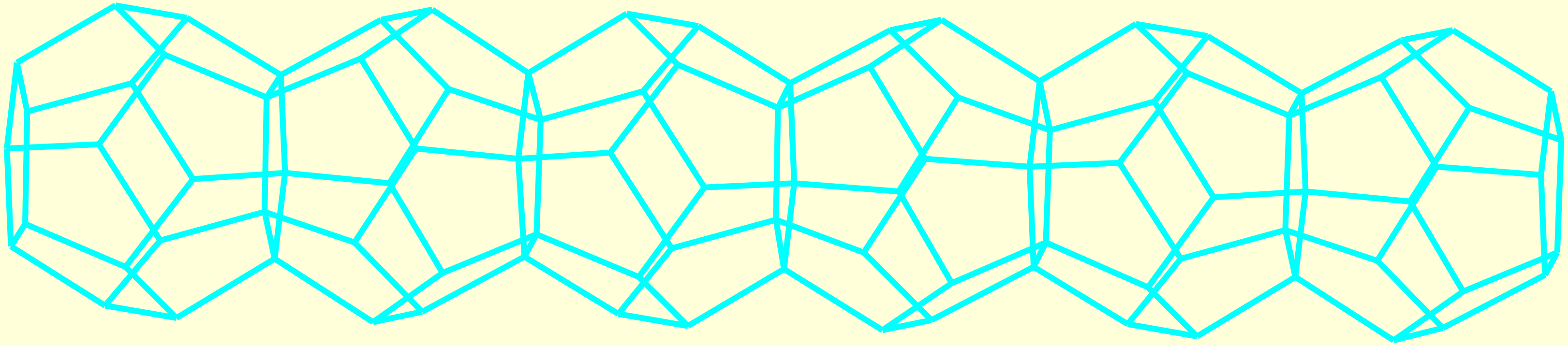
Calculated UV-VIS spectrum

nm

Nanostructure design for apps

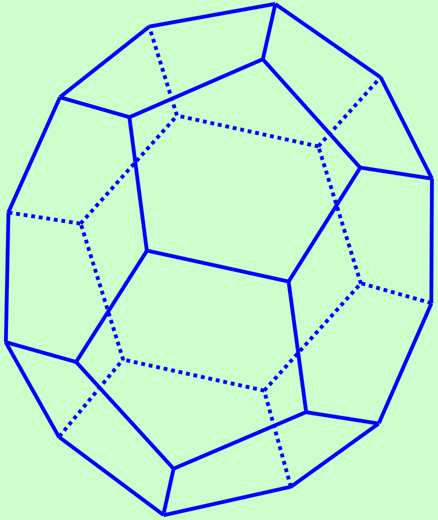




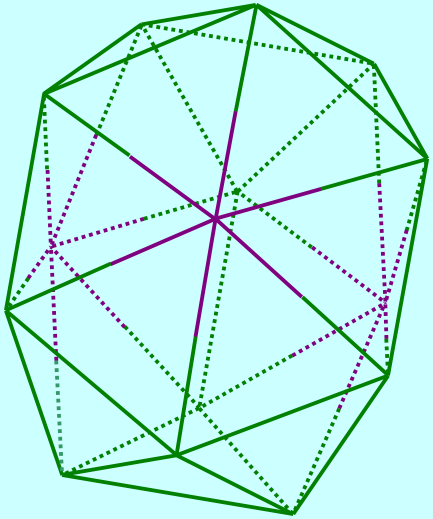


Map operations (on C26 fullerene)

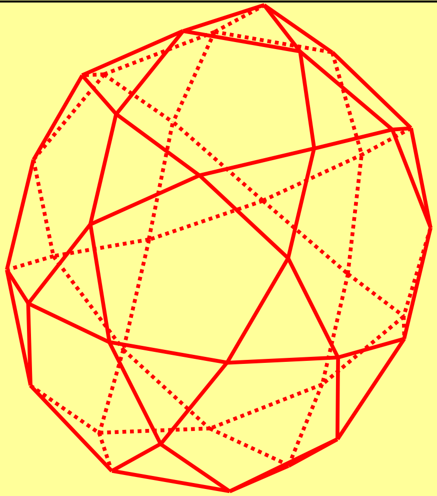
Map(C_{26})



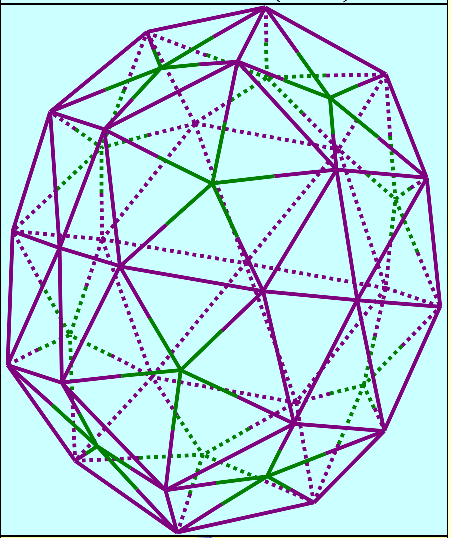
Dual(C_{26})

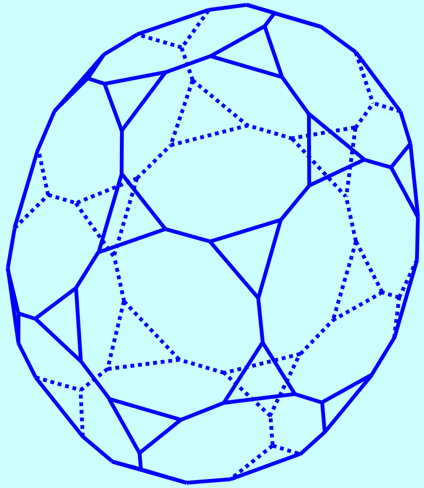


Medial(C_{26})

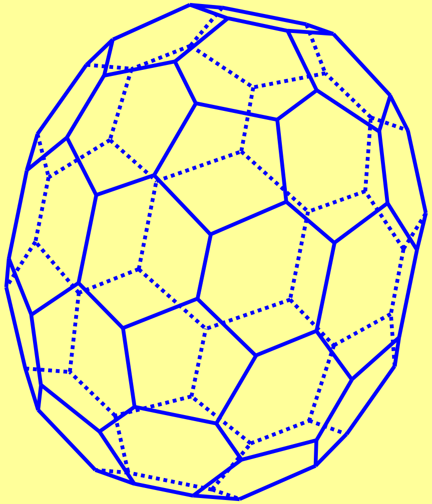


Stellation(C_{26})

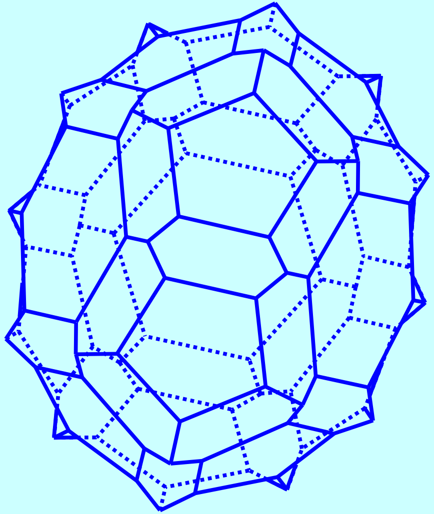




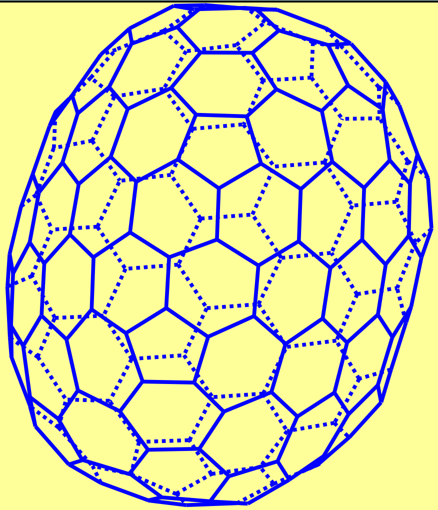
Truncation(C_{26})



Leapfrog(C_{26})



Quadrupling(C_{26})



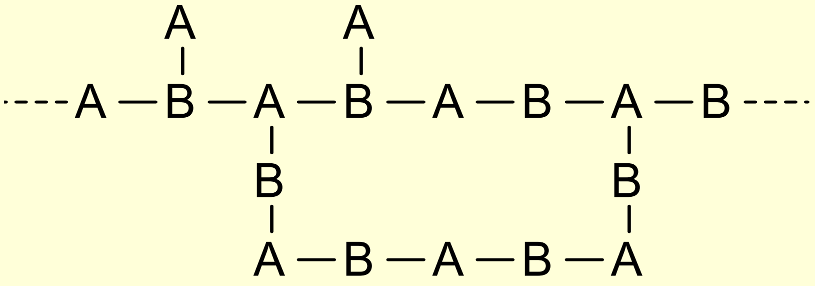
Capra(C_{26})

Polymers

- Polymer=$[\text{Monomer}]_n$; natural & synthetic
- Repeated unit:
  - A single structural unit are repeated → homopolymers
  - Two different structural unit are repeated → copolymers
  - Three different structural unit are repeated → terpolymers
- Number of repetitions:
  - Short polymers: $n \leq 50$ (ex. “peptides”; $n > 50$ → “proteins”)
  - Usual: $10^3 \leq n \leq 10^4$
  - Long: $10^5 < n$

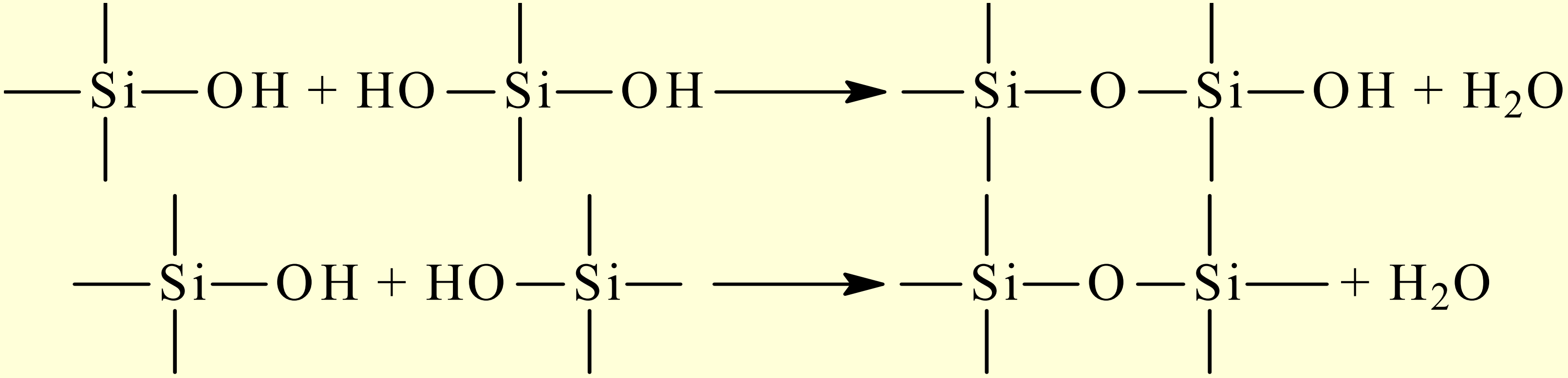
Copolymers

- Alternating monomer units: A-B-A-B-A-B-etc; general formula: $[AB]_m$;
- Periodic groups of monomer units: AAABBAAABBetc; general formula: $[A_mB_n]_p$;
- Random or statistically determined arrangement of monomer units; no general formula, only ratios and rules of arrangement (AABAAABABBBAetc);
- Block groups of monomer units: AAAAAABBBBBBetc; general formula: $[A_mB_n etc]$;
- Graft (grafted polymers): with one of the above rule but with tree structure with/without cycles:



Polymers properties

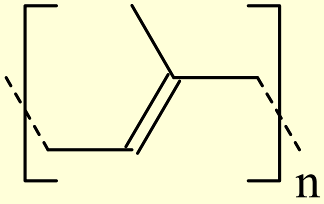
- Polymers only in rare cases posses a regular alternation of the two monomers and less often a deterministic length. Therefore solid state polymers are generally amorphous substances.
- Certain properties have a clear rule of variation with number of units; impact resistance and viscosity increases; chemical stability decreases; other properties are strongly dependent of the type of monomers; for instance boiling point of alkanes, silanes and silicones increases with the chain length.



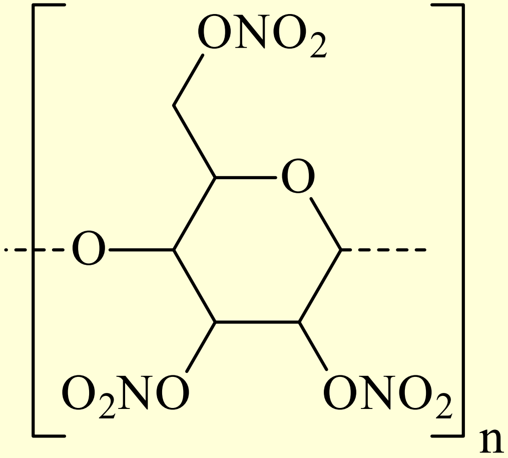
$$-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{HO}-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{OH} \longrightarrow -\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{H_2O}$$

$$-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{HO}-\underset{|}{\overset{|}{\mathrm{Si}}}- \longrightarrow -\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Si}}}- + \mathrm{H_2O}$$

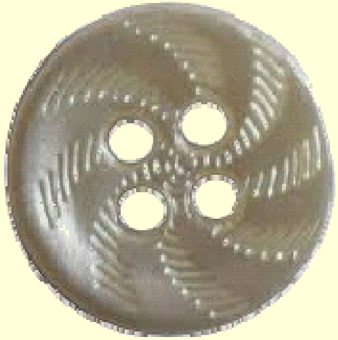
Natural sources of polymers



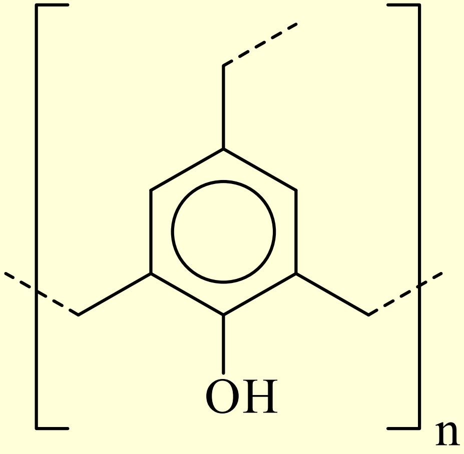
Latex is a natural polymer of isoprene. Typically, a small percentage (up to 5% of dry mass) of other materials, such as proteins, fatty acids, resins and inorganic materials (salts) are found in natural rubber. Discovered in 1736. Rubber - latex vulcanization (thermal treatment with sulfur) discovered in 1839.



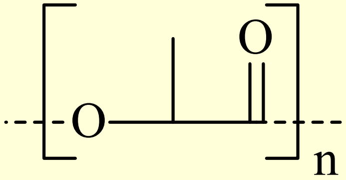
Guncotton. Obtained nitrating cellulose through exposure to nitric acid. Discovered in 1832. Precursor of celluloid ("plasticized" with camphor, in 1880).



Galalith (Plastic buttons from shirts) is a synthetic plastic material manufactured by the interaction of casein (about 80% of the proteins in cow milk) and formaldehyde. Discovered in 1897.



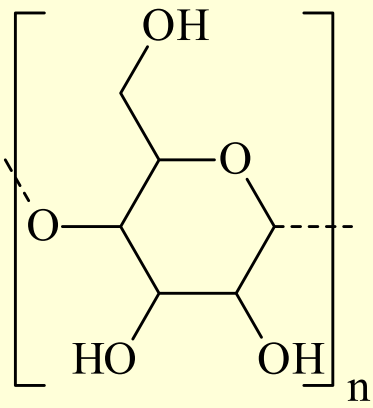
Bakelite. Formed from an elimination reaction of phenol with formaldehyde. Discovered in 1907.

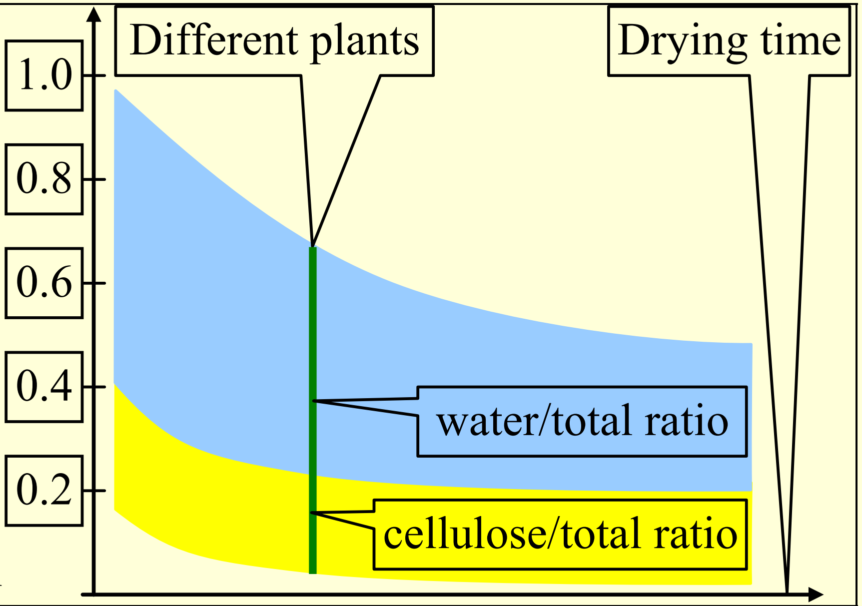


Polylactide. Derived from cornstarch, tapioca roots, or sugarcane. Discovered in 1932.

Biopolymers

Cellulose is the most common biopolymer. About 33% of plant dry matter is cellulose.
Cotton contains 90% cellulose while wood about 50%.





Peptide (20AA): Ala-Arg-Asn-Asp-Cys-Glu-Gln-Gly-His-Ile-Leu-Lys-Met-Phe-Pro-Ser-Thr-Trp-Tyr-Val

DNA strain:
(A=Ala; C=Cys; G=Gly; T=Thr)

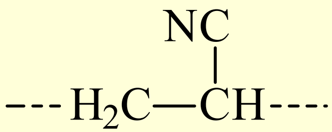
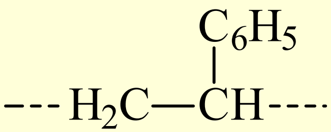
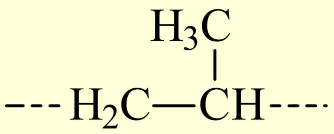
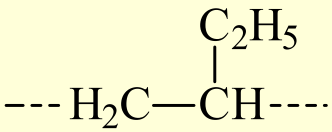
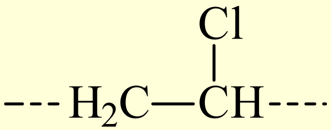
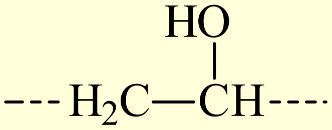
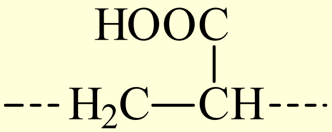
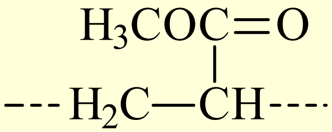
…	CTTTTCATT	
	CTGACTGCA	
	ACGGGCAAT	…

AA	Formula
His	$C_6H_9N_3O_2$
Ile	$C_6H_{13}NO_2$
Leu	$C_6H_{13}NO_2$
Lys	$C_6H_{14}N_2O_2$
Met	$C_5H_{11}NO_2S$
Phe	$C_9H_{11}NO_2$
Thr	$C_4H_9NO_3$
Trp	$C_{11}H_{12}N_2O_2$
Val	$C_5H_{11}NO_2$
Arg	$C_6H_{14}N_4O_2$

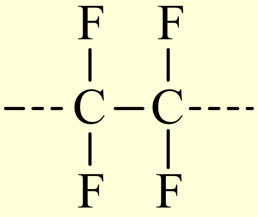
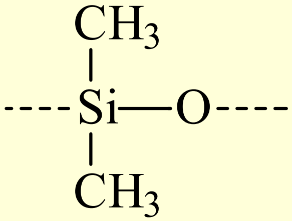
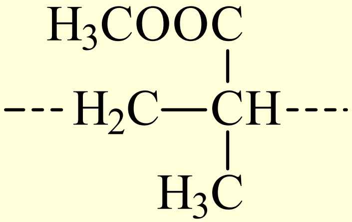
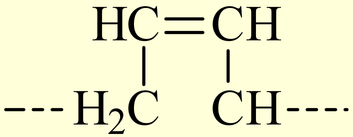
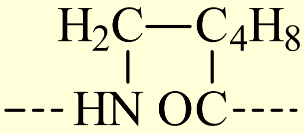
AA	Formula
Cys	$C_3H_7NO_2S$
Gln	$C_5H_{10}N_2O_3$
Pyl	$C_{12}H_{21}N_3O_3$
Orn	$C_5H_{12}N_2O_2$
Pro	$C_5H_9NO_2$
Sec	$C_3H_7NO_2Se$
Ser	$C_3H_7NO_3$
Tau	$C_2H_7NO_3S$
Tyr	$C_9H_{11}NO_3$
Ala	$C_3H_7NO_2$

AA	Formula
Asn	$C_4H_8N_2O_3$
Asp	$C_4H_7NO_4$
Glu	$C_5H_9NO_4$
Gly	$C_2H_5NO_2$
Aib	$C_4H_9NO_2$
Cit	$C_6H_{13}N_3O_3$
Dha	$C_3H_5NO_2$
Gaba	$C_4H_9NO_2$
Hcy	$C_4H_9NO_2S$
Hyp	$C_5H_9NO_3$

Synthetic polymers (1/2)

Monomer, polymer & its uses		
Polyacrylonitrile. Ultra filtration membranes, hollow fibers for reverse osmosis, fibers for textiles, oxidized flame retardant fibers	←	 $---H_2C-\overset{NC}{\overset{\vert}{C}}H---$
Polystyrene. Disposable cutlery, housings; flow if heated above 100°C, behavior exploited for plastic models, molding, and extrusion	←	 $---H_2C-\overset{C_6H_5}{\overset{\vert}{C}}H---$
Polypropylene. Packaging and labeling, reusable containers, laboratory equipment, textiles, banknotes	←	 $---H_2C-\overset{H_3C}{\overset{\vert}{C}}H---$
Poly-1-butene. Pressure piping, flexible packaging, water heaters, hot melt adhesives	←	 $---H_2C-\overset{C_2H_5}{\overset{\vert}{C}}H---$
Polyvinyl chloride. Pipes for residential sewerage and water supply systems	←	 $---H_2C-\overset{Cl}{\overset{\vert}{C}}H---$
Polyvinyl alcohol. Hard contact lens solution as lubricant	←	 $---H_2C-\overset{HO}{\overset{\vert}{C}}H---$
Polyacrylic acid. Disposable diapers and for to thicken, disperse, suspend and emulsify pharmaceuticals and cosmetics	←	 $---H_2C-\overset{HOOC}{\overset{\vert}{C}}H---$
Polyvinyl acetate. Component of widely used glue type (wood glue, white glue, carpenter's glue, school glue)	←	 $---H_2C-\overset{H_3COC{=}O}{\overset{\vert}{C}}H---$

Synthetic polymers (2/2)

<table>
<tr><td colspan="8">Monomer, polymer & its uses</td></tr>
<tr><td colspan="2" rowspan="2">Polyoxymethylene. Precision parts that require high stiffness, low friction and excellent dimensional stability</td><td>←</td><td>$---CH_2-O----$</td><td>$---CH_2-CH_2----$</td><td>→</td><td colspan="2" rowspan="2">Polyethylene. Packaging (plastic bag, plastic films, membranes, containers including bottles)</td></tr>
<tr><td colspan="2" rowspan="2">Polytetrafluoroethylene. Teflon; water and water-containing substances do not wet it; very low friction coefficient against any solid</td><td colspan="2" rowspan="2">Polydimethylsiloxane. Silicones; inert, non-toxic and non-flammable; contact lenses, medical devices, elastomers; present in shampoos (makes hair shiny and slippery), lubricating oils, and heat-resistant tiles</td></tr>
<tr><td> $---\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}----$</td><td>→</td><td>←</td><td> $----\underset{CH_3}{\overset{CH_3}{Si}}-O----$</td></tr>
<tr><td colspan="2" rowspan="2">Poly(methyl methacrylate). Lightweight and shatter-resistant alternative to glass</td><td>←</td><td> $---H_2C-\underset{H_3C}{\overset{H_3COOC}{CH}}---$</td><td> $\begin{array}{c} HC=CH \\ ---H_2C\quad CH---- \end{array}$</td><td>→</td><td colspan="2">Polybutadiene. Synthetic rubber for automobile tires</td></tr>
<tr><td colspan="6" rowspan="2">Nylon 6. Bristles for toothbrushes, surgical sutures, strings for acoustic and classical musical instruments (guitars, sitars, violins, violas, and cellos), threads, ropes, filaments, nets, tire cords, and hosiery and knitted garments</td></tr>
<tr><td> $\begin{array}{c} H_2C-C_4H_8 \\ ---HN\quad OC---- \end{array}$</td><td>→</td></tr>
</table>

Q & R

In connection with polymers:		
	1	Teflon is a synthetic polymer
	0	Teflon is a natural polymer
	1	Polystyrene is a synthetic polymer
	0	Polystyrene is a natural polymer
	0	The peptides are synthetic polymers
	1	The peptides are natural polymers
	0	Cellulose is a synthetic polymer
	1	Cellulose is a natural polymer

Polymers apps

- Rheological fluids - suspensions of non-conducting particles in an electrically insulating fluid at which viscosity changes reversibly by an order of up to 100,000 in response to an electric field. Apps: flexible electronics (rollable screens and keypads), shock absorbers (bulletproof vests).
- Thermoplasts - pliable or moldable above a specific temperature, and reversible return to solid state upon cooling. Apps: gluings, plugging holes in asphalt and walls
- Elastomers – transverse elasticity modulus does not change appreciably and has values in the range 1..10 daN/cm^2. Apps: rubbers, flexible control devices, seals, adhesives and molded flexible parts
- Duroplasts – elasticity modulus does not change appreciably and has values over 100 daN/cm^2. Being light, flexible, and strong are recommended for apps exploiting these qualities.

Plastic materials

- Polymers are mixed with auxiliary materials in order to obtain plastics:
  - plasticisers: minimize polymer intramolecular forces of attraction which add irreversibly changes the physical properties of polymers;
  - stabilizers: mitigate or eliminate reactions that cause degradation;
  - packing materials (such as dust, threads, fibers, paper, textiles) - modify certain physicochemical properties;
  - reinforcement materials - fillers that increase resistance;
  - dyes - organic and inorganic pigments;
  - lubricants - is applied on surfaces to facilitate separation of plastics and metals;
  - antistatic substances - prevent accumulation of electrostatic charges;
  - flame retardants - increase the fire resistance;
  - fungistatic agents - increase resistance to the action of microorganisms on auxiliary materials;
  - blowing agents - to obtain porous plastics;
  - odorization agents - to cover the inadequate smell due to chemical constitution, auxiliaries or oxidation processes;

Reaction types and conservation laws

Type	Reaction	Example
Rearranging	A → B	cyclopropane ↔ propene
Combustion	$C_aH_bN_cO_d + (a+{}^{b}/_{4}-{}^{d}/_{2})O_2 \rightarrow (a)CO_2 + ({}^{b}/_{2})H_2O + ({}^{c}/_{2})N_2$	
	$C_aH_bS_f + (a+{}^{b}/_{4}+{}^{3f}/_{2})O_2 + (116f-{}^{b}/_{2})H_2O \rightarrow (a)CO_2 + (f)[H_2SO_4\cdot 115H_2O]$	
	$C_aH_bP_e + (a+{}^{b}/_{4}+{}^{5e}/_{2})O_2 \rightarrow (a)CO_2 + ({}^{b}/_{2}-{}^{3e}/_{2})H_2O + (e)H_3PO_4$	
Synthesis	A + B → AB	$8Fe + S_8 \rightarrow 8FeS$
Decomposition	AB → A + B	$H_2CO_3 \rightarrow H_2O + CO_2$
Displacement	AB + CD → AD + CB	$Pb(NO_3)_2 + 2KI \rightarrow PbI_2 + 2KNO_3$

Conservation	Law	Exceptions
Mass	Total ("rest") mass before and after reaction are equal	Reaction between "heavy particles" (bradyons) of matter and antimatter
Number of atoms	For each species (element) the number of atoms before and after reaction are equal	Fission and fusion reactions
Electric charge	The total number of electrons before and after reaction are equal	Reactions involving induced electric current (electrolysis, electrochemical cells)

Q & R

In connection with the types of chemical reactions:		
	1	$AB + CD \rightarrow AD + CB$ defines a displacement
	0	$AB + CD \rightarrow AD + CB$ defines a decomposition
	0	$AB \rightarrow A + B$ defines a displacement
	1	$AB \rightarrow A + B$ defines a decomposition
	1	$A + B \rightarrow AB$ defines a synthesis
	0	$A + B \rightarrow AB$ defines a rearrangement
	0	$A \rightarrow B$ defines a synthesis
	1	$A \rightarrow B$ defines a rearrangement

Q & R (see & Course3)

Determine if processes are properly defined by the chemical reactions:		
	1	Dissociation: $MgCl_2(aq) \rightleftharpoons Mg^{2+}(aq) + 2Cl^-(aq)$
	0	Reaction: $MgCl_2(aq) \rightleftharpoons Mg^{2+}(aq) + 2Cl^-(aq)$
	0	Dissociation: $MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$
	1	Reaction: $MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$
	1	Dissociation: $NaOH(aq) \rightleftharpoons Na^+(aq) + HO^-(aq)$
	0	Dissolving: $NaOH(aq) \rightleftharpoons Na^+(aq) + HO^-(aq)$
	0	Dissociation: $NaOH(s) \rightarrow NaOH(aq)$
	1	Dissolving: $NaOH(s) \rightarrow NaOH(aq)$

Elementary reactions

- An elementary (chemical) reaction is when one or more of the chemical species react directly to form products in a single reaction step and with a single transition state.

$$R_1 + R_2 + \ldots + R_m \to P_1 + P_2 + \ldots + P_n,$$

$$\upsilon = k[R_1]\cdot[R_2]\cdot\ldots\cdot[R_m]$$

- Example:

  $2A + B \to A + C$ (“C”=“B”+”A”)

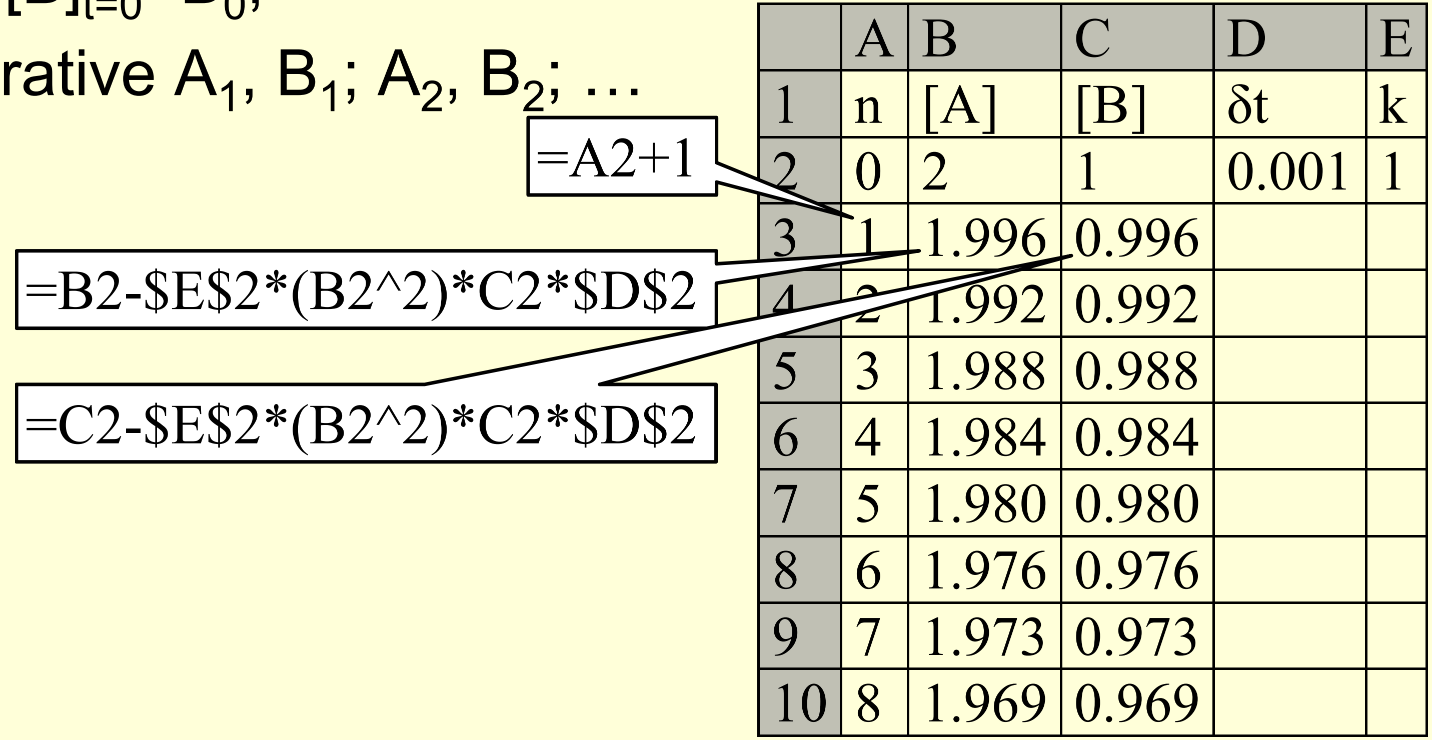
  $d[A]/dt=-k[A]^2[B]$; $d[B]/dt=-k[A]^2[B]$; $d[C]/dt=k[A]^2[B]$;

  To solve:

$$A \cdot \ddot{A} - 2 \cdot \dot{A}^2 + k \cdot A^3 \cdot \dot{A} = 0$$

Iterative approach

- Example (again): $2A + B \rightarrow A + C$
- $dt \rightarrow \delta t$; $d[A]/dt \rightarrow (A_{n+1}-A_n)\delta t$; $d[B]/dt \rightarrow (B_{n+1}-B_n)\delta t$
- $d[A]/dt=-k[A]^2[B] \rightarrow A_{n+1} = A_n + (-kA_n{}^2B_n)\cdot\delta t$
- $d[B]/dt=-k[A]^2[B] \rightarrow B_{n+1} = B_n + (-kA_n{}^2B_n)\cdot\delta t$
- $[A]_{t=0}=A_0$; $[B]_{t=0}=B_0$;
- $n \geq 1 \rightarrow$ iterative A_1, B_1; A_2, B_2; …



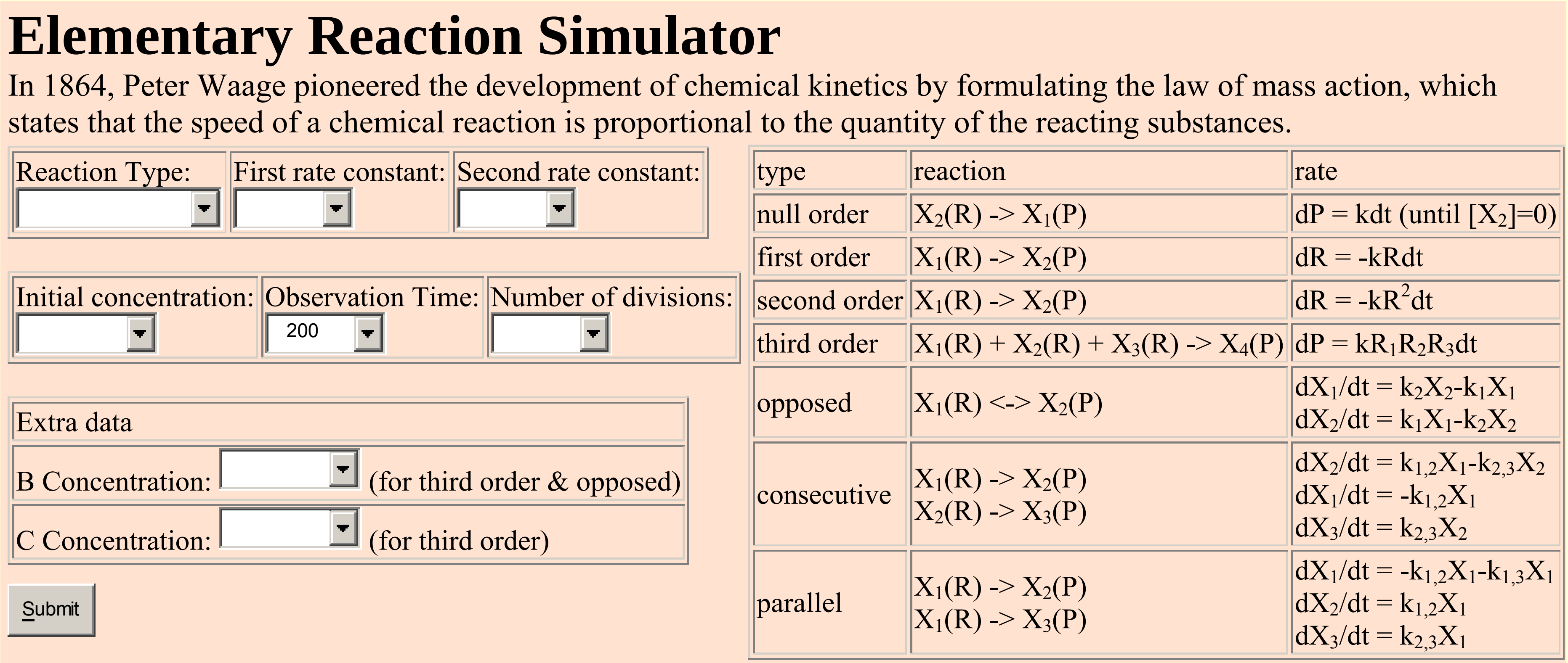
=A2+1

=B2-$E$2*(B2^2)*C2*$D$2

=C2-$E$2*(B2^2)*C2*$D$2

	A	B	C	D	E
1	n	[A]	[B]	δt	k
2	0	2	1	0.001	1
3	1	1.996	0.996		
4	2	1.992	0.992		
5	3	1.988	0.988		
6	4	1.984	0.984		
7	5	1.980	0.980		
8	6	1.976	0.976		
9	7	1.973	0.973		
10	8	1.969	0.969		

http://l.academicdirect.org/Education/Training/reaction_kinetics/



Elementary Reaction Simulator

In 1864, Peter Waage pioneered the development of chemical kinetics by formulating the law of mass action, which states that the speed of a chemical reaction is proportional to the quantity of the reacting substances.

Reaction Type:	First rate constant:	Second rate constant:

Initial concentration:	Observation Time: 200	Number of divisions:

Extra data

B Concentration: (for third order & opposed)

C Concentration: (for third order)

type	reaction	rate
null order	$X_2(R) \rightarrow X_1(P)$	$dP = kdt$ (until $[X_2]=0$)
first order	$X_1(R) \rightarrow X_2(P)$	$dR = -kRdt$
second order	$X_1(R) \rightarrow X_2(P)$	$dR = -kR^2dt$
third order	$X_1(R) + X_2(R) + X_3(R) \rightarrow X_4(P)$	$dP = kR_1R_2R_3dt$
opposed	$X_1(R) \leftrightarrow X_2(P)$	$dX_1/dt = k_2X_2-k_1X_1$ $dX_2/dt = k_1X_1-k_2X_2$
consecutive	$X_1(R) \rightarrow X_2(P)$ $X_2(R) \rightarrow X_3(P)$	$dX_2/dt = k_{1,2}X_1-k_{2,3}X_2$ $dX_1/dt = -k_{1,2}X_1$ $dX_3/dt = k_{2,3}X_2$
parallel	$X_1(R) \rightarrow X_2(P)$ $X_1(R) \rightarrow X_3(P)$	$dX_1/dt = -k_{1,2}X_1-k_{1,3}X_1$ $dX_2/dt = k_{1,2}X_1$ $dX_3/dt = k_{2,3}X_1$

Michaelis-Menten mechanism

1. Writing of elementary reactions; writing of reaction rates equations

(1): $S + E \rightarrow_{k1} C$, $v_{(1)} = k_1 \cdot s \cdot e$	(2): $C \rightarrow_{k2} S + E$, $v_{(2)} = k_2 \cdot c$	(3): $C \rightarrow_{k3} P + E$, $v_{(3)} = k_3 \cdot c$

2. Applying of atoms conservation principle

(S): $\dot{s} = v_{(2)} - v_{(1)}$	(E): $\dot{e} = v_{(2)} + v_{(3)} - v_{(1)}$	(C): $\dot{c} = v_{(1)} - v_{(2)} - v_{(3)}$	(P): $\dot{p} = v_{(3)}$

3. Suppositions and notations

$s(0) = s_0$	$e(0) = e_0$	$c(0) = 0$	$p(0) = 0$	$e = e_0 - c$

4. Equations to solve

$\dot{s} = k_2 c - k_1 s(e_0 - c)$	$\dot{c} = k_1 s(e_0 - c) - (k_2 + k_3)c$

5. General case

implicit equation → has no analytical solution!	phases space	$\frac{dy}{dx} = b\frac{x - y - xy}{-x + ay + xy}$
explicit equations; substitutions: $t = k_1 e_0 \tau$, τ initial time	$0 < a < 1$ $b > 0$	$a = \frac{k_2}{k_2 + k_3}$; $b = \frac{k_2 + k_3}{k_1 e_0}$; $x = \frac{k_1 s}{k_2 + k_3}$; $y = \frac{c}{e_0}$ $\dot{x} = -x + ay + xy$; $\dot{y} = b(x - y - xy)$;

6. Solving numerically (i=1..n)

$x_0 = 3$ $y_0 = 0$	$x_{i+1}=x_i+\delta(-x_i+ax_i+x_iy_i)$ $y_{i+1}=y_i+b\delta(x_i-y_i-x_iy_i)$	$\delta=10^{-2}$ $n=3000$	$a \in \{\frac{1}{5}, \frac{2}{5}, \frac{3}{5}, \frac{4}{5}\}$	$b \in \{\frac{250}{25}, \frac{50}{25}, \frac{10}{25}, \frac{4}{25}\}$

7. Excel sheet:

	A	B	C	D	E	F
1	x0=	3		i	xi	yi
2	y0=	0		=0	=B1	=B2
3	δ=	1.0e-2		=D2+1	=E2+$B$3*(-E2+$B$4*E2+E2*F2)	=F2+$B$5*$B$3*(E2-F2-E2*F2)
4	a=	0.2		…	…	…
5	b=	10		…	…	…

Lindemann - Hinshelwood mechanism

1. Writing of elementary reactions; writing of reaction rates equations

(1): $R + R \rightarrow R^* + R$, $v_{(1)}=k_1[R]^2$	$R^* + R \rightarrow R + R$, $v_{(2)}=k_2[R][R^*]$	$R^* \rightarrow P$, $v_{(3)}=k_3[R^*]$

2. Applying of atoms conservation principle (unknowns [R] = x; [R*] = y; [P] = z):

(R): $\dot{x} = -v_{(1)} + v_{(2)}$	(R*): $\dot{y} = v_{(1)} - v_{(2)} - v_{(3)}$	(P): $\dot{z} = v_{(3)}$

3. Suppositions and notations

$r(0) = r_0$	$r^*(0) = 0$	$p(0) = 0$	$k_1 = a$	$k_2 = b$	$k_3 = c$

4. Equations to solve

$\dot{x} = -ax^2 + bxy$	$\dot{y} = ax^2 - bxy - cy$	$\dot{z} = cy$

5. Wrong approach

The search for an analytical solution is unsuccessfully.

6. Solving numerically (i=1..n)

$x_0 = 3$ $y_0 = 0$ $z_0 = 0$	$x_{i+1}=x_i+\delta(-ax_i^2+bx_iy_i)$ $y_{i+1}=y_i+\delta(ax_i^2-bx_iy_i-cy_i)$ $z_{i+1}=z_i+\delta cy_i$	$\delta=10^{-2}$ $n=3000$	$a=10^{-1}$ $b=10^{-2}$ $c=10^{-3}$

7. Excel sheet:

	A	B	C	D	E	F	G
1	x0=	1		i	xi	yi	zi
2	y0=	0		=0	=B1	=B2	=B3
3	z0=	0		=D2+1	=E2+(-B$1*E2^2+B$2*E2*F2)*B$4	=F2+(B$1*E2^2-B$2*E2*F2-B$3*F2)*B$4	=G2+B$3*F2*B$4
4	δ=	1e-2		…	…	…	…
5	a=	1e-1		…	…	…	…
6	b=	1e-2		…	…	…	…
7	c=	1e-3		…	…	…	…

Autocatalysis mechanism

1. Writing of elementary reactions; writing of reaction rates equations

$$(1):\ R \rightarrow P,\ v_{(1)} = k\cdot[R]\cdot[P]$$

2. Applying of atoms conservation principle (unknowns [R] = x; [R*] = y; [P] = z):

(R): $\dot{r} = -v_{(1)} = -k_1 rp$	(P): $\dot{p} = v_{(1)} = k_1 rp$

3. Suppositions and notations

[R] = r	[P] = p	$k_1 = a$	$r+p=r_0+p_0=b$	$r(0)=r_0$	$p(0)=p_0$

4. Equations to solve

$\dot{p} = a(b-p)p$	$\dot{r} = -ar(b-r)$

5. Approach - exists analytical solution

$$\dot{p} = a(b-p)p \Rightarrow \frac{dp}{p(b-p)} = adt \Rightarrow \frac{1}{b}\ln\frac{p}{b-p} = at+c \Rightarrow \frac{p}{b-p} = e^{b(k_1t+c)} \Rightarrow$$

$$p = \frac{b}{1+e^{-b(k_1t+c)}} = \frac{b}{1+e^{-bk_1t}e^{-bc}}$$

6. Constants "b" and "c" - from initial values of the concentrations (at time = 0).

$$\frac{1}{b}\ln\frac{p(0)}{b-p(0)} = a0+c \Rightarrow \frac{1}{b}\ln\frac{p_0}{r_0} = c\ ;\ bc = \ln\frac{p_0}{r_0}\ ;\ -bc = \ln\frac{r_0}{p_0}\ ;\ e^{-bc} = \frac{r_0}{p_0}$$

7. Analytical solution and its interpretation

$p = p(t) = p_0\dfrac{r_0+p_0}{r_0e^{-(r_0+p_0)k_1t}+p_0}$; $r = r_0 + p_0 - p$	if $p_0 = 0$ then $p = 0$ and thus no evolution if $r_0 = 0$ then $p = p_0$ and thus no evolution

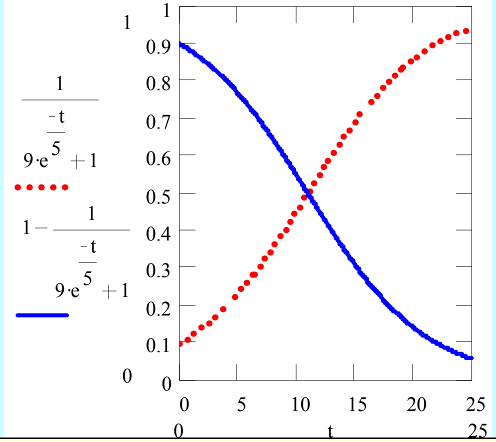
8. Plot of $p_0 \neq 0$ şi $r_0 \neq 0$ case (numerical application, using MathCad)

if $p_0 = 0.1$; $r_0 = 0.9$; $k_1 = 0.2$ then

$$p(t) = \frac{1}{9e^{-0.2t}+1}$$

and

$$r(t) = 1 - \frac{1}{9e^{-0.2t}+1}$$



Lotka - Volterra mechanism

1. Writing of elementary reactions; writing of reaction rates equations

$R + X \rightarrow 2X$, $v_{(1)} = k_1rx$	$X + Y \rightarrow 2Y$, $v_{(2)} = k_2xy$	$Y \rightarrow P$, $v_{(3)} = k_3y$	$P \rightarrow$, $v_{(4)} = k_4p$

2. Equations to solve

$\dot{x} = v_{(1)} - v_{(2)} = k_1rx - k_2xy$	$\dot{y} = v_{(2)} - v_{(3)} = k_2xy - k_3y$	$\dot{p} = v_{(3)} + v_{(4)} = k_3y + k_4p$

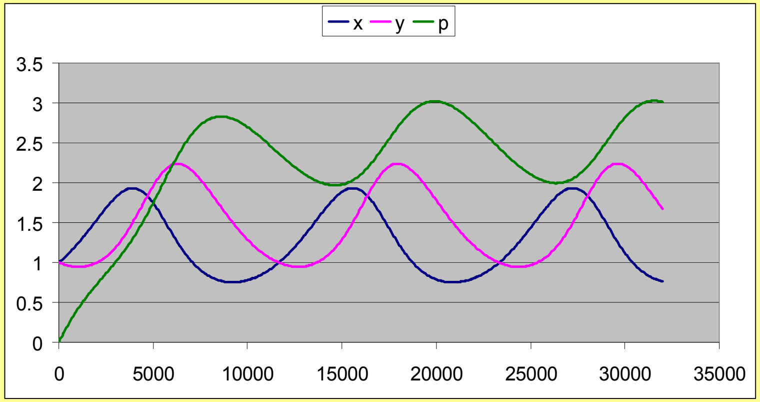
3. Solving numerically (i=1..n)

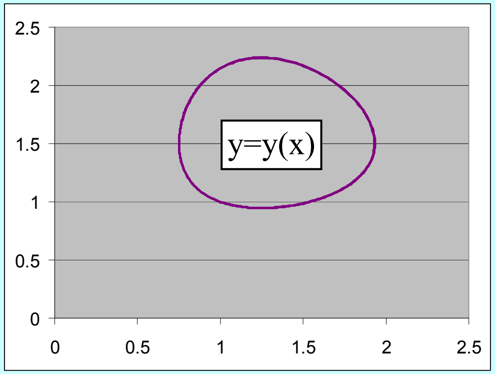
$x_0 = 3$ $y_0 = 0$ $z_0 = 0$	$x_{i+1} = x_i(1+(k_1r-k_2y_i)\delta)$ $y_{i+1} = y_i(1+(k_2x_i-k_3)\delta)$ $p_{i+1} = p_i+(k_3y_i-k_4p_i)\delta$	$\delta=10^{-2}$ $n=5\cdot10^5$	$k_1=3$ $k_2=4$ $k_3=5$	$k_4=3$ $r=1$

7. Excel sheet:

	A	B	C	D	E	F	G
1	x0=	1		i	xi	yi	pi
2	y0=	1		=0	=B1	=B2	=B3
3	p0=	0		=D2+1	=D2*(1+(B$5*B$4 -B$6*E2)*B$9)	=E2*(1+(B$6*D2-B$7)*B$9)	= F2+(B$7*E2 -B$8*F2)*B$9
4	r=	2		…	…	…	…
5	k1=	3		…	…	…	…
6	k2=	4		…	…	…	…
7	k3=	5		…	…	…	…
8	k4=	3		…	…	…	…
9	δ=	1e-4		…	…	…	…

8. Plots:





Remarks: the y=y(x) equation is almost impossible to be extracted analitically, but we may extract it aproximately (numerically). Thus, for the simulated mechanism above, the y=y(x) equation is:

$$(x-1.32)^2+0.824\cdot(y-1.57)^2 = 0.35\pm0.05$$

Brusselator mechanism

1. Writing of elementary reactions and of reaction rates equations ([R]=r, [X]=x, [Y]=y, [P]=p):

$R \to X$, $v_{(1)} = k_1 r$

$X + 2Y \to 3Y$, $v_{(2)} = k_2 x y^2$

$Y \to P$, $v_{(3)} = k_3 y$

2. Applying of atoms conservation principle (unknowns [X] = x; [Y] = y):

(X): $\dot{x} = v_{(1)} - v_{(2)} = k_1 r - k_2 x y^2$

(Y): $\dot{y} = \upsilon_{(2)} - \upsilon_{(3)} = k_2 x y^2 - k_3 y$

(P): $\dot{p} = k_3 y$

3. Approach (simplifying r = 1, $k_1 = 1$ and $k_3 = 1$):

$\dot{x} = 1 - k_2 x y^2$

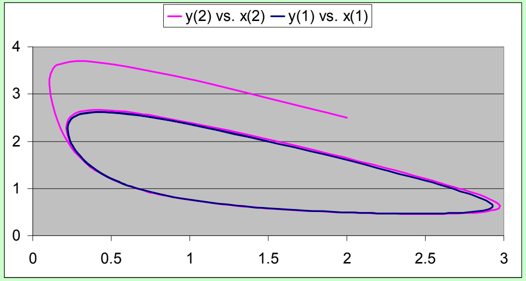
$\dot{y} = k_2 x y^2 - y$

4. Solving numerically (i=1..n):			Case 1	Case 2
$k_2 = 0.88$	$x_{n+1} = x_n + (1 - k_2 x_n y_n^2)\delta$ $y_{n+1} = y_n + (k_2 x_n y_n^2 - y_n)\delta$	$\delta = 10^{-2}$ n=10000	$x_0 = 1.5$ $y_0 = 2$	$x_0 = 2$ $y_0 = 2.5$

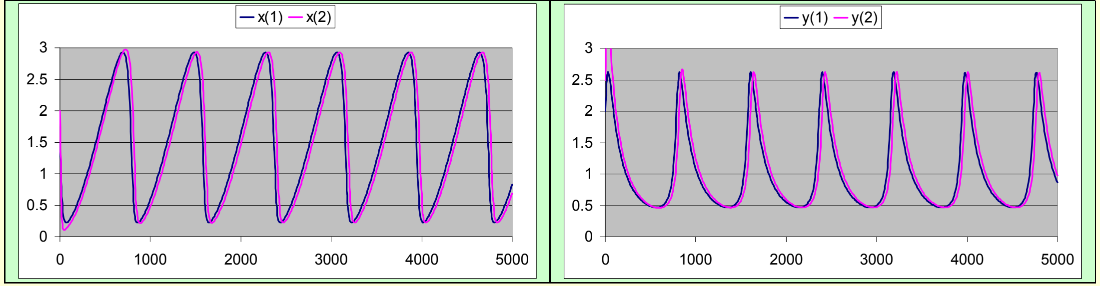
5. Excel sheet:

	A	B	C	D	E	F	G	H
1	k2=	0.88			Case 1		Case 2	
2	δ=	1e-2		i	xi	yi	xi	yi
3	Case	1		=0	=B4	=B5	=B7	=B8
4	x0=	1.5		=D2+1	=D3+(1-B$1*D3*E3^2)*B$2	=E3+(B$1*D3*E3^2-E3)*B$2	…	…
5	y0=	2		…	…	…	…	…
6	Case	2		…	…	…	…	…
7	x0=	2		…	…	…	…	…
8	y0=	2.5		…	…	…	…	…

6. Phases plot (n=1000):



7. Intermediaries plots (n=5000):



8. Simulation analysis

Not for any values the attractor appears. For a given k_2 (such is 0.88) exists minimum values of x_0 and y_0 ($x_{0\text{-min}}$, $y_{0\text{-min}}$) from which periodical oscillations occurs and the system tends to the attractor.

Oregonator mechanism

1. Writing of elementary reactions and of reaction rates equations ([X]=x, and idem for the rest of):

$A + Y \rightarrow X$	$X + Y \rightarrow P$	$A + X \rightarrow 2X + Z$	$2X \rightarrow Q$	$Z \rightarrow Y$
$v_{(1)} = k_1ay$	$v_{(2)} = k_2xy$	$v_{(3)} = k_3ax$	$v_{(4)} = k_4x^2$	$v_{(5)} = k_5z$

2. Applying of atoms conservation principle (unknowns [X] = x; [Y] = y, [Z] = z):

(X): $\dot{x} = k_1ay - k_2xy + k_3ax - 2k_4x^2$

(Y): $\dot{y} = -k_1ay - k_2xy + k_5z$

(Z): $\dot{z} = k_3ax - k_5z$

3. Solving numerically (i=1..n, after a long series of substitutions and rescaling):

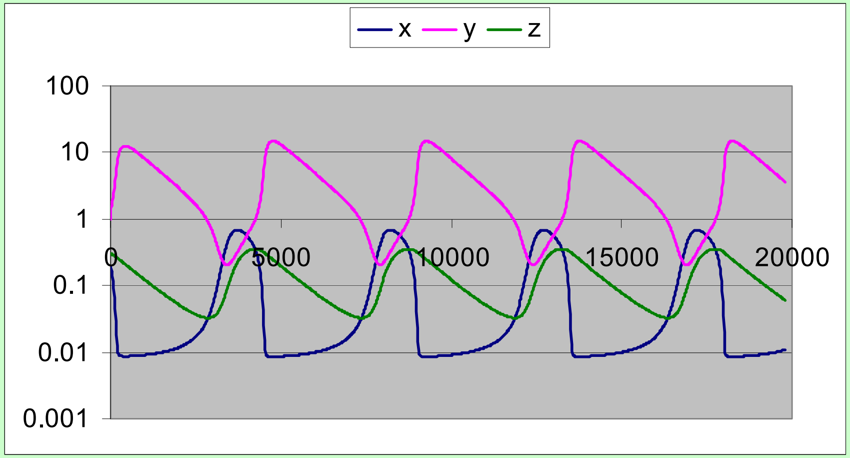
$$x_{n+1} = x_n+(qy_n-x_ny_n+x_n(1-x_n))\delta/\varepsilon$$
$$y_{n+1} = y_n+(-qy_n-x_ny_n+fz_n)\delta/\eta$$
$$z_{n+1} = z_n+(x_n-y_n)\delta$$

$x_0=0.2$ $y_0=1$ $z_0=0.3$	$\varepsilon= 8e-3$ $\eta=1e-1$	$q=2e-3$ $f=1$	$\delta=1e-3$ $n=19800$

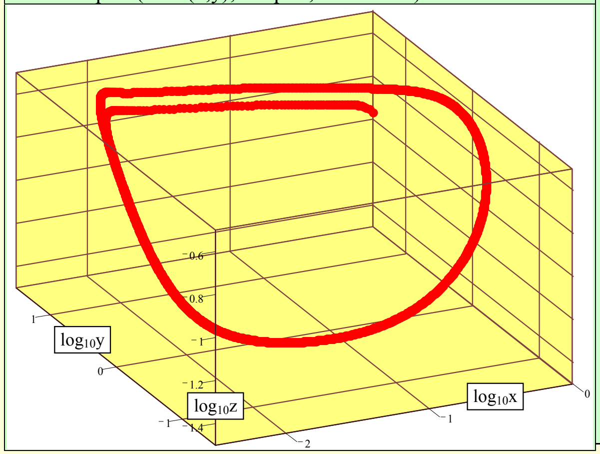
4. Excel sheet:

	A	B	C	D	E	F	F
1	q=	8e-3		i	xi	yi	zi
2	ε=	1e-1		=0	=B6	=B7	=B8
3	η=	2e-3		=D2+1	=IF(D2+(B$1*E2-D2*E2+D2*(1-D2))*B$5/B$2>0,D2+(B$1*E2-D2*E2+D2*(1-D2))*B$5/B$2,0)	=IF(E2+(-B$1*E2-D2*E2+B$4*F2)*B$5/B$3>0,E2+(-B$1*E2-D2*E2+B$4*F2)*B$5/B$3,0)	=IF(F2+(D2-F2)*B$5>0,F2+(D2-F2)*B$5,0)
4	f=	1		…	…	…	…
5	δ=	1e-3		…	…	…	…
6	x0=	0.2		…	…	…	…
7	y0=	1		…	…	…	…
8	z0=	0.3		…	…	…	…

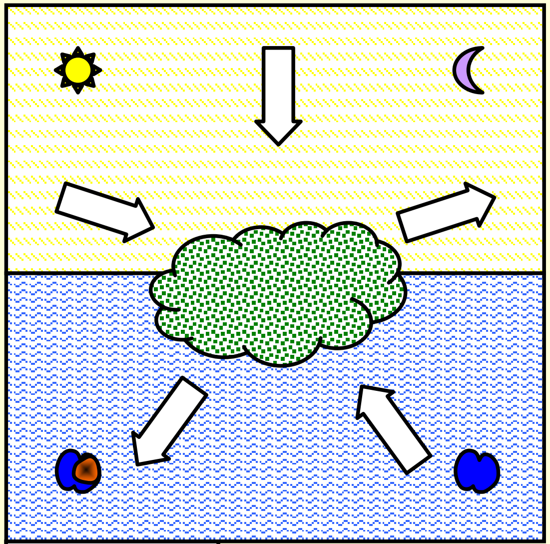
5. Intermediaries plots (n=1000):



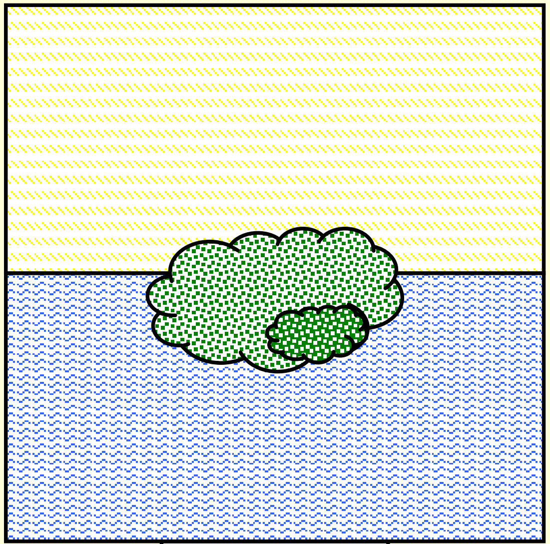
6. Phases plot (z = z(x,y); 3D plot, MathCad7):



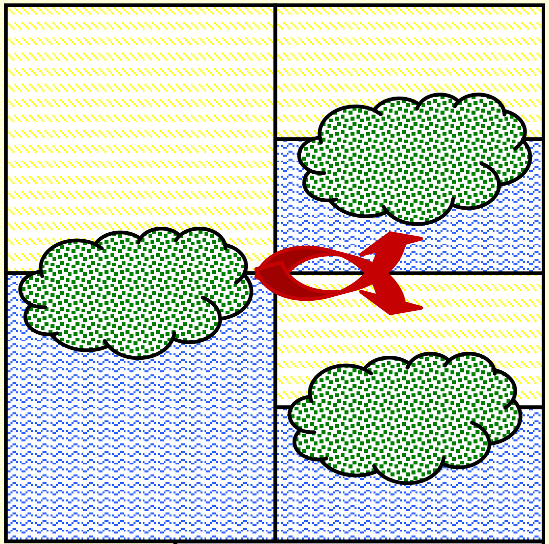
Cells functions



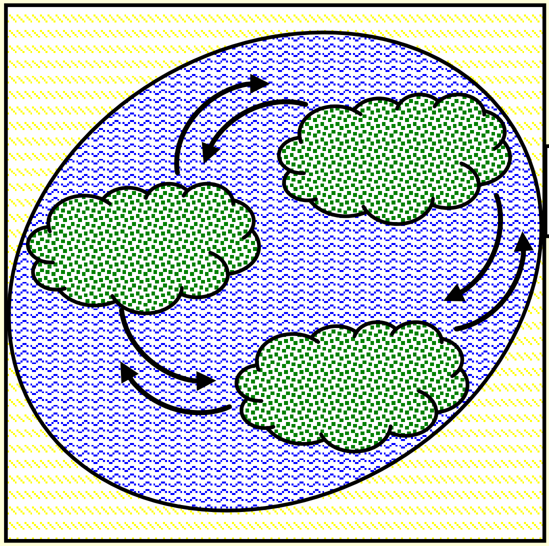
Feeding



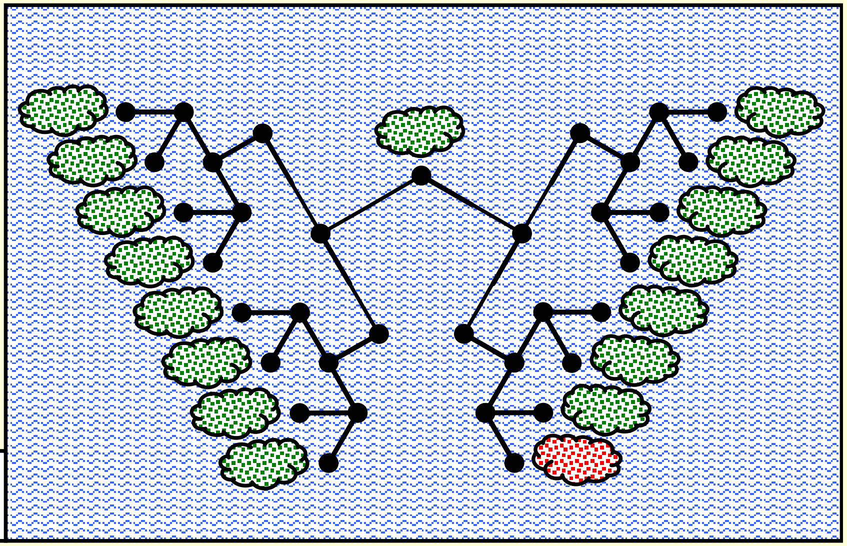
Copying



Multiplication

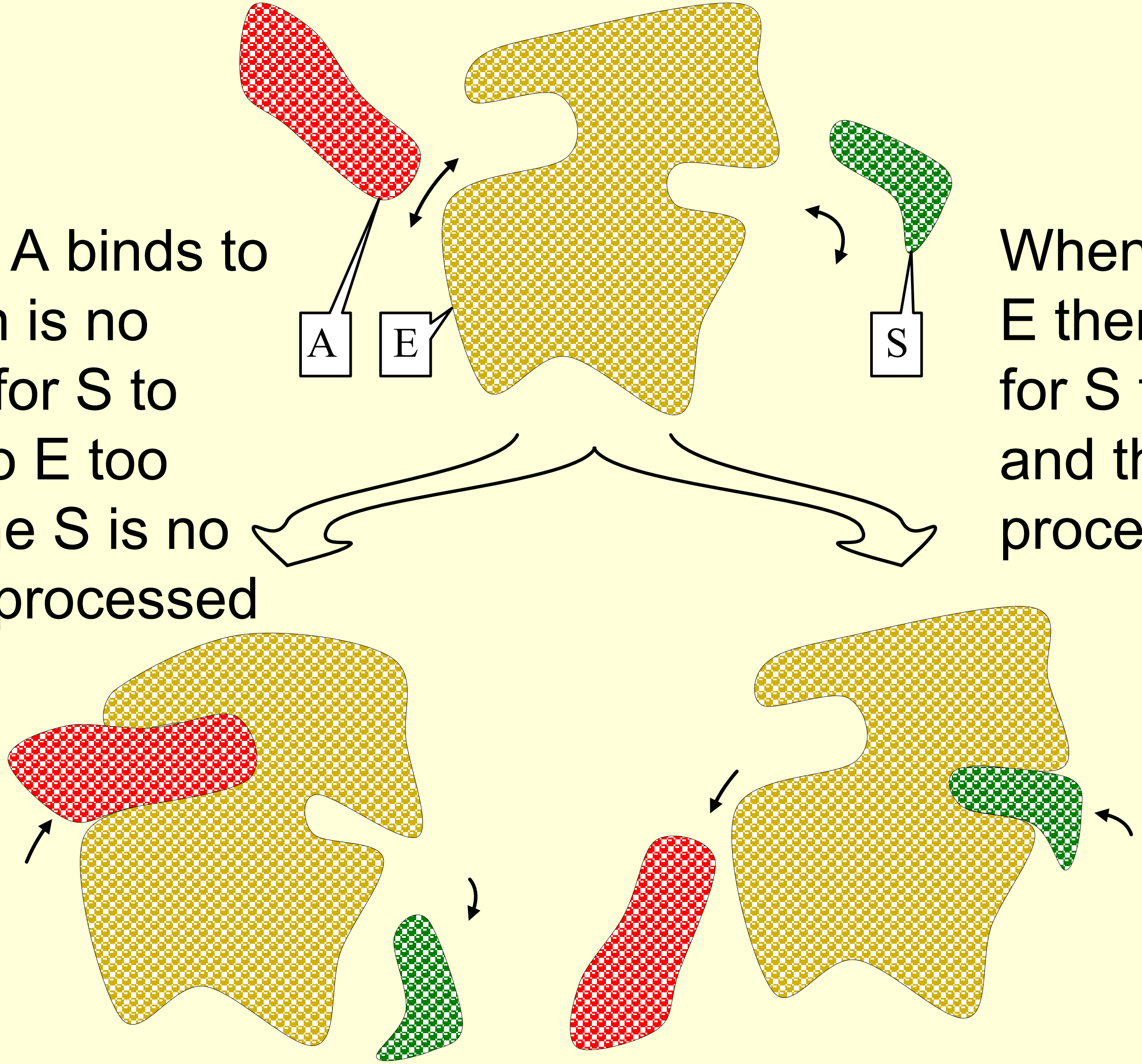


Signaling



Mutation

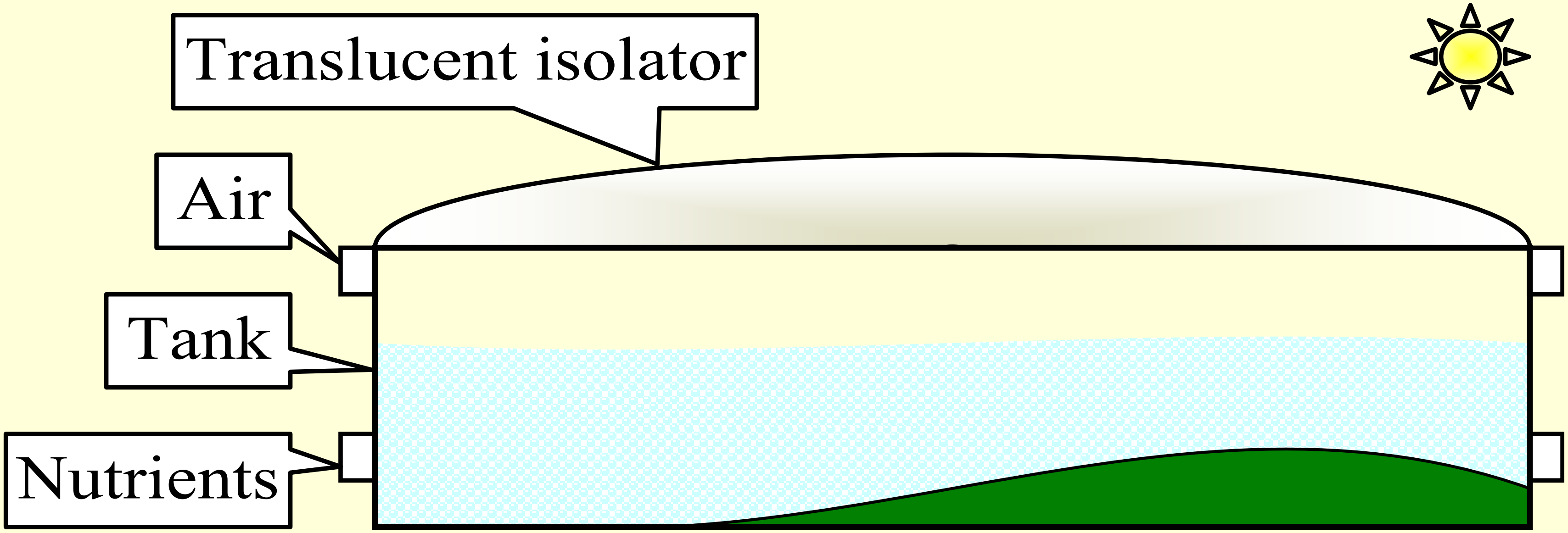
Enzyme action



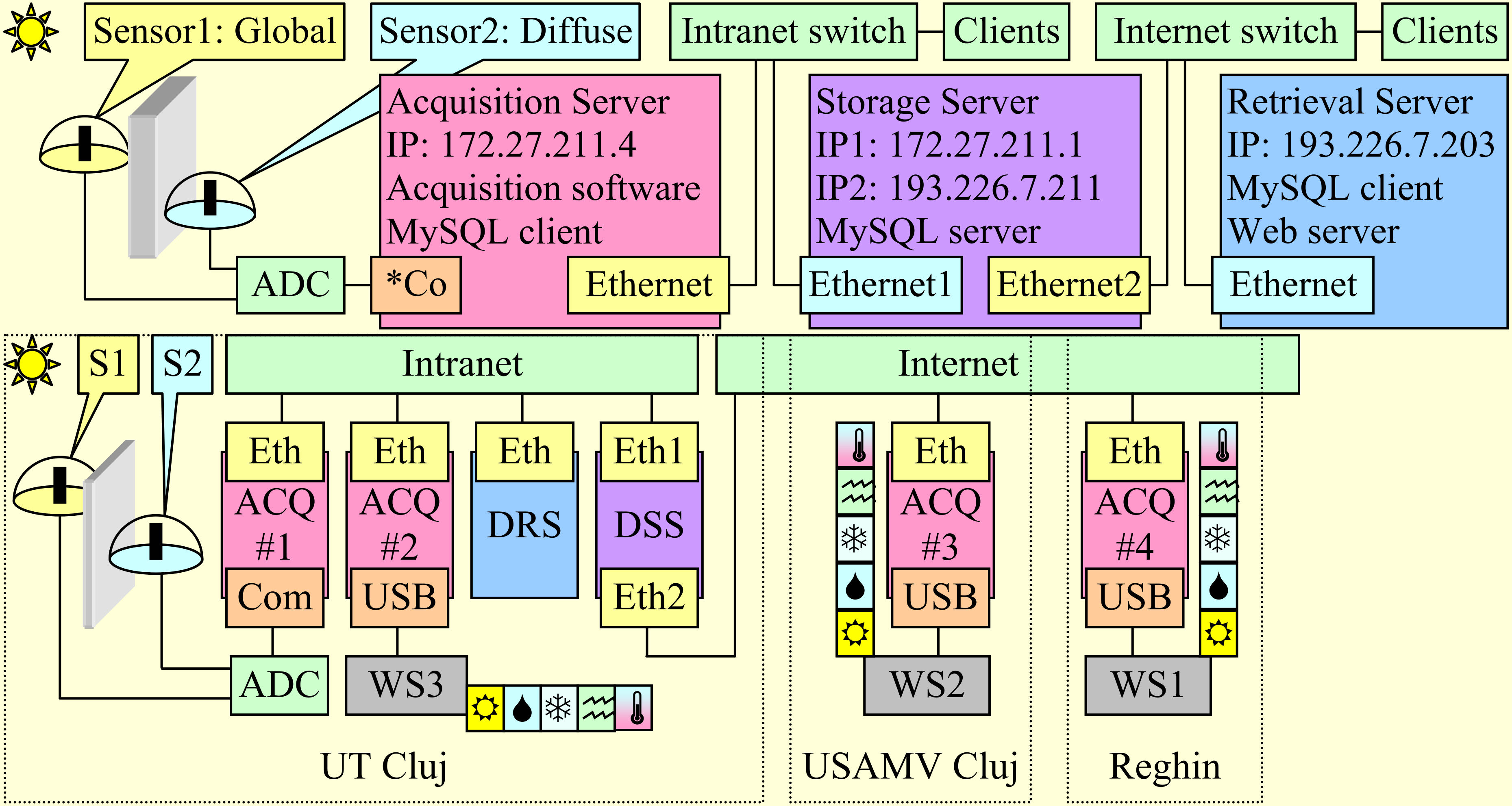
When A binds to E then is no room for S to bind to E too and the S is no more processed

When A leaves E then is room for S to bind to E and the S is processed

“Blue” biotechnology



Acquisition, storage, retrieval of sensor's data



Sensor1: Global

Sensor2: Diffuse

Intranet switch — Clients

Internet switch — Clients

Acquisition Server
IP: 172.27.211.4
Acquisition software
MySQL client

Storage Server
IP1: 172.27.211.1
IP2: 193.226.7.211
MySQL server

Retrieval Server
IP: 193.226.7.203
MySQL client
Web server

ADC

*Co

Ethernet

Ethernet1

Ethernet2

Ethernet

S1

S2

Intranet

Internet

Eth — ACQ #1 — Com

Eth — ACQ #2 — USB

Eth — DRS

Eth1 — DSS — Eth2

Eth — ACQ #3 — USB

Eth — ACQ #4 — USB

ADC

WS3

WS2

WS1

UT Cluj

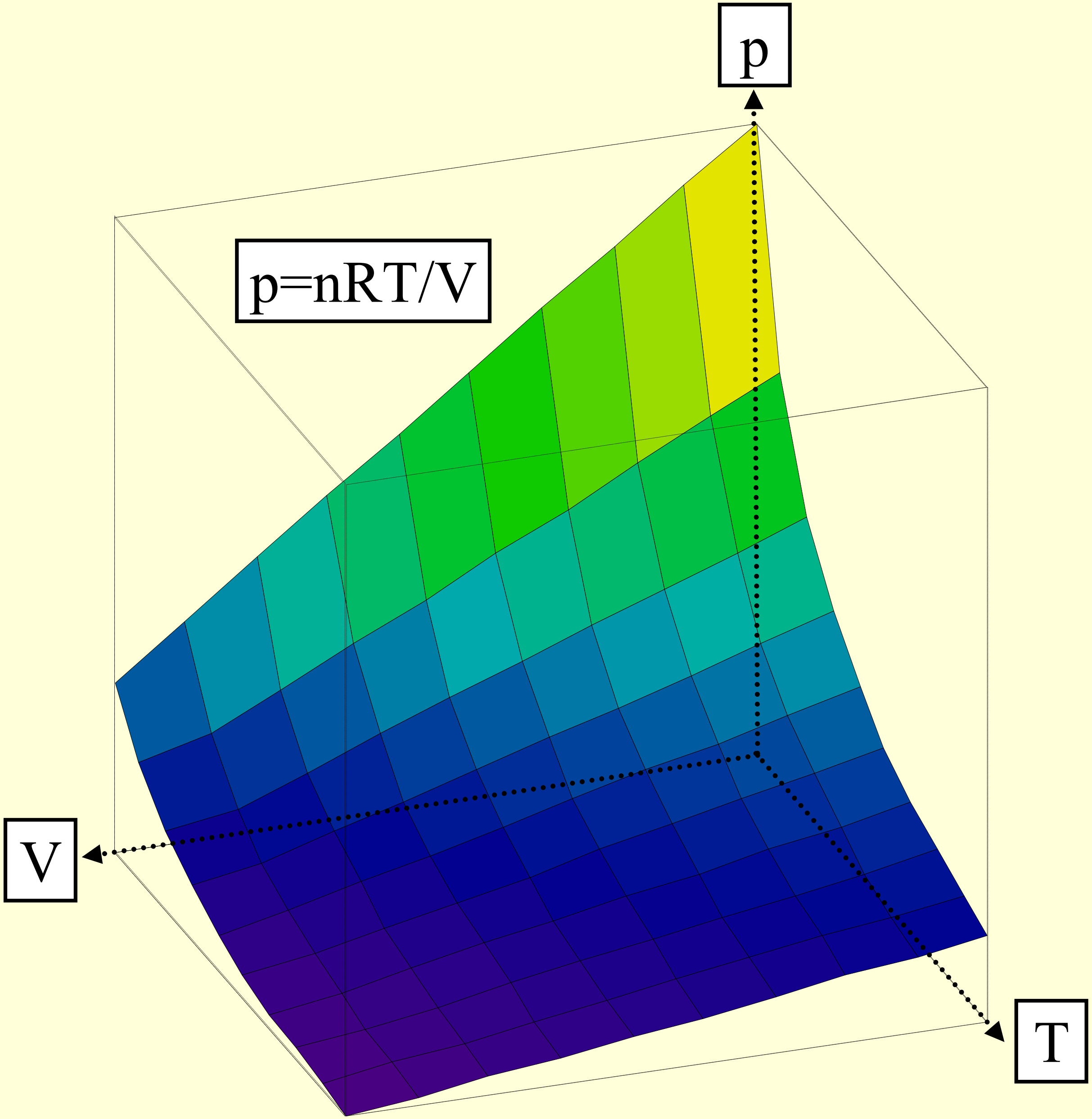
USAMV Cluj

Reghin

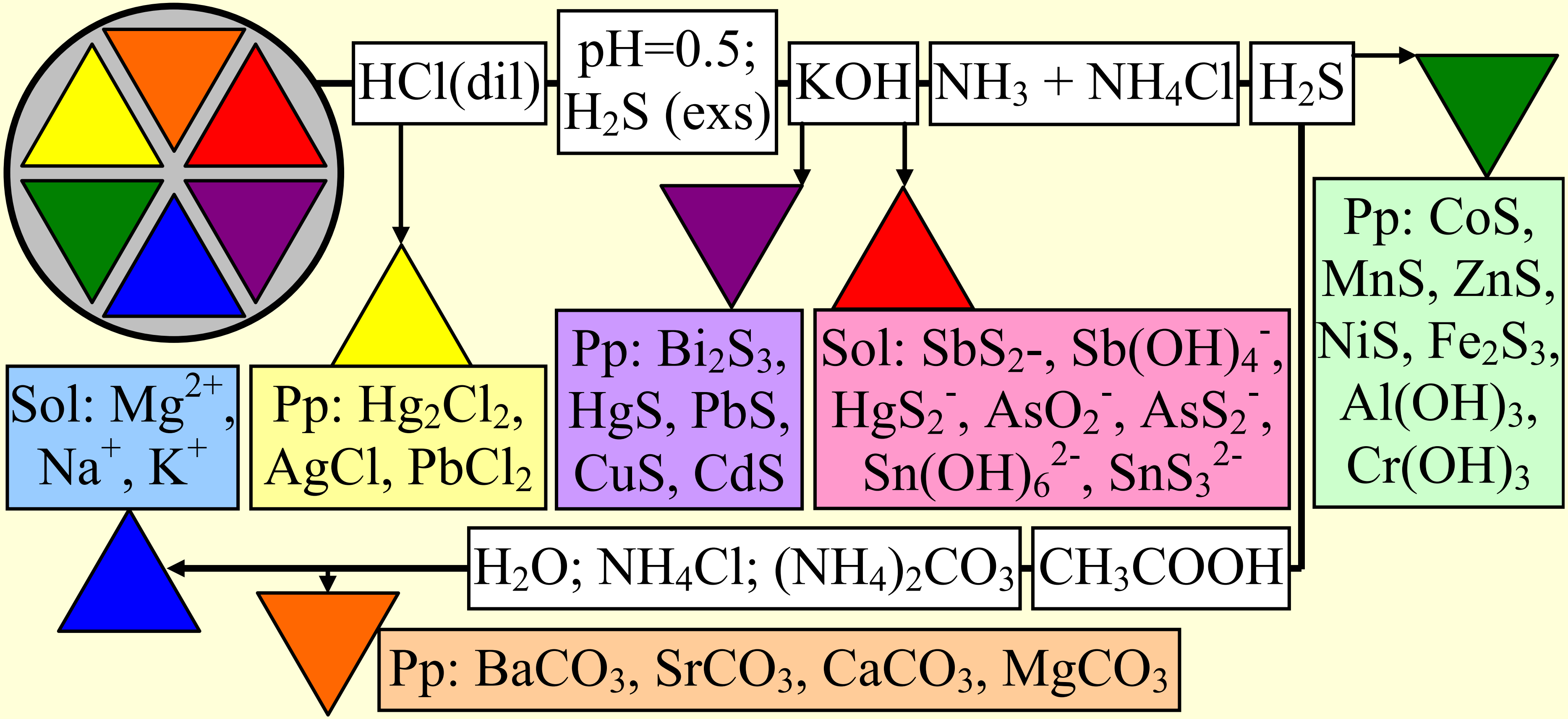
Course 14

Methods & models
Structure activity/property relationships

Ideal gas: the surface of possible states



Chemical separation methods



HCl(dil)

pH=0.5; H_2S (exs)

KOH

NH_3 + NH_4Cl

H_2S

Sol: Mg^{2+}, Na^+, K^+

Pp: Hg_2Cl_2, AgCl, $PbCl_2$

Pp: Bi_2S_3, HgS, PbS, CuS, CdS

Sol: SbS_2-, $Sb(OH)_4^-$, HgS_2^-, AsO_2^-, AsS_2^-, $Sn(OH)_6^{2-}$, SnS_3^{2-}

Pp: CoS, MnS, ZnS, NiS, Fe_2S_3, $Al(OH)_3$, $Cr(OH)_3$

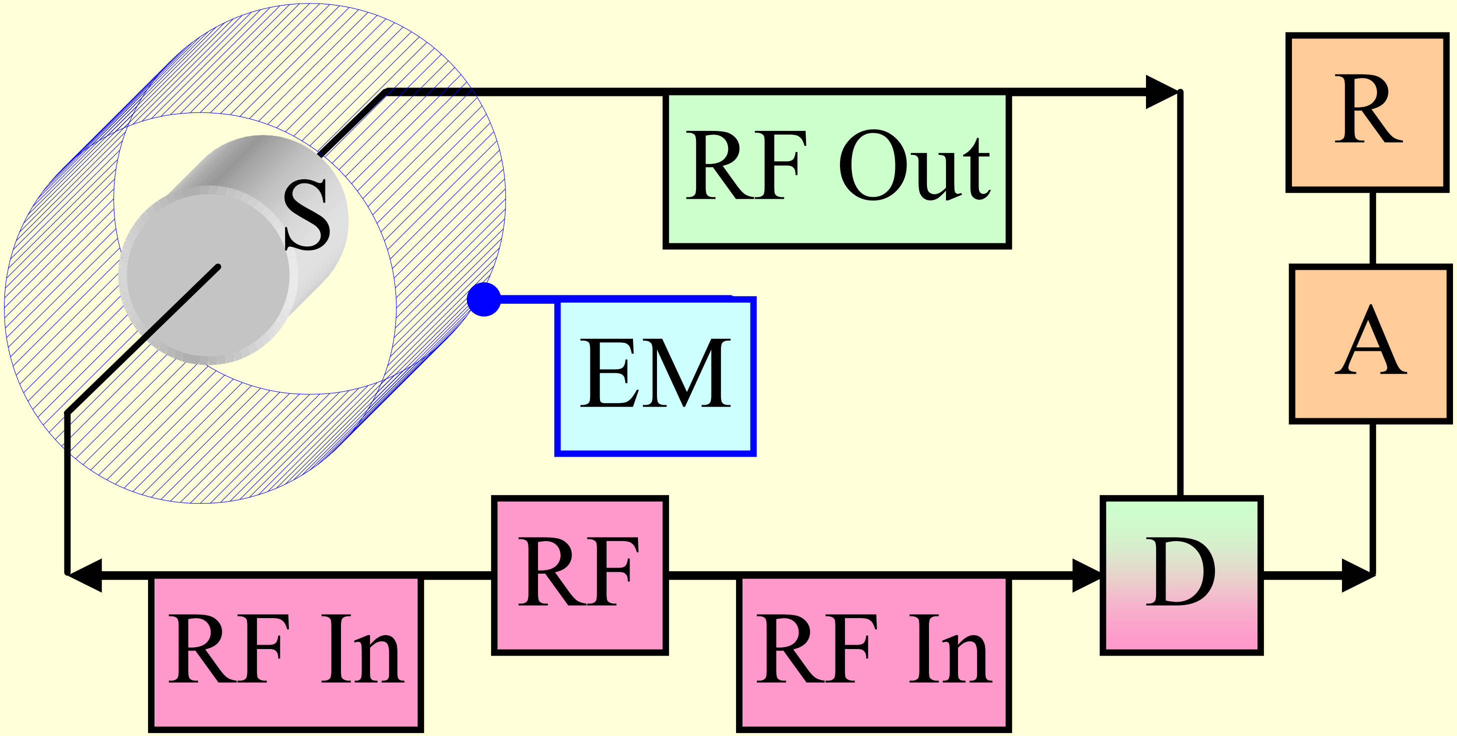
H_2O; NH_4Cl; $(NH_4)_2CO_3$

CH_3COOH

Pp: $BaCO_3$, $SrCO_3$, $CaCO_3$, $MgCO_3$

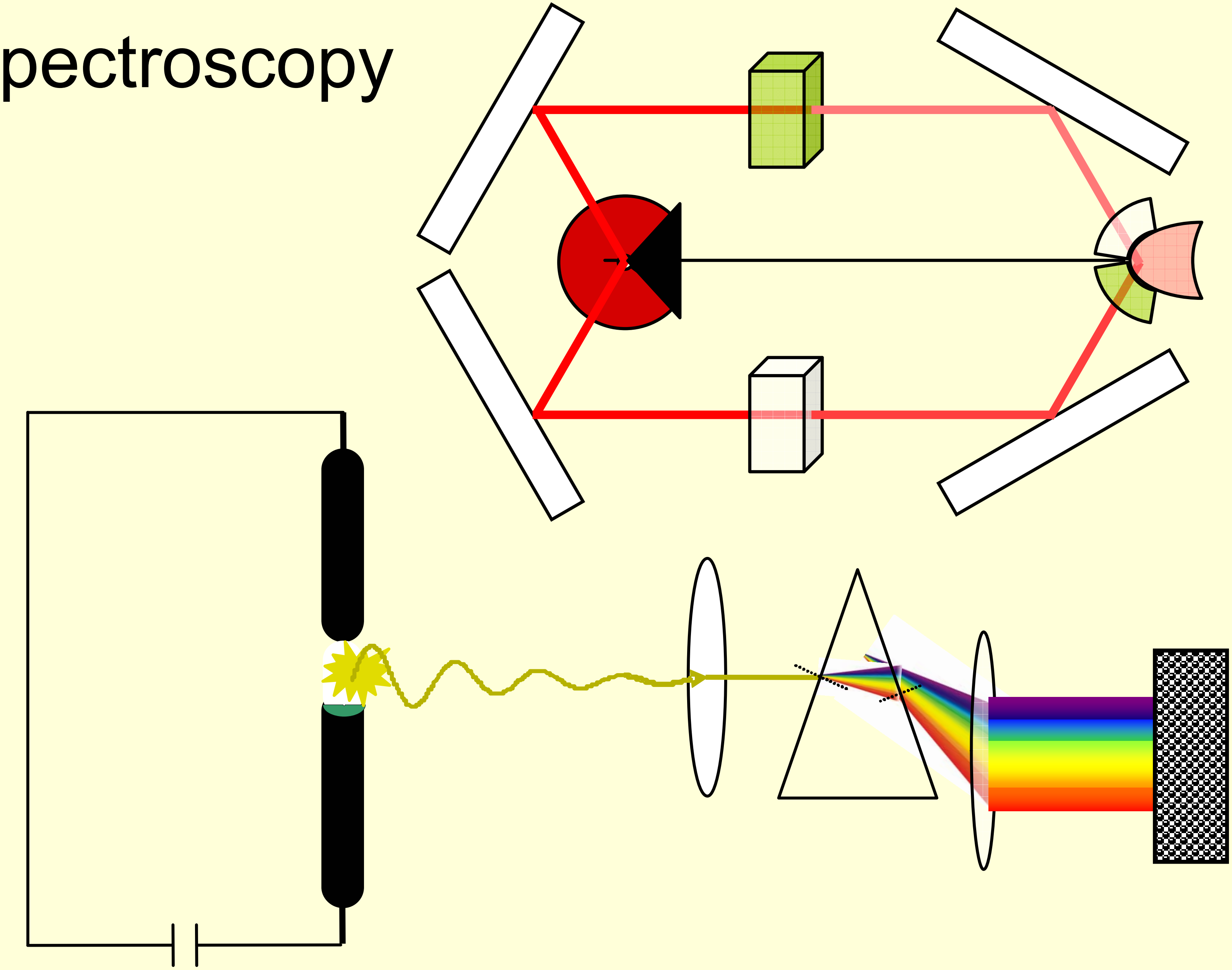
“H_2S schema”

NMR



S: Sample; RF: Radio Frequency
EM: Electromagnet; D: Detector
A: Analyser; R: Recorder

Spectroscopy

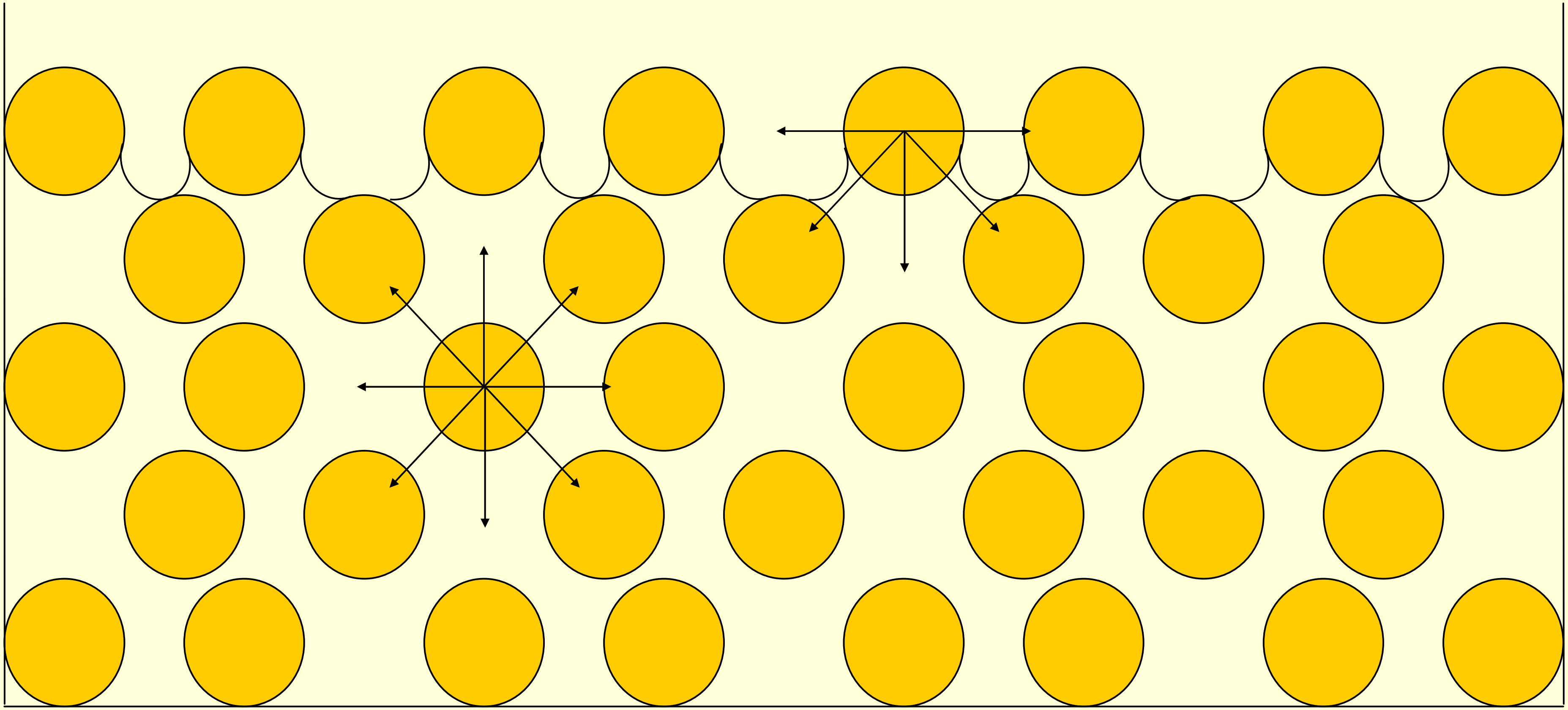


Liquids - surface tension (1/3)

- Liquids tend to take the form of minimum area with maximum number of molecules in the liquid and interactions between neighbors. Surface tension of liquids is the force that tends to minimize the surface of a liquid. In liquids, the distance between molecules is small and the scope of intermolecular forces is of the order of 10^{-6} cm. The force with which a unit of a liquid layer is drawn inwards internal pressure or pressure fluid is molecular.

Surface tension of liquids at 293 K

Substance	Benzene	Mercury	Methanol	Water
$\gamma(10^{-3}\cdot N/m)$	28.86	472	22.6	72.75



Distribution of attraction forces in a liquid

- Necessary work for σ surface variation by an dσ infinitesimal amount is proportional to dσ: $dw = \gamma \cdot d\sigma$

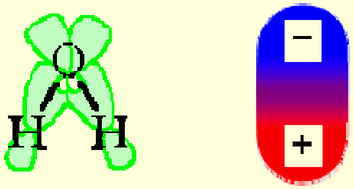
Liquids - surface tension (3/3)

- Liquid droplets tend to be spherical, spherical ensuring minimum surface/volume ratio. From this we can also provide mathematical relationship transformation applying Gauss - Ostogradsky integral over the volume V of a body to the surface S of the body and with the condition of minimum – we arrive at the fact that the position vector is collinear with the surface normal at any point of the surface S - it is obvious (geometric) the sphere.

$$\int_V \nabla\vec{r}\,dV = \oint_S \vec{r}\cdot\vec{n}\,dS = \min. \Rightarrow \vec{r}\cdot\vec{n} = 0 \Rightarrow \vec{r} \perp \vec{n}$$

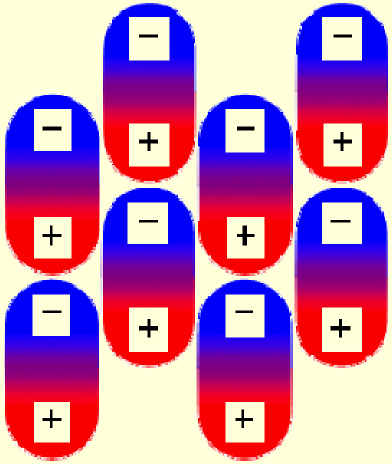
Polar solvents

- The most known polar solvent is water. Water molecule has an asymmetric electronic structure. Oxygen strongly electronegative element, moving toward him so that electrons of hydrogen atoms of water molecule is a polar molecule with polar negative charge near the oxygen atom and negatively charged pole near the hydrogen atoms.

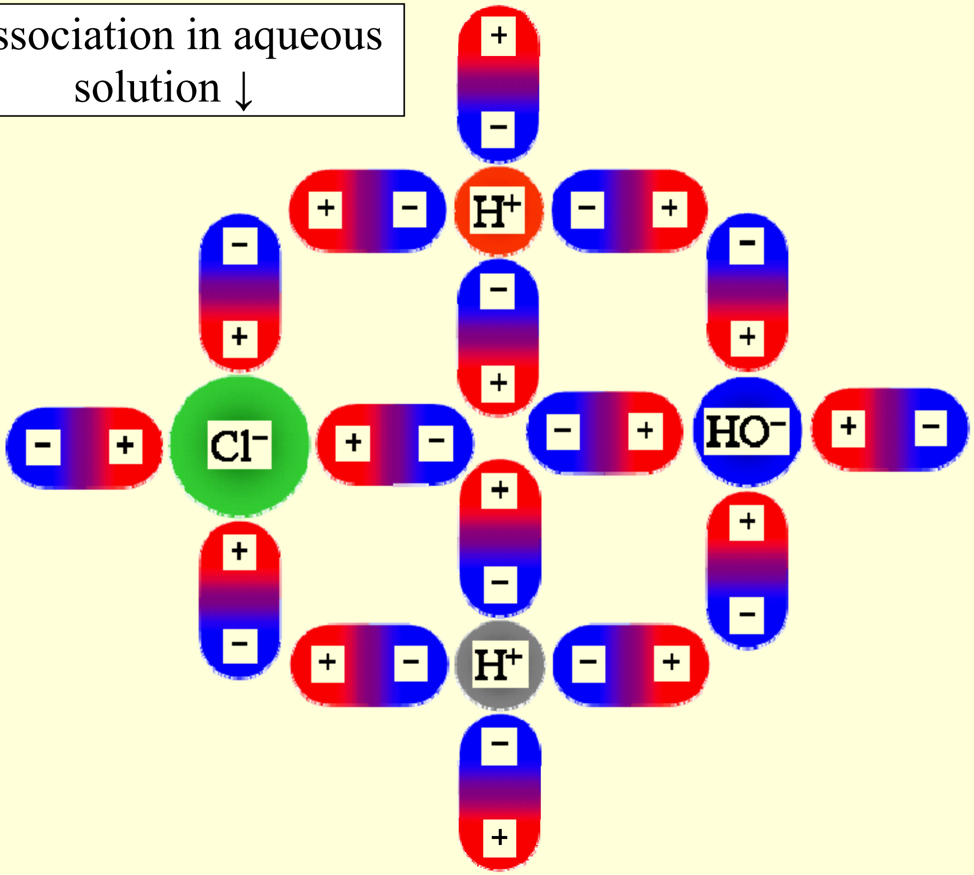


↑ Separation of charges in the water molecule

Stratification of the water molecules in the liquid phase →

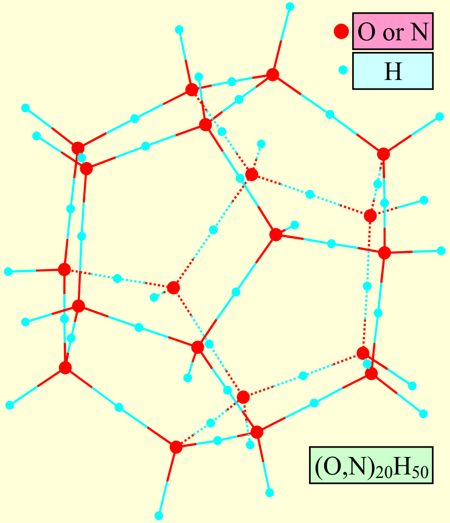


Dissociation in aqueous solution ↓



Ammonia in water

Pattern



Arrangements for $O_xN_{20-x}H_{50}$

Nr	Cluster	H_2O	NH_3	H_3O^+	HO^-	$[^+/^-]/H_2O$	Reaction of formation	N/(N+O) %
1	O_2N_{18}	2	18	8	0	+(8)/(2+8)	$18NH_3 + 10H_2O \rightarrow O_2N_{18}H_{50} + 8H_3O^+$	18/28=64.3
2	O_4N_{16}	4	16	6	0	+(6)/(6+4)	$16NH_3 + 10H_2O \rightarrow O_4N_{16}H_{50} + 6H_3O^+$	16/26=61.5
3	O_5N_{15}	5	15	5	0	+(5)/(5+5)	$15NH_3 + 10H_2O \rightarrow O_5N_{15}H_{50} + 5H_3O^+$	15/25=60.0
4	O_6N_{14}	6	14	4	0	+(4)/(4+6)	$14NH_3 + 10H_2O \rightarrow O_6N_{14}H_{50} + 4H_3O^+$	14/24=58.3
5	O_8N_{12}	8	12	2	0	+(2)/(2+8)	$12NH_3 + 10H_2O \rightarrow O_8N_{12}H_{50} + 2H_3O^+$	12/22=54.5
6	$O_{10}N_{10}$	10	10	0	0	(0)/(0+10)	$10NH_3 + 10H_2O \rightarrow O_{10}N_{10}H_{50}$	10/20=50.0
7	$O_{12}N_8$	12	8	0	2	-(2)/(2+12)	$8NH_3 + 14H_2O \rightarrow O_{12}N_8H_{50} + 2HO^-$	8/22=36.4
8	$O_{14}N_6$	14	6	0	4	-(4)/(4+14)	$6NH_3 + 18H_2O \rightarrow O_{14}N_6H_{50} + 4HO^-$	6/24=25.0
9	$O_{15}N_5$	15	5	0	5	-(5)/(5+15)	$5NH_3 + 20H_2O \rightarrow O_{15}N_5H_{50} + 5HO^-$	5/25=20.0
10	$O_{16}N_4$	16	4	0	6	-(6)/(6+16)	$4NH_3 + 22H_2O \rightarrow O_{16}N_4H_{50} + 6HO^-$	4/26=15.4
11	$O_{18}N_2$	18	2	0	8	-(8)/(8+18)	$2NH_3 + 26H_2O \rightarrow O_{18}N_2H_{50} + 8HO^-$	2/28=07.1

t(°C)	$(N/(N+O))_{sat}$	K_b	K_w	pH
0	0.460	$1.37\cdot10^{-5}$	$1.14\cdot10^{-15}$	12.5
10	0.401	$1.57\cdot10^{-5}$	$2.93\cdot10^{-15}$	12.1
20	0.334	$1.71\cdot10^{-5}$	$6.81\cdot10^{-15}$	11.6
30	0.279	$1.82\cdot10^{-5}$	$1.47\cdot10^{-14}$	11.3
40	0.232	$1.86\cdot10^{-5}$	$2.92\cdot10^{-14}$	10.9
50	0.179	$1.89\cdot10^{-5}$	$5.48\cdot10^{-14}$	10.6

Calculus based on observed data

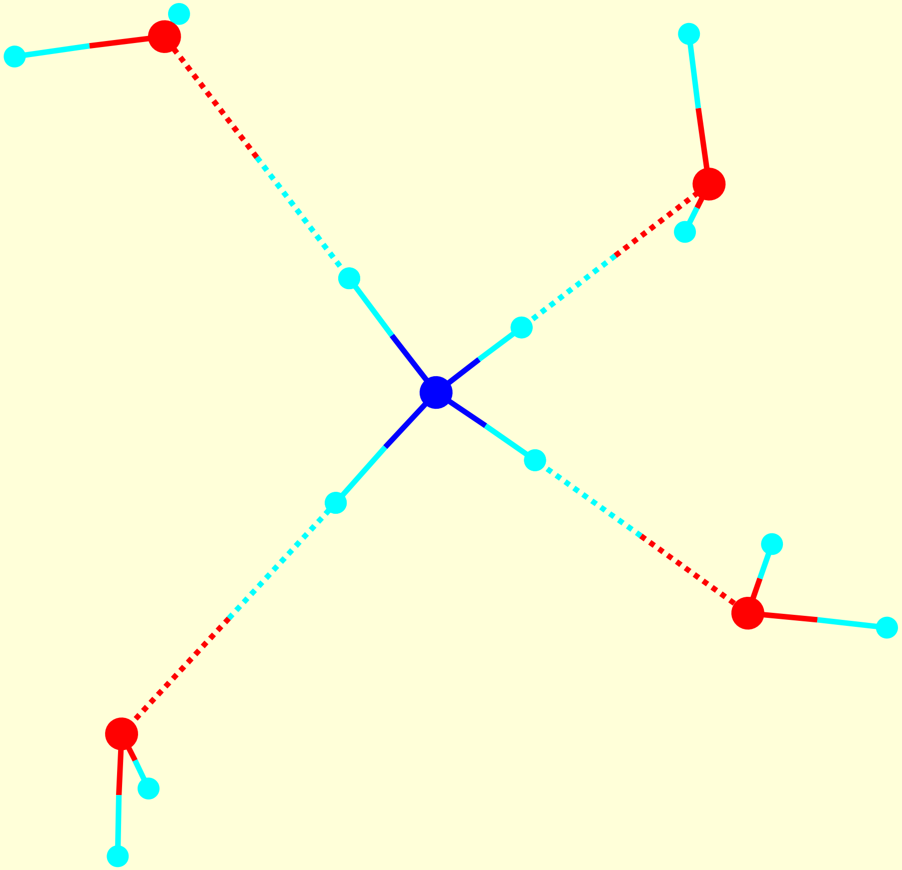
$w := 5.48\cdot10^{-14}$ $\quad n := 1.89\cdot10^{-5}$ $\quad f := 0.179$ $\quad x := 10^{-3}$ $\quad y := 10^{-12}$ $\quad$ Given

$$x\cdot(x+y) = n\cdot(1-x)\cdot\left(\frac{1-f}{f} - x - 2\cdot y\right) \qquad y\cdot(x+y) = w\cdot\left(\frac{1-f}{f} - x - 2\cdot y\right)^2 \qquad vec := \mathrm{Find}(x,y)$$

$$vec = \begin{pmatrix} 9.3\times10^{-3} \\ 1.2\times10^{-10} \end{pmatrix} \qquad z := \frac{\left(vec^T\right)^{\langle 0\rangle} + \left(vec^T\right)^{\langle 1\rangle}}{\frac{1-f}{f} - \left(vec^T\right)^{\langle 0\rangle} - 2\cdot\left(vec^T\right)^{\langle 1\rangle}} \qquad z = 2\times10^{-3} \qquad pH := -\log\left(\frac{w}{z}\right)$$

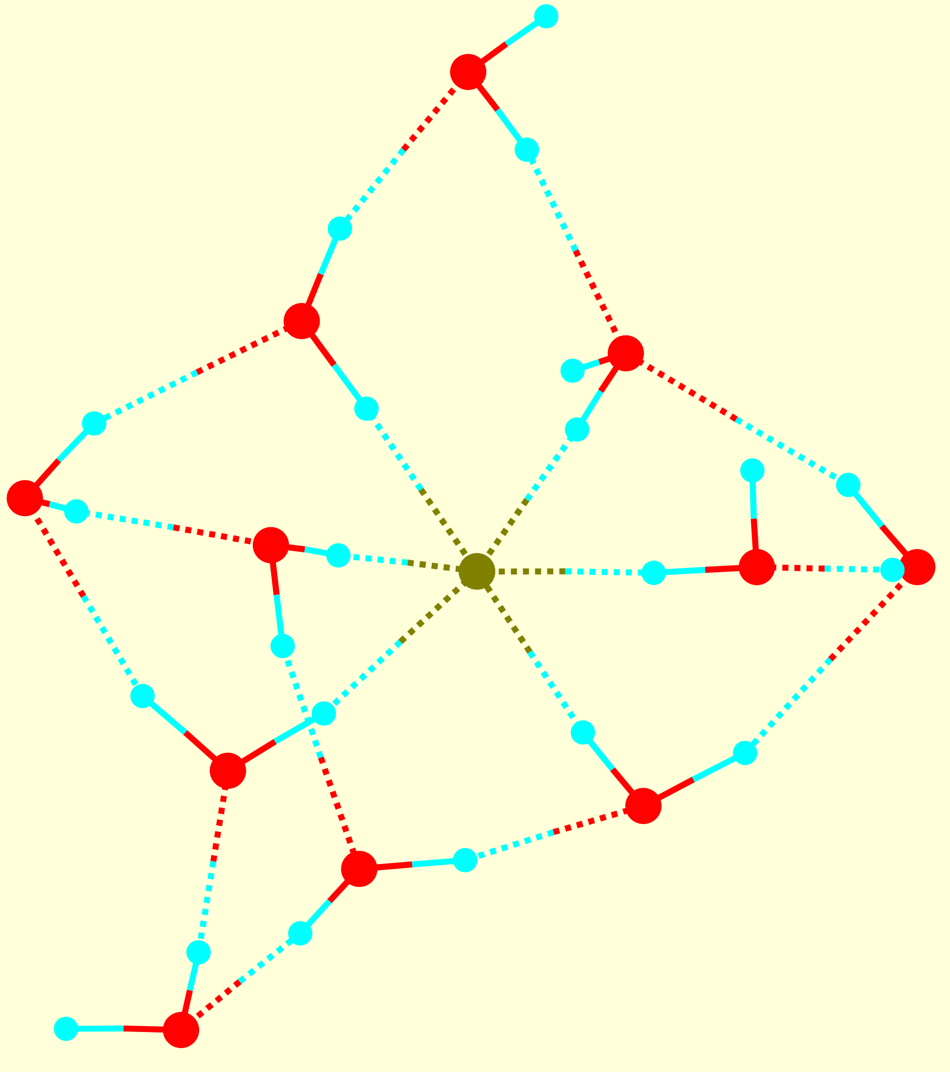
$$pH = 10.6$$

$NH_4^+ \cdot 4H_2O$

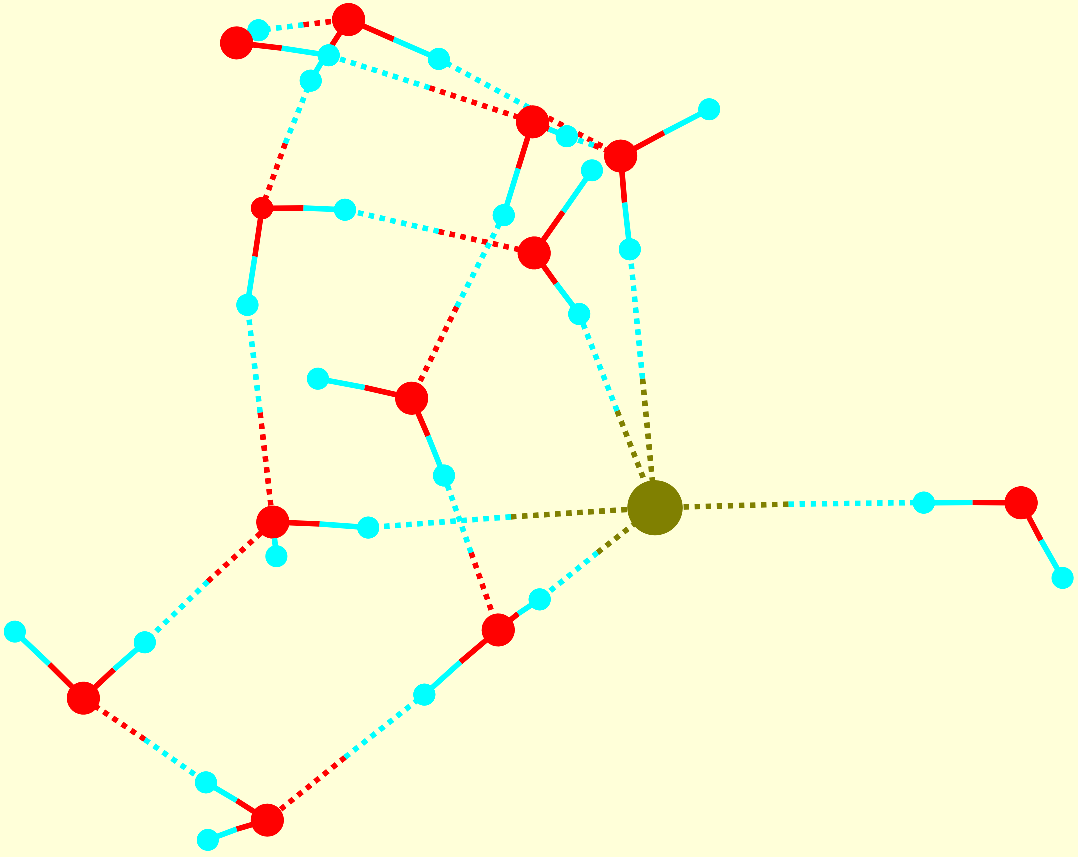
Model, distances (pm) and angles (°)	O-H	95
	N-H	101
	O…H	208
	H-O-H	$\angle(95,95) = 105°$
	H-N-H	$\angle(101,101) = 109°$
	H-O…H	$\angle(95,208) = 113°$

Restricted Hartree-Fock 6-31G* Charge=+1; Solvation=Water (SM8)

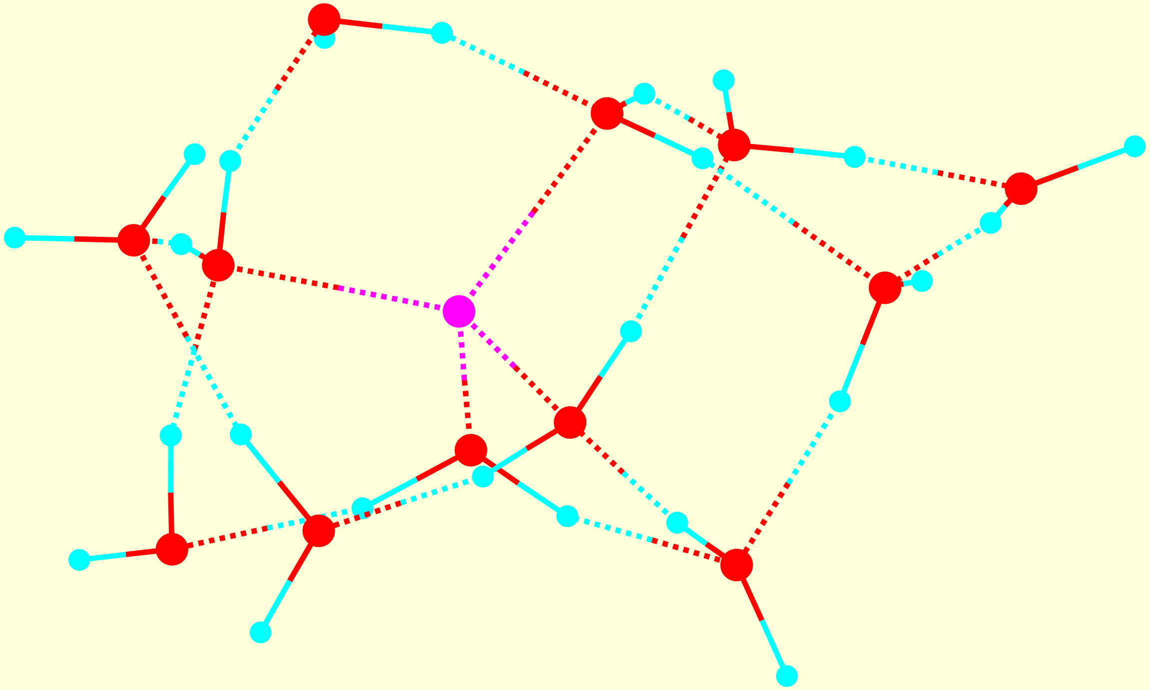
$F^{-} \cdot 6H_2O$

Model, distances (pm) and angles (°)	H…F	H…F…H
	179	∠(179,184) = 77°
	182	∠(184,187) = 85°
	183	∠(182,183) = 85°
	184	∠(179,183) = 86°
	185	∠(185,187) = 87°
	187	∠(183,184) = 88°
		∠(179,182) = 89°
		∠(184,185) = 89°
		∠(179,185) = 90°
		∠(183,187) = 93°
		∠(182,185) = 98°
		∠(182,187) = 109°
		∠(179,187) = 162°
		∠(182,184) = 165°
		∠(183,185) = 177°
Restricted Hartree-Fock 6-31G* Charge=-1; Solvation=Water (SM8)		

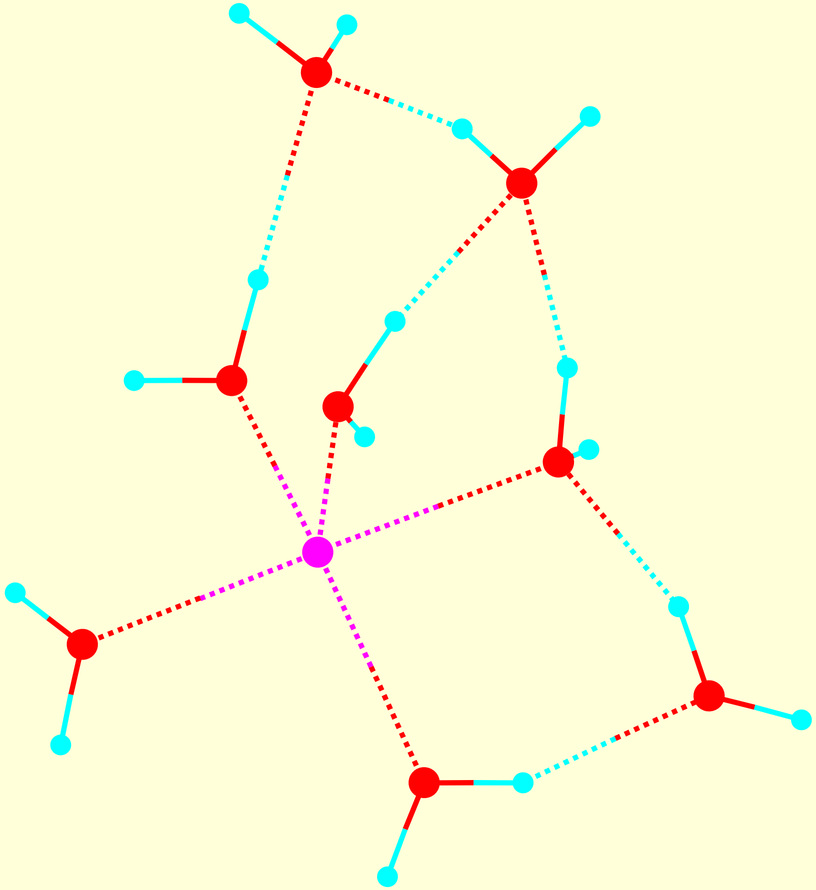
$Cl^{-} \cdot 5H_2O$

Model, distances (pm) and angles (°)	H…Cl	H…Cl…H
	265	∠(281,307) = 67°
	274	∠(274,307) = 76°
	281	∠(281,284) = 82°
	284	∠(274,284) = 82°
	307	∠(265,307) = 89°
		∠(274,281) = 96°
		∠(265,274) = 101°
		∠(265,284) = 129°
		∠(284,307) = 140°
		∠(265,281) = 146°
Restricted Hartree-Fock 6-31G* Charge=-1; Solvation=Water (SM8)		

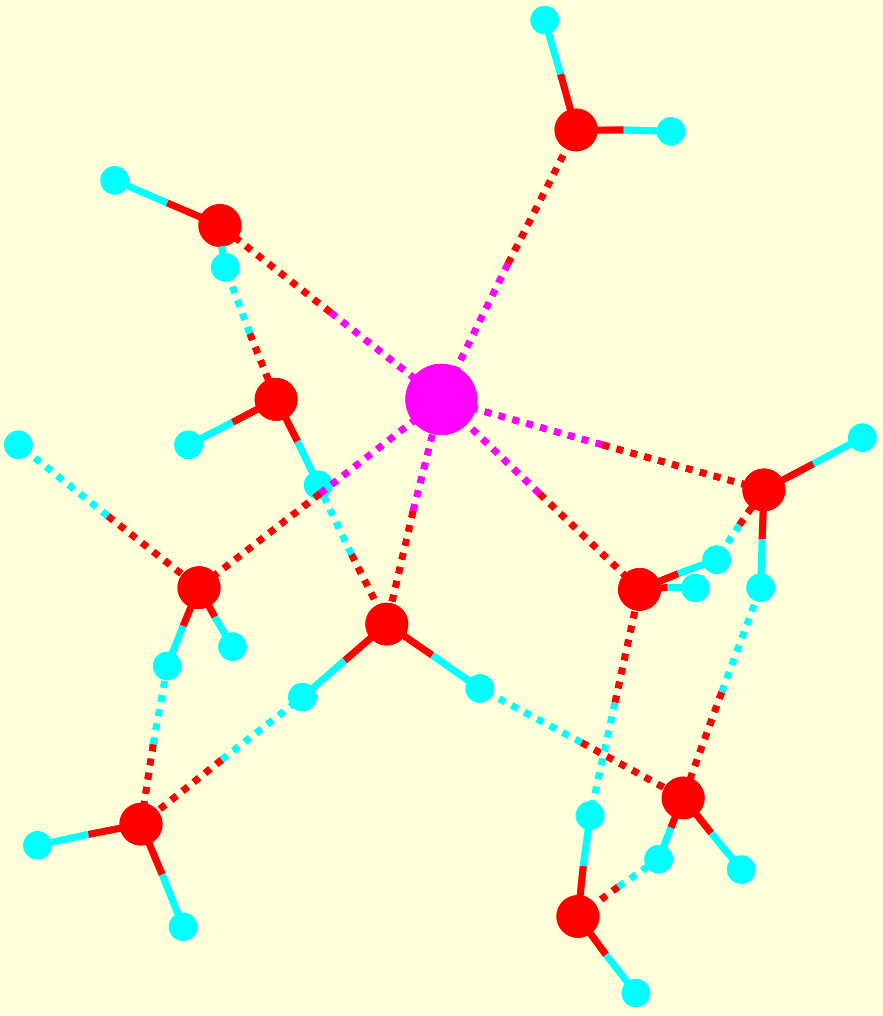
$Li^+ \cdot 4H_2O$

Model, distances (pm) and angles (°)	Li…O	O…Li…O
	193	∠(193,196) = 99°
	194	∠(194,200) = 104°
	196	∠(196,200) = 110°
	200	∠(193,200) = 111°
		∠(194,196) = 116°
		∠(193,194) = 117°
Restricted Hartree-Fock 6-31G* Charge=+1; Solvation=Water (SM8)		

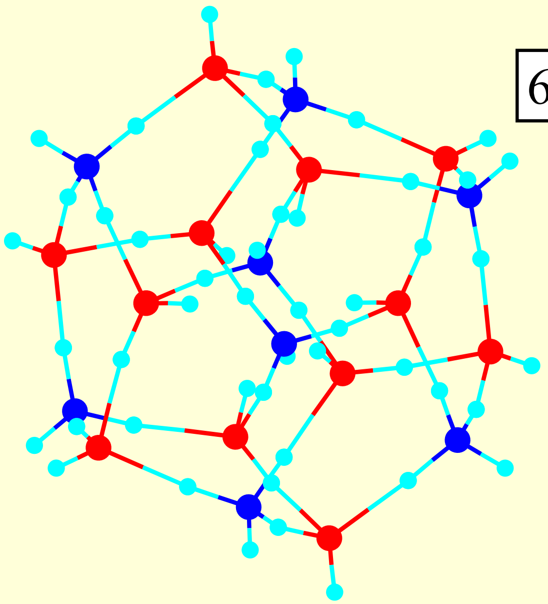
$Na^+ \cdot 5H_2O$

Model, distances (pm) and angles (°)	Na…O	O…Na…O
	231	∠(234,239) = 84°
	234	∠(236,239) = 85°
	235	∠(231,239) = 88°
	236	∠(231,235) = 93°
	239	∠(235,236) = 94°
		∠(234,235) = 97°
		∠(231,234) = 100°
		∠(234,236) = 123°
		∠(231,236) = 135°
		∠(231,235) = 178°
Restricted Hartree-Fock 6-31G* Charge=+1; Solvation=Water (SM8)		

$K^+ \cdot 6H_2O$

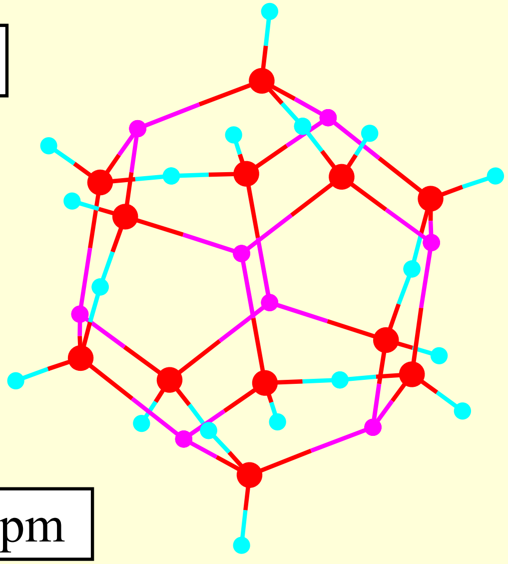
Model, distances (pm) and angles (°)	O…K	O…K…O
	278	∠(285,293) = 58.1°
	279	∠(281,285) = 79.0°
	281	∠(284,293) = 79.1°
	284	∠(278,281) = 80.8°
	285	∠(281,284) = 81.3°
	293	∠(279,293) = 86.2°
		∠(279,285) = 86.3°
		∠(278,279) = 92.5°
		∠(278,284) = 94.4°
		∠(281,293) = 100.5°
		∠(279,284) = 121.6°
		∠(284,285) = 127.8°
		∠(278,285) = 128.8°
		∠(279,281) = 157.1°
		∠(278,293) = 173.0°
Restricted Hartree-Fock 6-31G* Charge=+1; Solvation=Water (SM8)		

Most probable clusters in water



6 O-H in & 6 O-H out

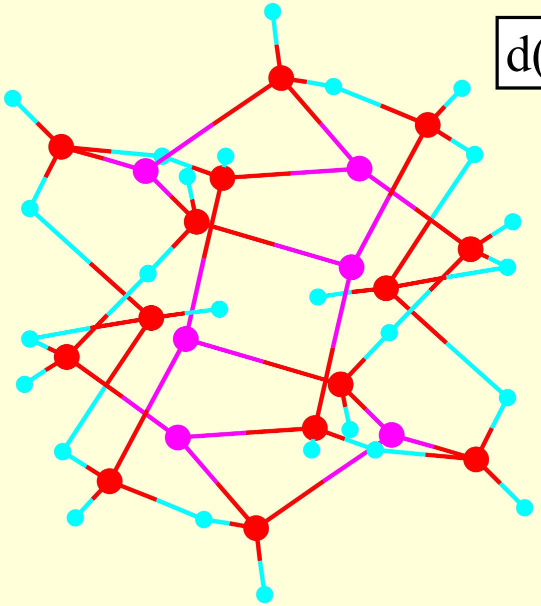
$O_{12}N_8H_{50}$; stable



d(Li,O) = 179±1 pm

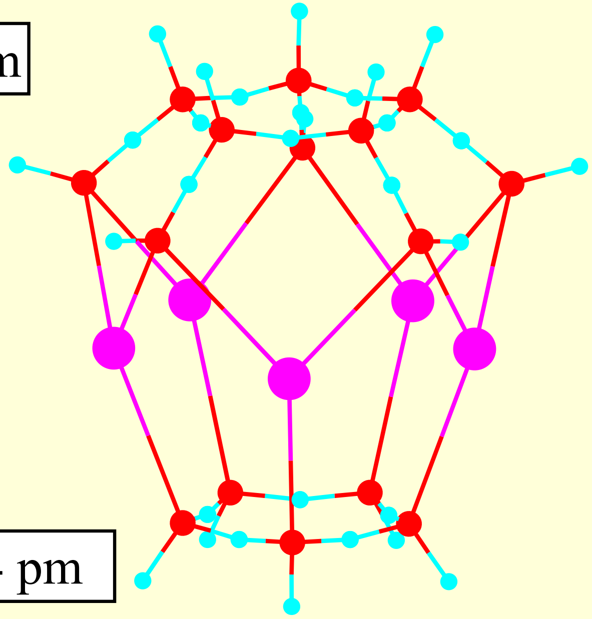
$O_{12}Li_8H_{18}$; stable

$O_{14}Na_6H_{26}$; instable



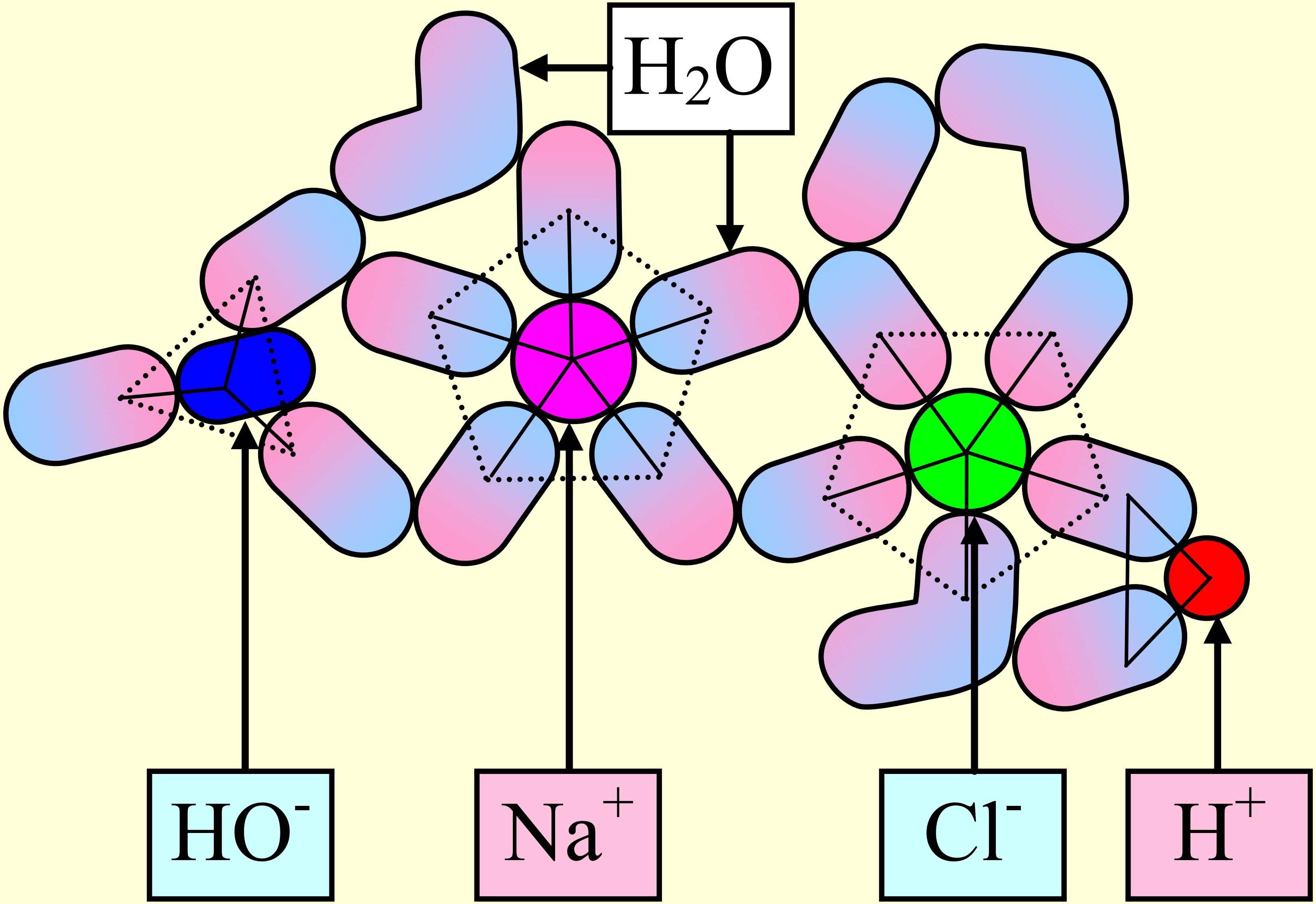
d(Na,O) = 275±46 pm

$O_{15}K_5H_{29}$; stable



d(K,O) = 270±4 pm

NaCl aqueous solution



H_2O

HO^-

Na^+

Cl^-

H^+

Q & R

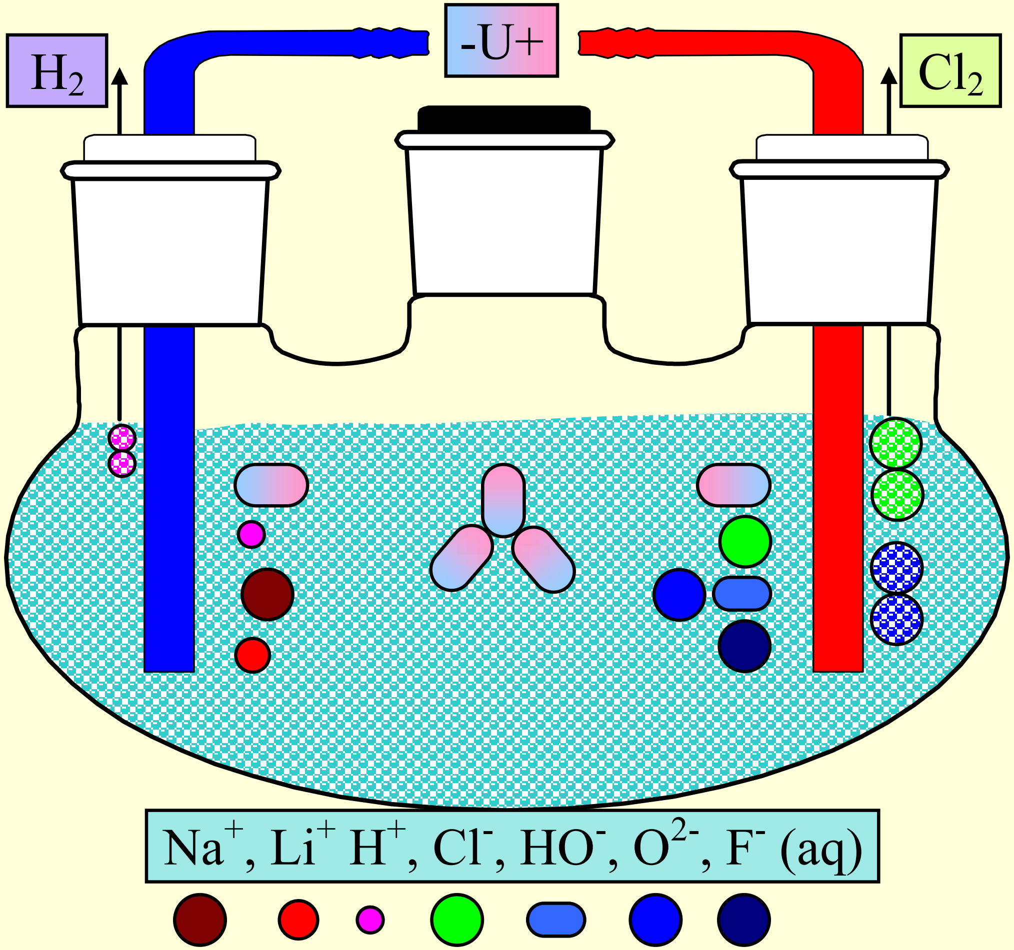
In connection with the ions dissolved in water:		
	1	K^+ is surrounded by 6 molecules of H_2O
	1	Na^+ is surrounded by 5 molecules of H_2O
	0	Li^+ is surrounded by 6 molecules of H_2O
	0	Li^+ is surrounded by 5 molecules of H_2O
	1	Li^+ is surrounded by 4 molecules of H_2O
	0	Cl^- is surrounded by 6 molecules of H_2O
	1	Cl^- is surrounded by 5 molecules of H_2O
	0	F^- is surrounded by 5 molecules of H_2O
	1	F^- is surrounded by 6 molecules of H_2O
	0	NH_4^+ is surrounded by 5 molecules of H_2O
	0	NH_4^+ is surrounded by 3 molecules of H_2O
	1	NH_4^+ is surrounded by 4 molecules of H_2O

Electrolysis in water

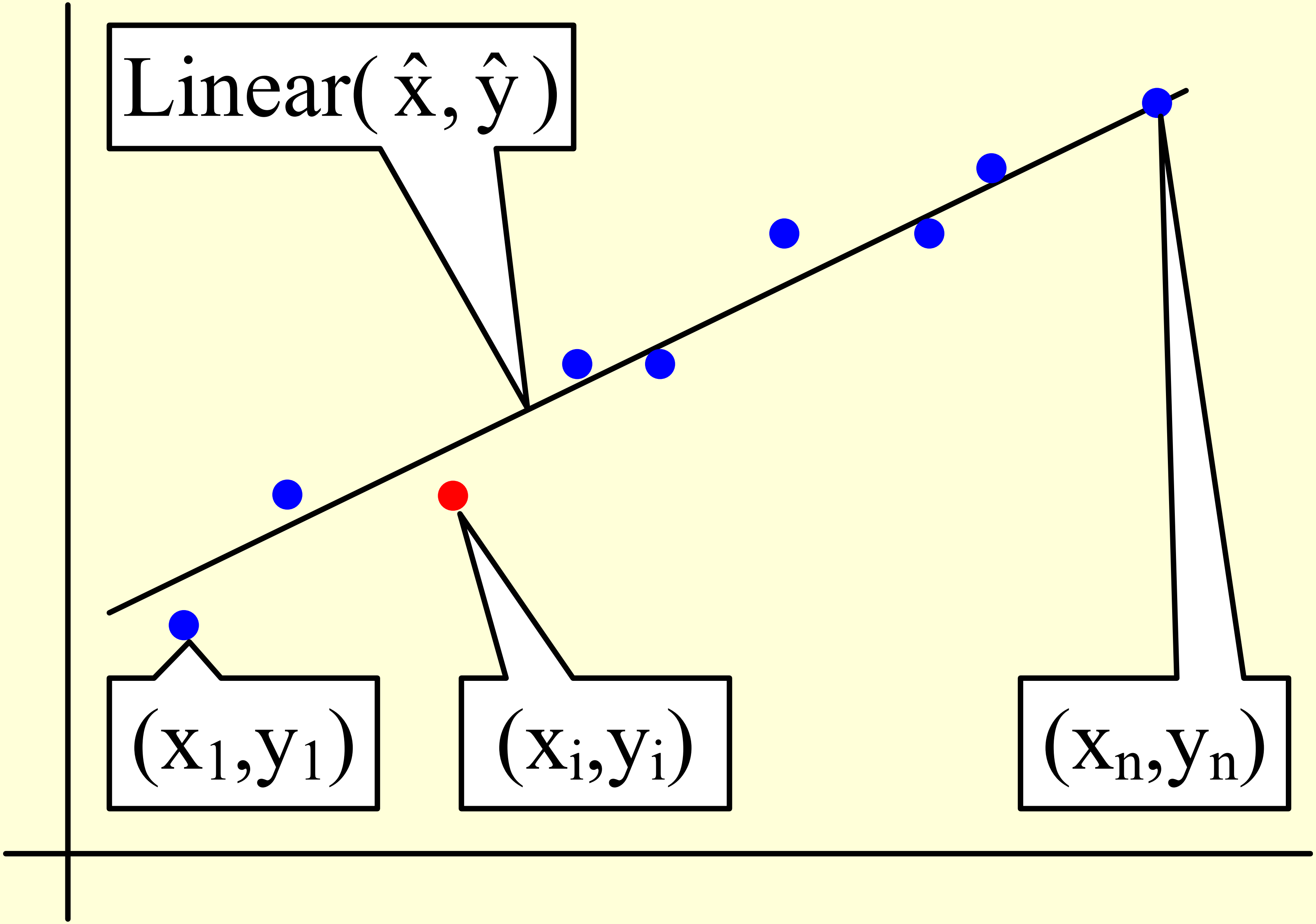
Element	F	O	Cl	H	Li	Na
Electronegativity	3.98	3.44	3.16	2.20	0.98	0.93

Electrode	Reaction
Cathode (-):	$\text{ox} + ne^- \rightarrow \text{red}$
Anode (+):	$\text{red} - ne^- \rightarrow \text{ox}$

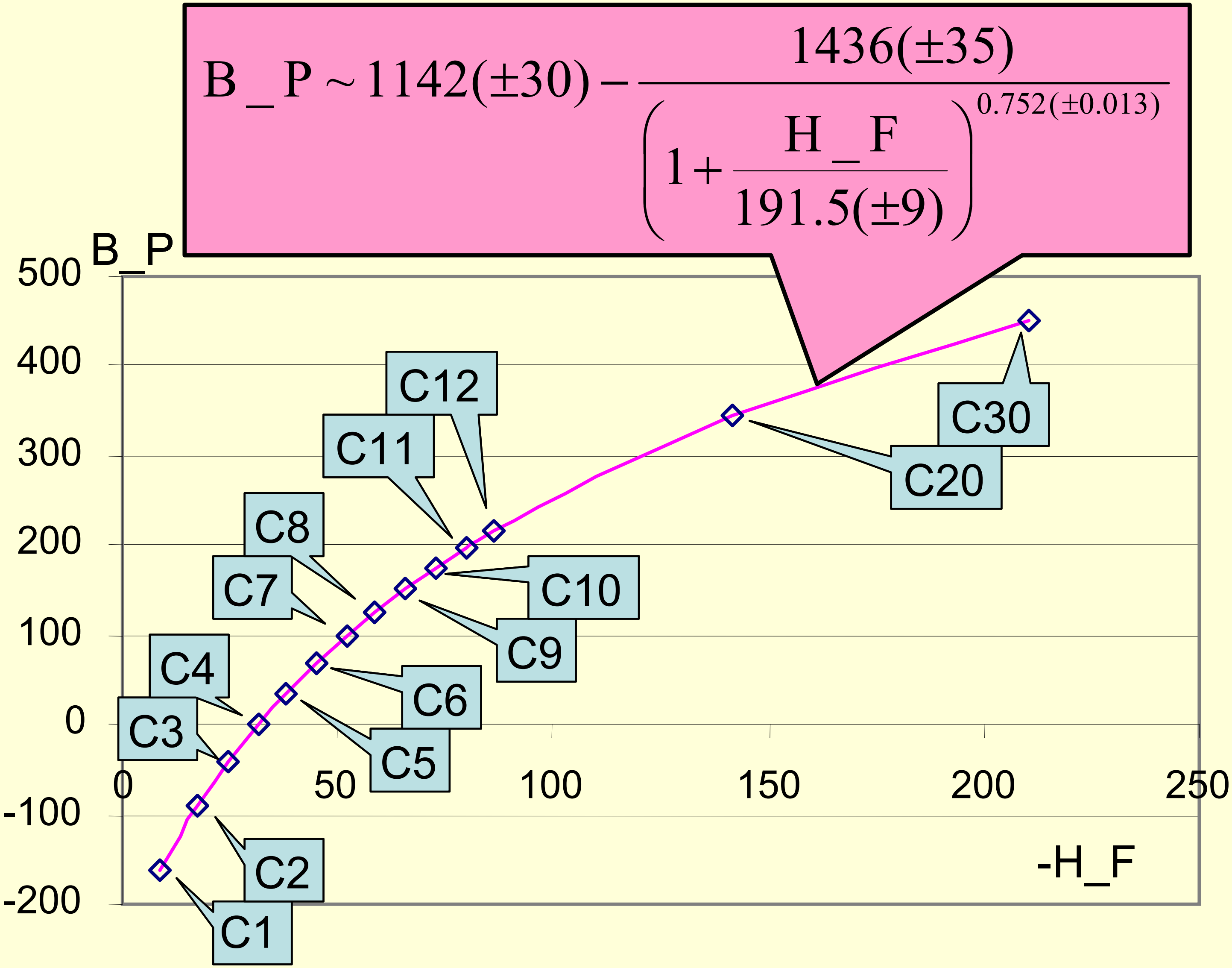
Reactions & potentials	V
$2Li^+ + 2e^- \rightarrow 2Li(s)$	-3.04
$2F^- \rightarrow F_2(g) + 2e^-$	-2.87
$2Na^+ + 2e^- \rightarrow 2Na(s)$	-2.71
$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$	-1.78
$HO^- \rightarrow {}^1/_2O_2(g) + H^+ + 2e^-$	-1.73
$2Cl^- \rightarrow Cl_2(g) + 2e^-$	-1.36
$H_2O \rightarrow {}^1/_2O_2(g) + 2H^+ + 2e^-$	-1.23
$2H_2O + 2e^- \rightarrow H_2(g) + 2HO^-$	-0.83
$H_2O_2 \rightarrow O_2(g) + 2H^+ + 2e^-$	-0.70
$2HO^- \rightarrow {}^1/_2O_2(g) + H_2O + 2e^-$	-0.40
$2H^+ + 2e^- \rightarrow H_2(g)$	-0.00



Linear regressions



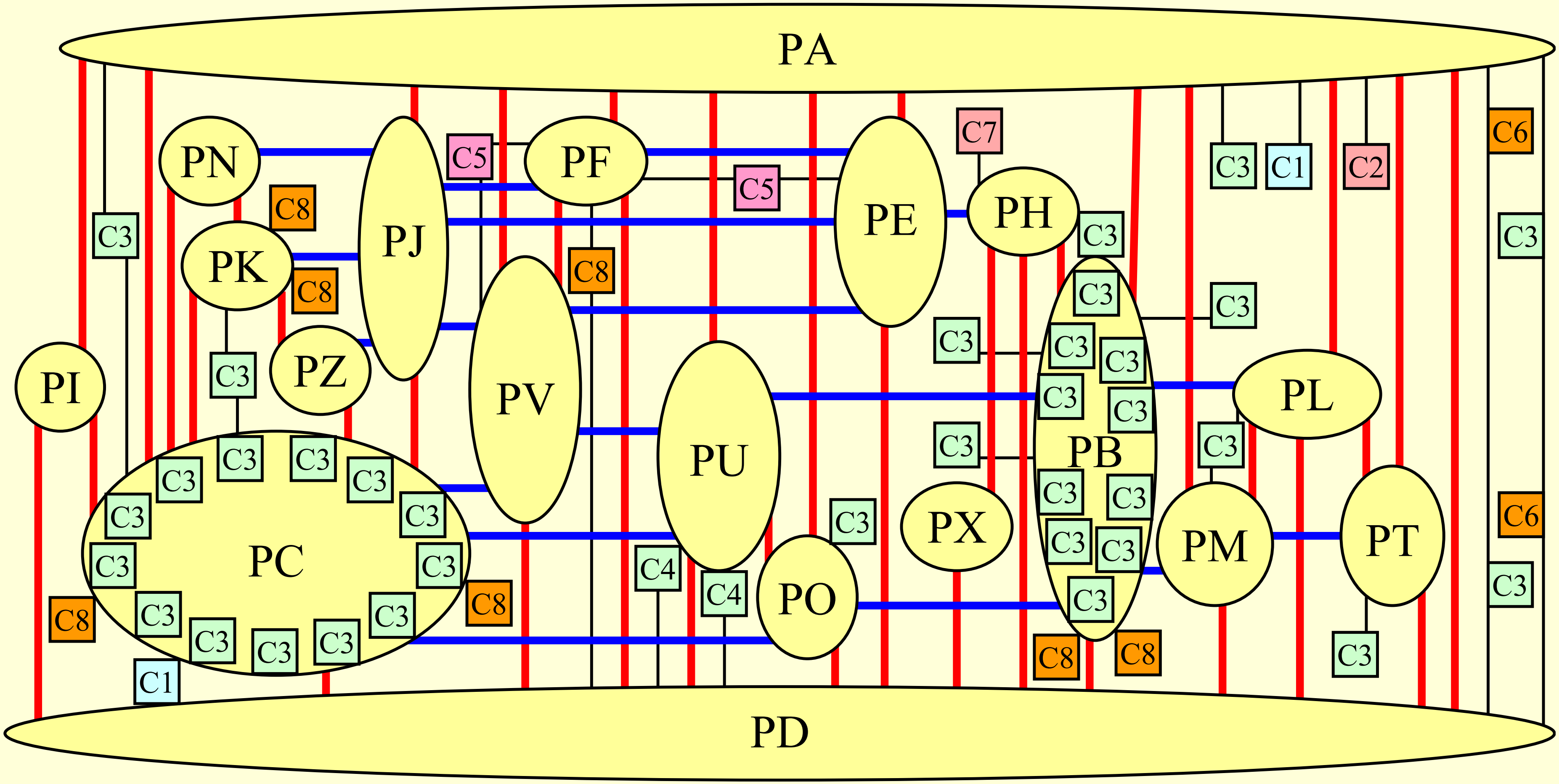
B.p. vs. H.f. of normal alkanes



$$B\_P \sim 1142(\pm30) - \frac{1436(\pm35)}{\left(1+\frac{H\_F}{191.5(\pm9)}\right)^{0.752(\pm0.013)}}$$

Image from: Studia Universitatis Babeş-Bolyai. Series Chemia LV(4):61-68.
URL: http://studia.ubbcluj.ro/download/pdf/581.pdf

Plants “photosystem II”



PA…PX: different proteins	C3: chlorophyll A	C5: haem like	C8: β-carotene

http://www.ncbi.nlm.nih.gov/Structure/mmdb/mmdbsrv.cgi?Dopt=s&uid=26605

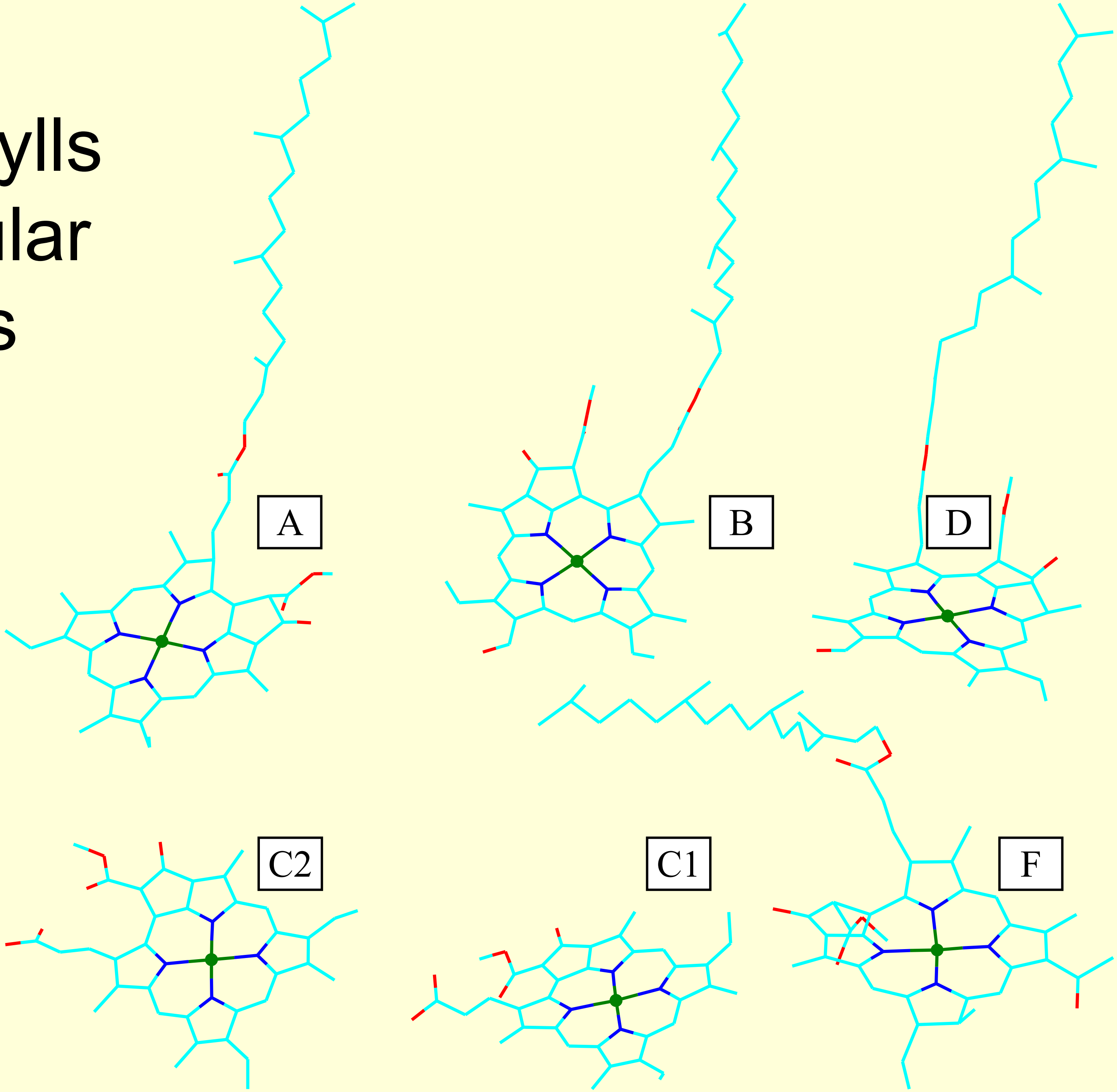
Chlorophylls - natural solar cells

- Chlorophylls are small molecules containing a Magnesium atom responsible for conversion of the solar energy into chemical energy and represent the engine of any vegetal living organism. A in-vitro approach of molecular design was conducted on the series of six chlorophylls in order to relate the chemical properties with their natural occurrence.

By combining many reports on chlorophylls, we may conclude that their occurrence is not equal, and this diversity may be arisen from a long evolution and adaptation process. Table gives a guess about the occurrence of chlorophylls.

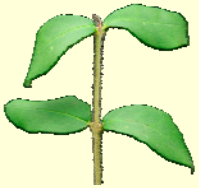
Chlorophyll	ChemSpider ID	Occurrence
a	16736115	universal
b	16739843	many plants
d	16736116	cyanobacteria
f	2763140	cyanobacteria
c1	391649	different algae
c2	17229531	different algae

Chlorophylls – molecular models



Chlorophylls – molecular analysis

- Method: Extract from PM3 structure models the Molecular Orbitals → calculate energies of electronic transitions (OMO-UMO)
- Analysis: Relate occurrence with e-density(HOMO)*ΣEntropy(UMO)
- Results: showed that the in-vitro molecular orbital states of chlorophylls are in good agreement with the observed natural occurrences of chlorophylls

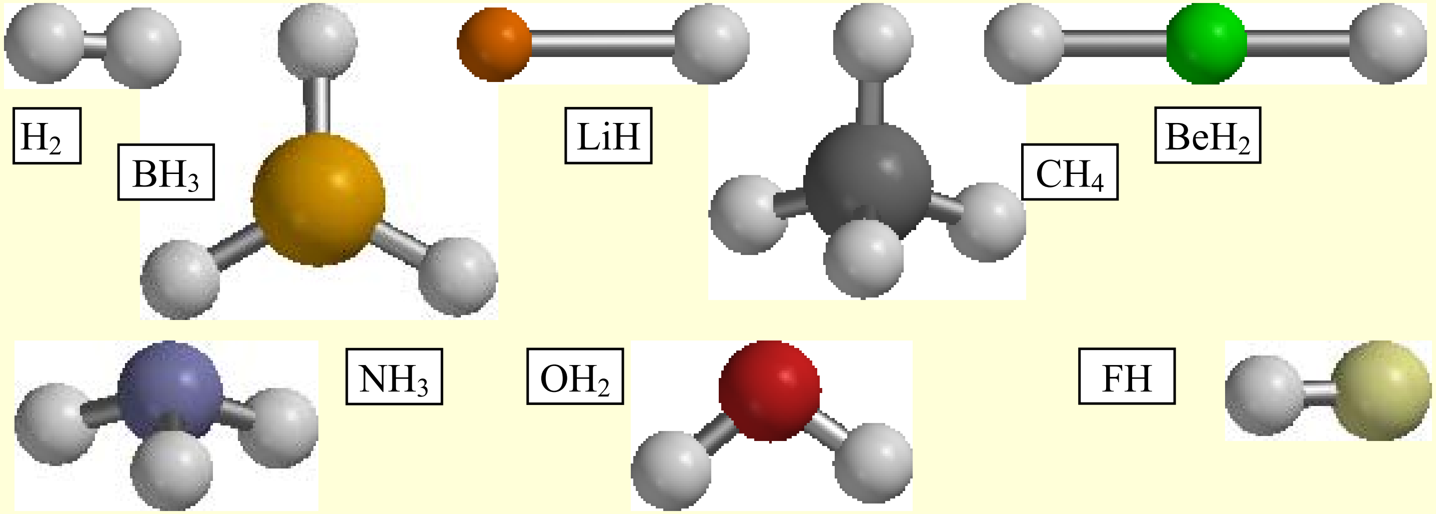


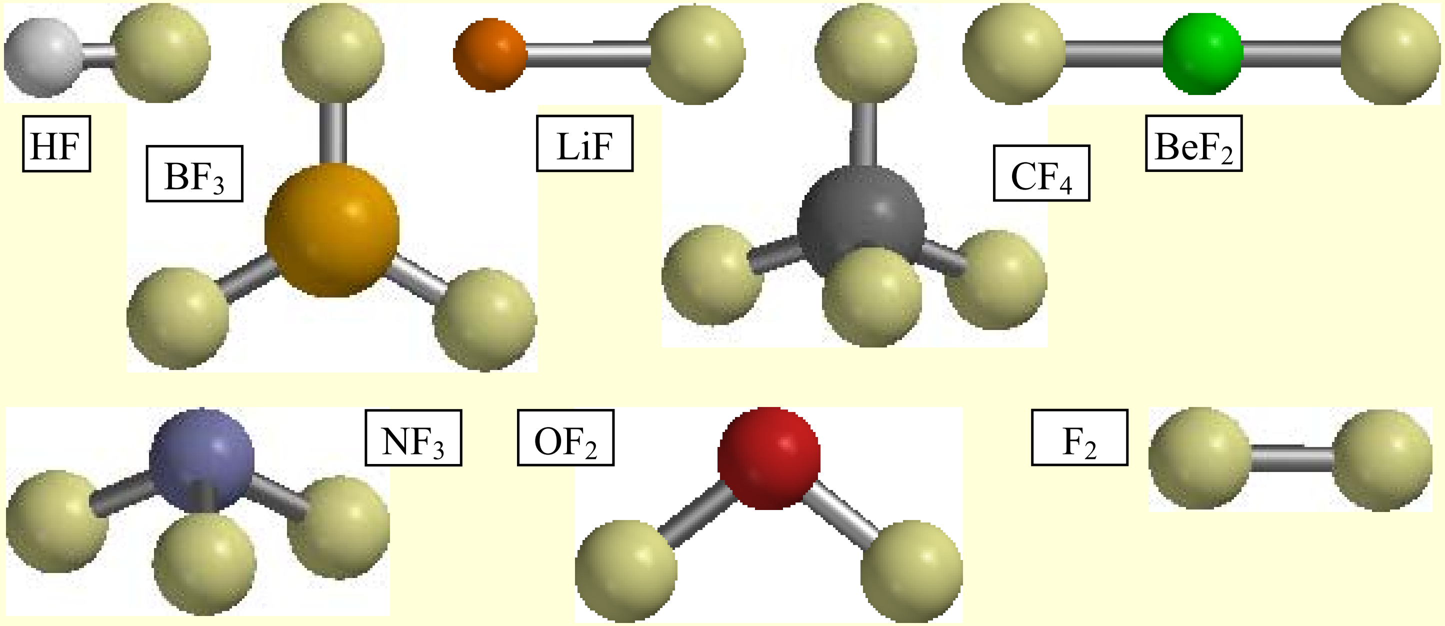
	Observed Occurrence	$\rho_{HOMO} \cdot \Sigma H_{UMO}$	Estimated occurrence	Observations
a	universal	1.84	****	Probability to be different from the mean of {1.54, 1.38, 1.21, 1.33, 1.38} is over 99.9%
b	many plants	1.54	***	Probability to be different from the mean of {1.38, 1.21, 1.33, 1.38} is over 99.4%
d	cyanobacteria	1.38	**	Probability to be different one to each other is less than 22%
c1	different algae	1.33	**	
c2	different algae	1.38	**	
f	cyanobacteria	1.21	*	Probability to be different from the mean of {1.84, 1.54, 1.38, 1.33, 1.38} is over 96.1%

Polarity vs. polarizability

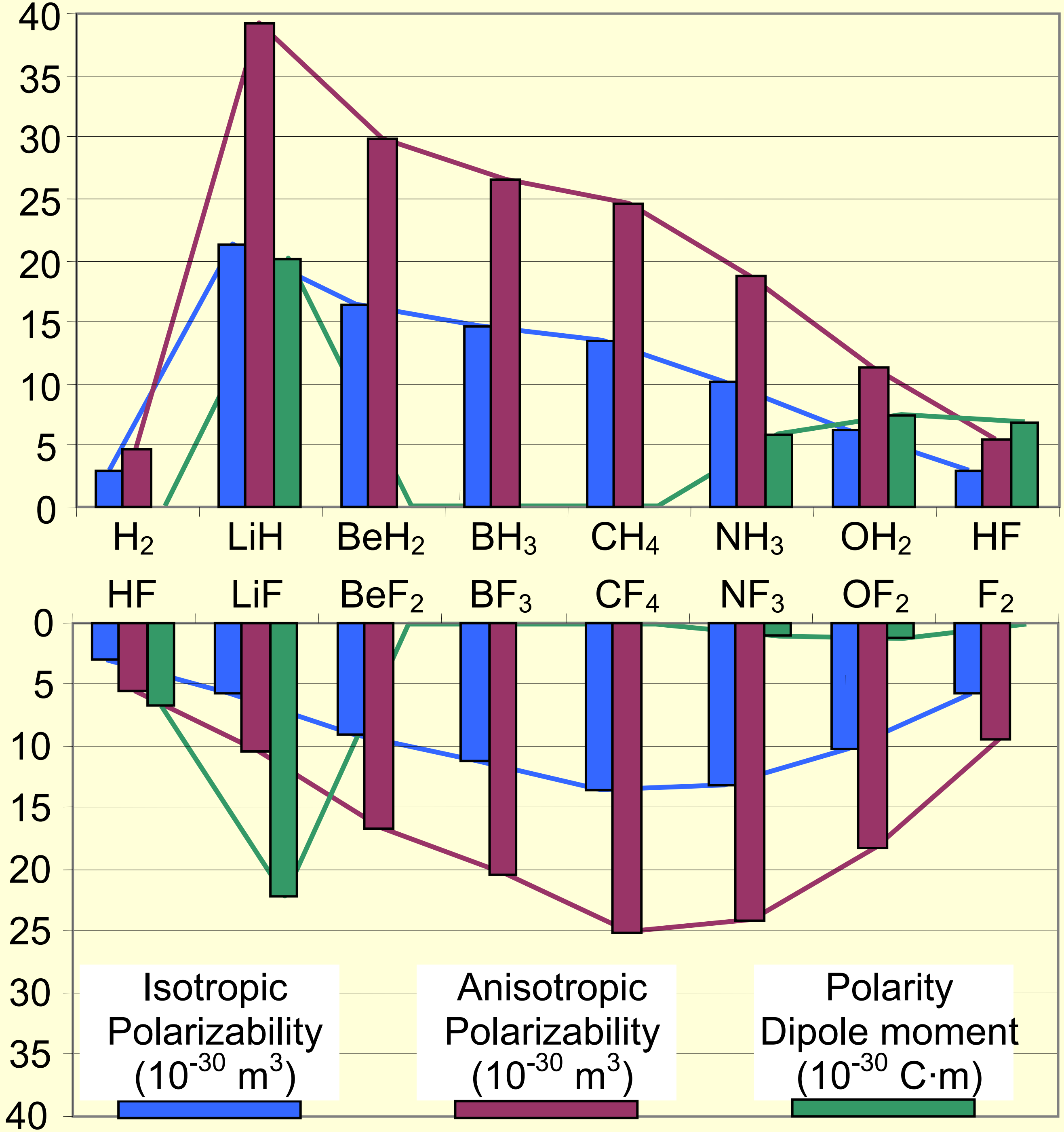
- Polarity is separation of electric charge leading to an electric dipole or multipole and its moment in the molecule.
- Polarizability is measure the change in electron distribution in response to an applied electric field.
- Dipole
  - Permanent: independent of the environment
  - Induced: when one molecule with a permanent dipole induces a dipole in other molecule
- Dipole moment: the product of magnitude of charge on a molecule and the distance between two charges of equal magnitude with opposite sign.
- The electronic polarizability is the ratio of the induced dipole moment of an atom to the electric field that produces this dipole moment (DM/E).

Polarity & polarizability: two series of molecules



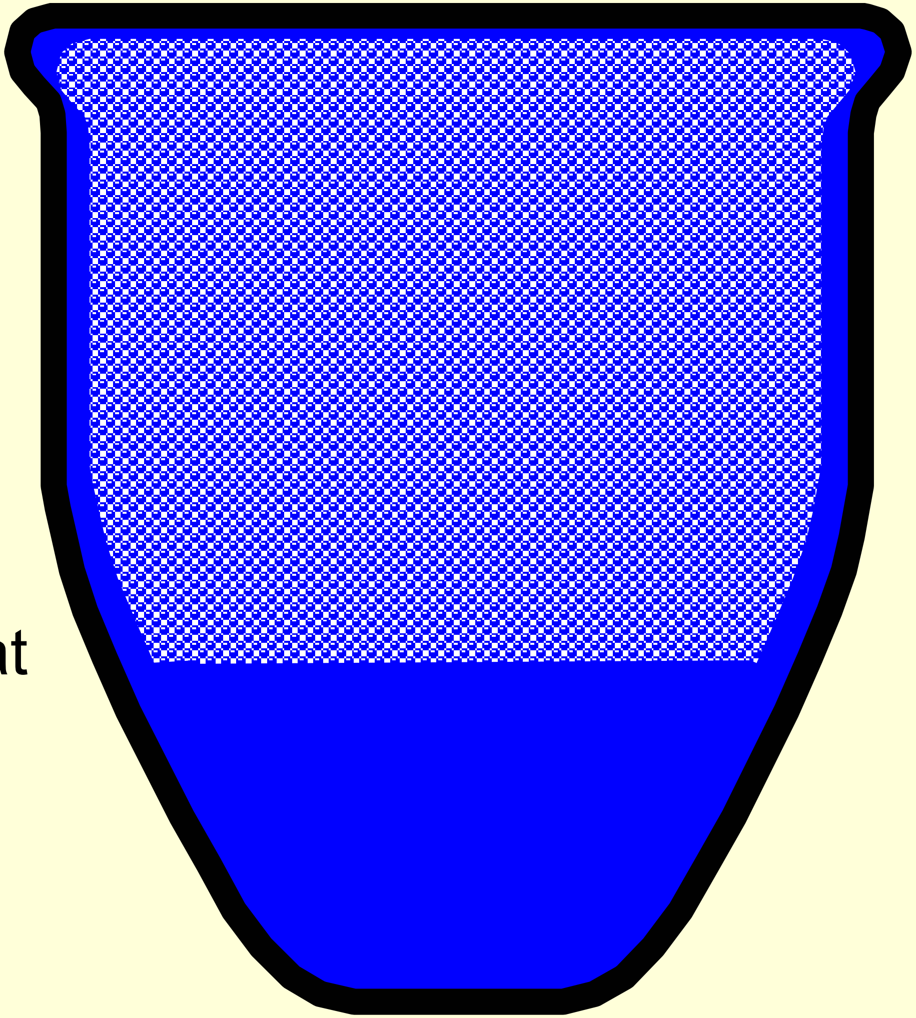


Polarity & polarizability: values



London dispersion forces

- Molecules without dipole and without exterior polarization field still interact due to the nonsymmetrical charge distribution surrounding the nucleus. The forces keeping together the atoms are called London dispersion forces.
- Only for Helium ($1s^2$ $2s^2$) these forces are so small, that liquid helium surrounds all surfaces of the vessel in which are kept.



References

for General Chemistry

Periodic system; periodic properties; electronic structure

- Delia M. GLIGOR, Lorentz JÄNTSCHI, 2005. *Periodic System of Elements Database and Its Applications*. Oradea University Annals, Chemistry Fascicle 12: 180-194.
- Ossi HOROVITZ, Costel SÂRBU, Horia F. POP, 2000. *Rational classification of chemical elements*. Cluj-Napoca: Editura Dacia.
- Mircea V. DIUDEA, Ioan SILAGHI-DUMITRESCU, 1989. *Valence group electronegativity as a vertex discriminator*. Revue Roumaine de Chimie 34(5):1175-1182.
- Lorentz JÄNTSCHI, 2004. *MDF - A New QSAR/QSPR Molecular Descriptors Family*. Leonardo Journal of Sciences 3(4): 68-85.
- David YOUNG, 2001*. Appendix A (A.1.6 p.330, SPARTAN)* In: *Computational Chemistry*. New York: Wiley-Interscience.

Abundance of elements; chemical formulas; stoechiometry

- Lorentz JÄNTSCHI, 2012. *Structure vs. Property: Algorithms and Models*. Habilitation Thesis in Chemistry (principal), Mathematics (secondary) and Informatics (secondary). CNADTCU: Bucharest.
- Lorentz JÄNTSCHI, 2012. *Structure vs. Property: Algorithms and Models: Habilitation Thesis Presentation*. Defended on Sept. 24. Cluj-Napoca: Babeş-Bolyai University.
- Lorentz JÄNTSCHI, Sorana D. BOLBOACĂ, Mugur C. BĂLAN, Radu E. SESTRAŞ, 2011. *Chlorophylls - natural solar cells*. BUASVM. Agriculture 68(1):181-187.
- Lorentz JÄNTSCHI, 2000. *Prediction of Physical, Chemical and Biological Properties using Mathematical Descriptors*. Philosophy Degree Thesis in Chemistry (PhD Advisor: Prof. Dr. Mircea V. DIUDEA). Cluj-Napoca: Babeş-Bolyai University.
- Radu E. SESTRAŞ, Lorentz JÄNTSCHI, Sorana D. BOLBOACĂ, 2012. *Quantum Mechanics Study on a Series of Steroids Relating Separation with Structure*. JPC - Journal of Planar Chromatography - Modern TLC 25(6):528-533.

Minerals; Physical and chemical properties; Chemical reactions

- Lorentz JÄNTSCHI, Mihaela L. UNGUREŞAN, 2001. *Special Chapters of Chemistry for Automatics (in Romanian)*. Cluj-Napoca: UTPres.
- Elena M. PICĂ, 2009. *Principles and Experiences in Chemistry*. Cluj-Napoca: UTPres.

Hydrogen, Oxygen, Water

- Liana T. MARTA, 2003. *Inorganic chemistry for engineers (In Romanian)*. Cluj-Napoca: UTPres.
- Gavril NIAC, 2001. *Physical Chemistry (In Romanian)*. Cluj-Napoca: UTPres.
- Lorentz JÄNTSCHI, 2003. *Microbiology and Toxicology. Phytochemistry Studies (in Romanian)*. Cluj-Napoca: Amici.

Alkali and alkali-earth metals

- Liana T. MARTA, 2003. *Inorganic chemistry for engineers (In Romanian)*. Cluj-Napoca: UTPres.

Blocul “p^3-p^6” (grupele 15 - 18); blocul “d^1-d^5”; blocul “d^6-d^{10}”

- Liana T. MARTA, 2003. *Inorganic chemistry for engineers (In Romanian)*. Cluj-Napoca: UTPres.
- Horea I. NASCU, 1991. *General chemistry and technical analysis*. Bucharest: Editura Didactica si Pedagogica.
- Lorentz JÄNTSCHI, 2005. *Microbiology and Toxicology and Phytochemistry Studies (in Romanian)*. Cluj-Napoca: AcademicDirect.
- Lorentz JÄNTSCHI, Mihaela Ligia UNGUREŞAN, 2001. *Physical Chemistry. Molecular Kinetic and Dynamic (in Romanian)*. Cluj-Napoca: Mediamira.

“f” block

- Lorentz JÄNTSCHI, 2002. *Chemical and Instrumental Analysis (in Romanian)*. Cluj-Napoca: UTPres.
- Lorentz JÄNTSCHI, Sorana Daniela BOLBOACĂ, 2003. *Applied Chemical and Instrumental Analysis (in Romanian)*. Cluj-Napoca: AcademicDirect.
- Lorentz JÄNTSCHI, Horea I. NAŞCU, 2009. *Analytical and Instrumental Chemistry (in Romanian)*. Cluj-Napoca: AcademicPres.
- Mihaela L. UNGUREŞAN, Lorentz JÄNTSCHI, 2003. *Interactive Students Training and Evaluation Software For Radioisotopes*. Studia Universitatis Babes-Bolyai, Physics XLVIII(1 - Special Issue): 274-277.

Boron group; Carbon group

- Sorana BOLBOACĂ, Lorentz JÄNTSCHI, 2013. *Porphyrin photovoltaic functionalization of the fullerene*. Nano-Science in Mathematics, Physics, Chemistry and Biology (21st March, Cluj-Napoca, Romania, Oral presentation, 14:40-15:00).
- Lorentz JÄNTSCHI, 2013. *Cyclic Polyynes*. Nano-Science in Mathematics, Physics, Chemistry and Biology (21st March, Cluj-Napoca, Romania, Oral presentation, 14:20-14:40).
- Mircea V. DIUDEA, Csaba L NAGY, 2012. C 20-related structures: Diamond D 5. Diamond and Related Materials 23: 105-108.
- Lorentz JÄNTSCHI, Sorana D. BOLBOACĂ, 2010. *The relationship between energy calculations and boiling points of n-alkanes*. Studia Universitatis Babeş-Bolyai. Series Chemia LV(4): 61-68.

Ceramics; Semiconductors; Superconductors

- Lorentz JÄNTSCHI, Mihaela L. UNGUREŞAN, 2001. *Special Chapters of Chemistry for Automatics (in Romanian)*. Cluj-Napoca: UTPres.
- Traian PETRIŞOR, Lelia CIONTEA, 2004. *Properties of ceramic materials*. Cluj-Napoca: UTPres.

Materiale avansate; Polimeri & plastice Reactii & mecanisme; Biomolecule

- Lorentz JÄNTSCHI, Mihaela L. UNGUREŞAN, 2001. *Special Chapters of Chemistry for Automatics (in Romanian)*. Cluj-Napoca: UTPres.
- Violeta POPESCU, 2005. *Polymeric materials and the environment (In Romanian)*. Cluj-Napoca: Mediamira.
- Lorentz JÄNTSCHI, 2003. *Kinetic Biochemistry*. Leonardo Journal of Sciences 2(2): 1-40.

Methods & models; Relations structure activity/property

- Lorentz JÄNTSCHI, 2000. *Prediction of Physical, Chemical and Biological Properties using Mathematical Descriptors*. Philosophy Degree Thesis in Chemistry (PhD Advisor: Prof. Dr. Mircea V. DIUDEA). Cluj-Napoca: Babeş-Bolyai University.
- Lorentz JÄNTSCHI, 2010. *Genetic algorithms and their applications.* Philosophy Degree Thesis in Horticulture (PhD Advisor: Prof. Dr. Radu E. SESTRAŞ). Cluj-Napoca: University of Agricultural Sciences and Veterinary Medicine.
- Lorentz JÄNTSCHI, 2012. *Structure vs. Property: Algorithms and Models*. Habilitation Thesis in Chemistry (principal), Mathematics (secondary) and Informatics (secondary). CNADTCU: Bucharest.

Update 2013-2016

- Lorentz JÄNTSCHI, Sorana D. BOLBOACĂ, **2016**. *Study of geometrical shaping of linear chained polymers stabilized as helixes*, ***Studia Universitatis Babes-Bolyai Chemia*** 61(4): 131-145.
- Lorentz JÄNTSCHI, Donatella BÀLINT, Lavinia L. PRUTEANU, Sorana D. BOLBOACĂ, **2016**. *Elemental factorial study on one-cage pentagonal faces nanostructure congeners*, ***Materials Discovery*** 5: 14-21, DOI 10.1016/j.md.2016.12.001.
- Sorana D. BOLBOACĂ, Lorentz JÄNTSCHI, **2016**. *Nano-quantitative structure-property relationship modeling on C42 fullerene isomers*, ***Journal of Chemistry*** 2016: 1791756 (8p.), DOI: 10.1155/2016/1791756.
- Lavinia L. PRUTEANU, Lorentz JÄNTSCHI, Mihaela L. UNGUREŞAN, Sorana D. BOLBOACĂ, **2016**. *Models of monovalent ions dissolved in water*, ***Studia Universitatis Babes-Bolyai Chemia*** 61(1): 151-162.
- Mihaela L. UNGUREŞAN, Lavinia L. PRUTEANU, Lorentz JÄNTSCHI, Sorana D. BOLBOACĂ, **2016**. *Correlation study among boiling temperature and heat of vaporization*, ***Studia Universitatis Babes-Bolyai Chemia*** 61(1): 223-234.
- Lorentz JÄNTSCHI, Sorana D. BOLBOACĂ, **2016**. *Szeged Matrix Property Indices as descriptors to characterize fullerenes*, ***Ovidius University Annals of Chemistry*** 27(2): 73-80, DOI: 10.1515/auoc-2016-0010.
- Sorana D. BOLBOACĂ, Daniela D. ROŞCA, Lorentz JÄNTSCHI, **2014**. *Structure-activity relationships from natural evolution*, ***MATCH Communications in Mathematical and in Computer Chemistry*** 71(1): 149-172.
- Lorentz JÄNTSCHI, Sorana D. BOLBOACĂ, Mircea V. DIUDEA, **2013**. *Molecular design and QSARs with molecular descriptors family*, ***Current Computer-Aided Drug Design*** 9(2): 195-205, DOI: 10.2174/1573409911309020005.