TENTATIVE LECTURE SCHEDULE

		Date	Topic
1.	Mon	13.09.	Course Introduction & Short Review of the Elements
2.	Wed	15.09.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Fri	17.09.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Mon	20.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
5.	Wed	22.09.	Transition Metals: General Aspects
6.	Mon	27.09.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
7.	Wed	29.09.	Redox Chemistry
8.	Mon	04.10.	Crystal Field Theory
9.	Wed	06.10.	V, Nb, Ta & Metal Complexes & MOFs
10.	Fri	08.10.	Cr, Mo, W & 2D materials
11.	Mon	11.10.	Mn, Fe, Co, Ni, Cu & Magnetism & Superconductivity
12.	Wed	13.10.	EXTRA
13.	Fri	15.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Mon	18.10.	Lanthanoids + Actinoids & Pigments & Luminescence (Down/Upconversion)
15.	Wed	20.10.	Inorganic Materials Chemistry Research

EXAM: Thu Oct. 28, 2021

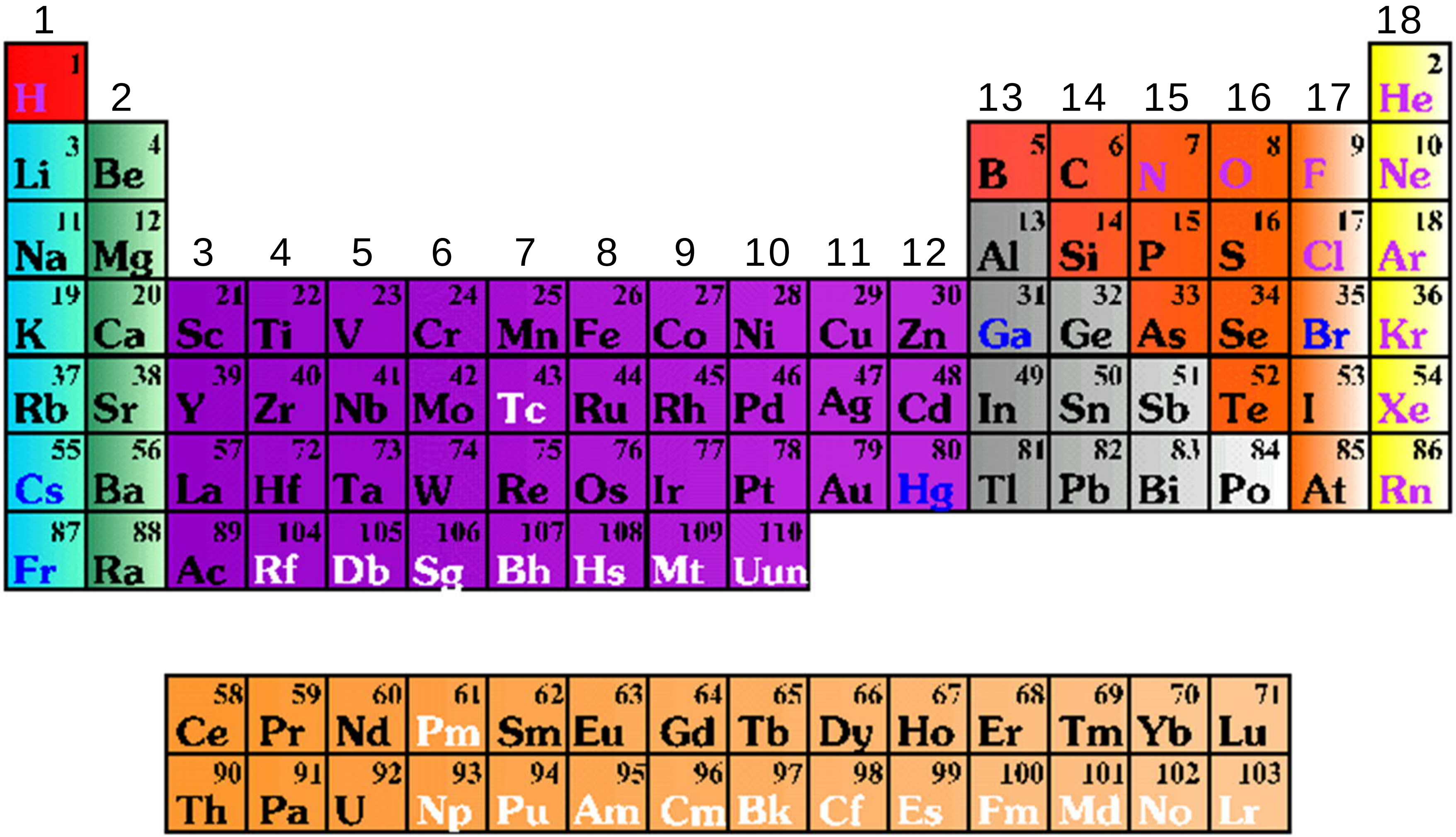
QUESTIONS: Lecture 2

Name your file Exe-2-Familyname; Return by noon tomorrow into MyCourses drop-box

1. Give the outer electron configuration for: Sc, Mn and Cu. Based on these configurations predict **(with short explanation !)** the most favourable oxidation state(s) of these elements.

2. Give the outer electron configuration for: Y, La, Ce, Sm, Gd and Yb. Based on these configurations predict **(with short explanation !)** which one of these elements would show the strongest magnetic properties.

3. Indicate **(with short explanation !)** for each of the following pairs the larger atom/ion: Na–K, K–Ca, Fe^{2+}–Fe^{3+}, Ti^{3+}–Ti^{4+}, Ti^{4+}–Zr^{4+}, La–Lu



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
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	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	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun								

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

Alkali metals
Alkaline earth metals
Halogens
Noble gases

Transition metals
Lanthanides
Actinides

ATOMIC MODEL & ELECTRON CONFIGURATIONS

IMPORTANT HISTORICAL STEPS

- **Thomson 1898-1903:** existence of electrons
- **Rutherford 1911:** small and dense nucleus + electron cloud
- **Einstein 1905:** wave and particle nature of electromagnetic radiation
- **Bohr 1913:** simple atom model (classical physics + some quantum theory features)
- **de Broglie 1924:** wave nature of particles
- **Davisson & Germes 1927:** diffraction of electrons
- **Heisenberg 1926:** uncertainty principle (exact position and momentum of electron)
- **Schrödinger 1926:**
  wave nature of electrons → quantum mechanical atom model
- **Compton 1921 and Goudsmit & Uhlenbeck 1925:** electron spin
- **Pauli 1925:** “exclusion principle”
- **Hund 1925:** minimum energy → maximum number of unpaired electrons

QUANTUM MECHANICAL ATOM MODEL

- Electrons have simultaneously both wave and particle nature
- In an atom electron behaves like standing wave
- Schrödinger wave function:
  - wavefunction ψ is a solution of Schrödinger equation
  - ψ describes the behaviour of electron
  - in chemistry: wavefunction → atomic orbital
  - Schrödinger equation has several possible solutions (= orbitals)
  - each orbital is described with a set of three quantum numbers: n, l and m
  - There is a certain energy corresponding to each wave function
  - Energy quantization is derived from the Schrödinger equation

QUANTUM NUMBERS

n	l	m	Orbital	Number
1	0	0	1s	1
2	0	0	2s	1
	1	-1, 0, 1	2p	3
3	0	0	3s	1
	1	-1, 0, 1	3p	3
	2	-2, -1, 0, 1, 2	3d	5
4	0	0	4s	1
	1	-1, 0, 1	4p	3
	2	-2, -1, 0, 1, 2	4d	5
	3	-3, -2, -1, 0, 1, 2, 3	4f	7

Principal quantum number (n): 1, 2, 3, …
- size and energy of the orbital

Angular momentum quantum number (l): 0, 1, … , (n-1)
- shape of the orbital

Magnetic quantum number (m): -l, (-l+1), …, (+l-1), +l
- orientation of the orbital in 3D space

Spin quantum number (s): -½, ½

Pauli’s exclusion principle

It is impossible for two electrons in the same atom to have the same set of quantum numbers: n, l, m and s

Aufbau (“building up”) principle

Orbitals are filled in the order of increasing energy:
1s–2s–2p–3s–3p–4s–3d–4p–5s–4d–5p–6s–4f–5d–6p–7s–5f–6d–7p

Hund’s rule (not necessarily obeyed when the energy levels splitted, ref. crystal field theory)

All orbitals in a subshell are first occupied with one electron before two electrons start to occupy the same orbital
(to minimize the electron-electron repulsions)

Atom orbitals

- ψ (wave function):

  does not tell the location or path of electron

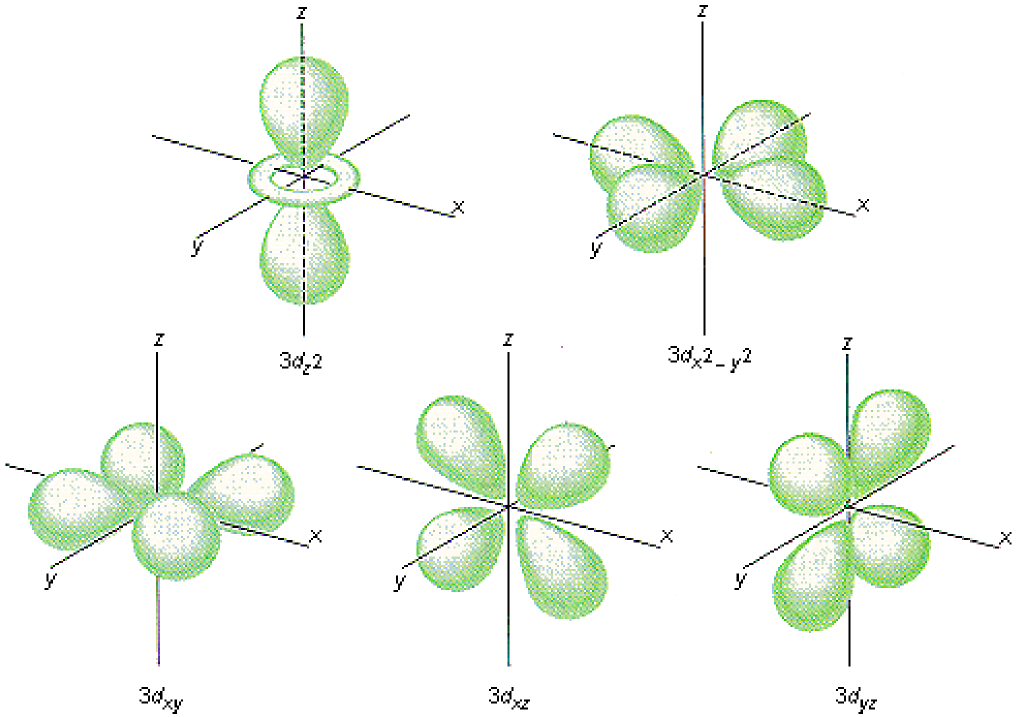
  (c.f. Heisenberg uncertainty principle)

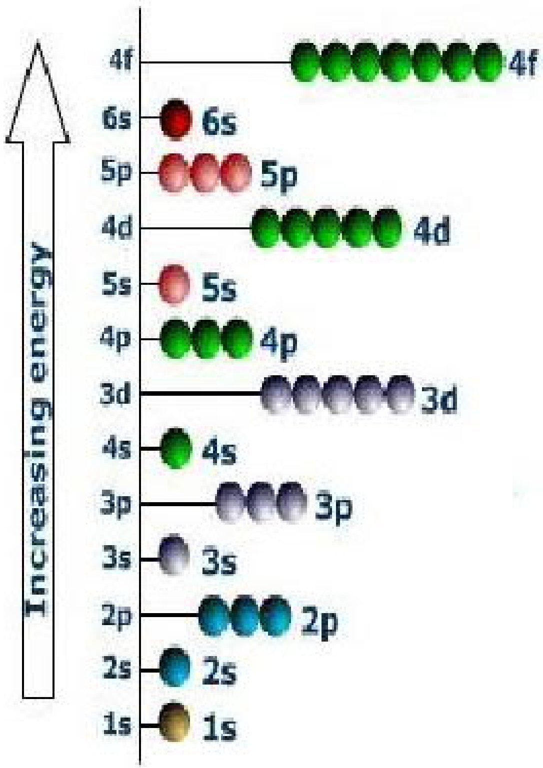
- ψ^2 (square of wave function):

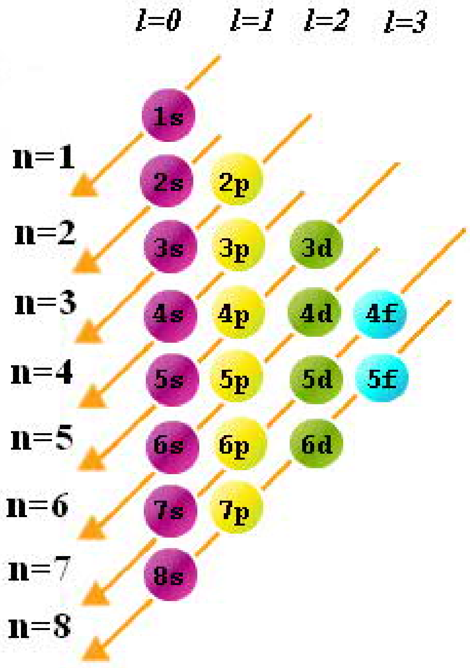
  probability of electron to be located in a certain location

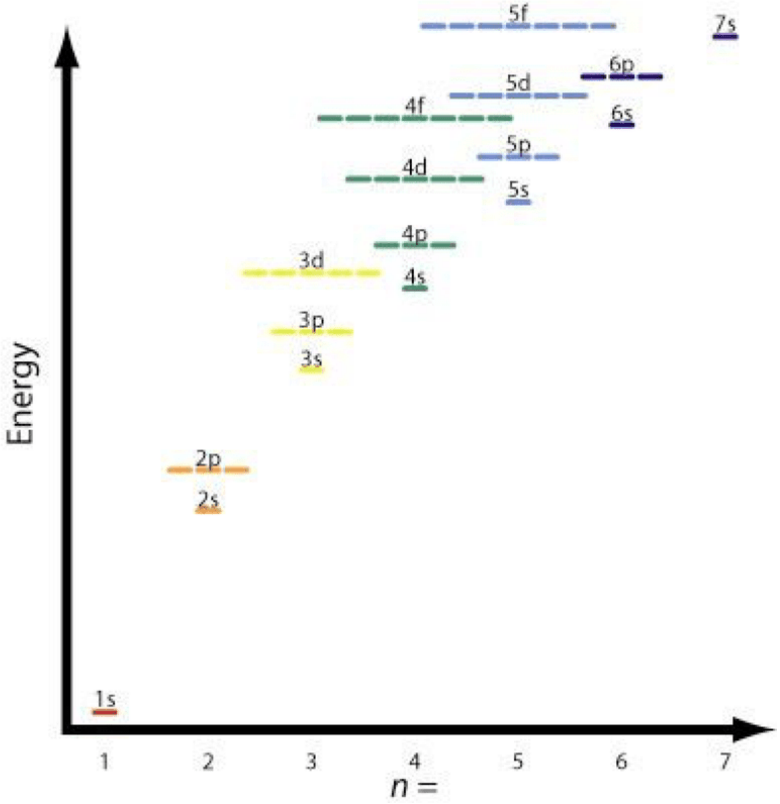
  → PROBABILITY DENSITY / ELECTRON DENSITY MAP

  → ”shape” of the orbital



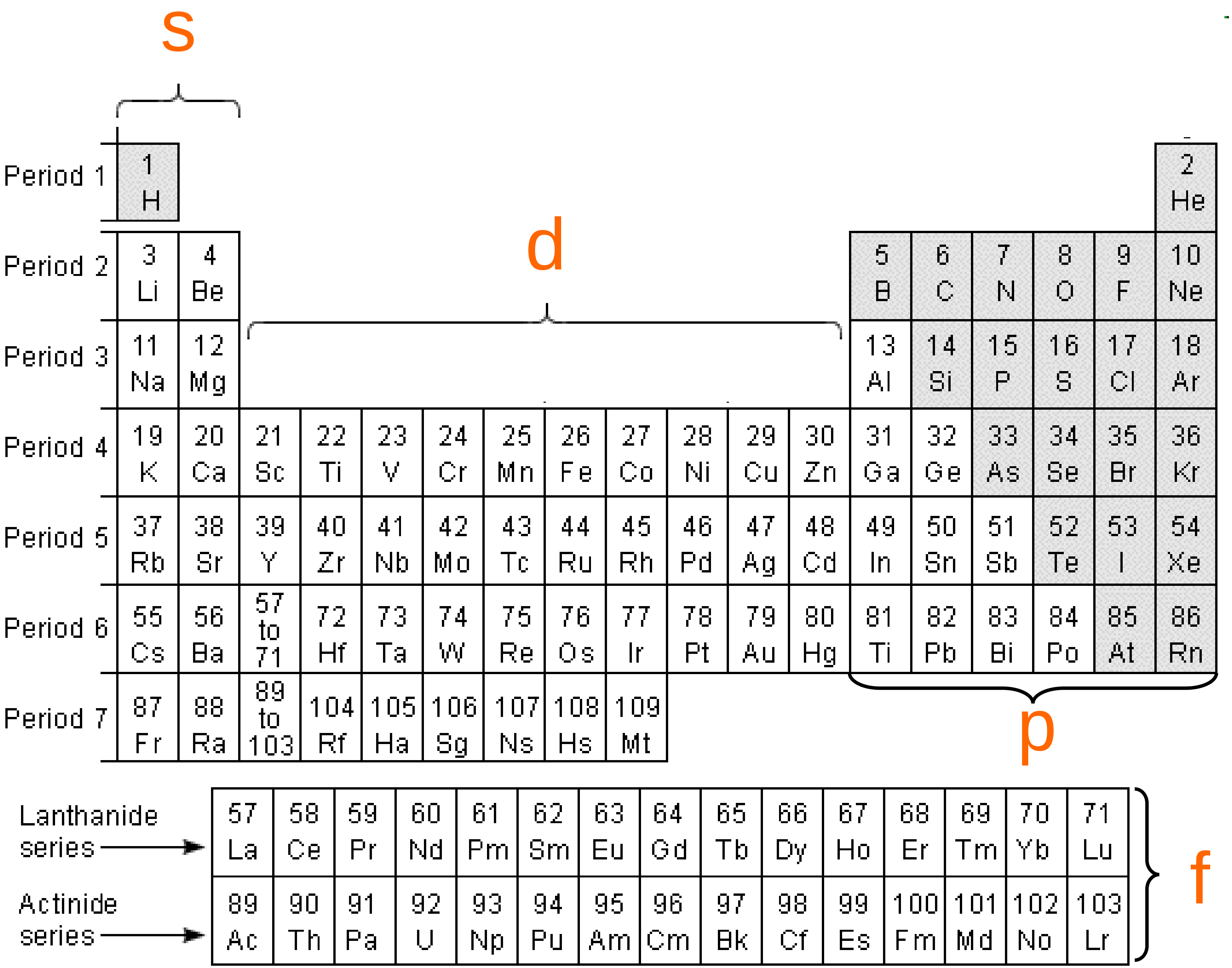






Relative Orbital Energies

- These diagrams show situation:
  - for empty orbitals
  - in a single separated atom
- Once an orbital is occupied by electron(s), its relative energy changes
- Once an atom is surrounded by neighbouring atoms, the energies of its (outer) d and f orbitals are splitted (*Crystal Field Splitting*)



Period 1	1 H																	2 He
Period 2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
Period 3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
Period 4	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
Period 5	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
Period 6	55 Cs	56 Ba	57 to 71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Ti	82 Pb	83 Bi	84 Po	85 At	86 Rn
Period 7	87 Fr	88 Ra	89 to 103	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt									

Lanthanide series →	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
Actinide series →	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

Electron configurations of 3d metals:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^x$$

			3d				4s
Scandium (Sc)	↑						↑↓
Titanium (Ti)	↑	↑					↑↓
Vanadium (V)	↑	↑	↑				↑↓
Chromium (Cr)	↑	↑	↑	↑	↑		↑
Manganese (Mn)	↑	↑	↑	↑	↑		↑↓
Iron (Fe)	↑↓	↑	↑	↑	↑		↑↓
Koboltti (Co)	↑↓	↑↓	↑	↑	↑		↑↓
Nikkeli (Ni)	↑↓	↑↓	↑↓	↑	↑		↑↓
Kupari (Cu)	↑↓	↑↓	↑↓	↑↓	↑↓		↑
[Sinkki (Zn)]	↑↓	↑↓	↑↓	↑↓	↑↓		↑↓

Electron configurations and oxidation states of lanthanoids

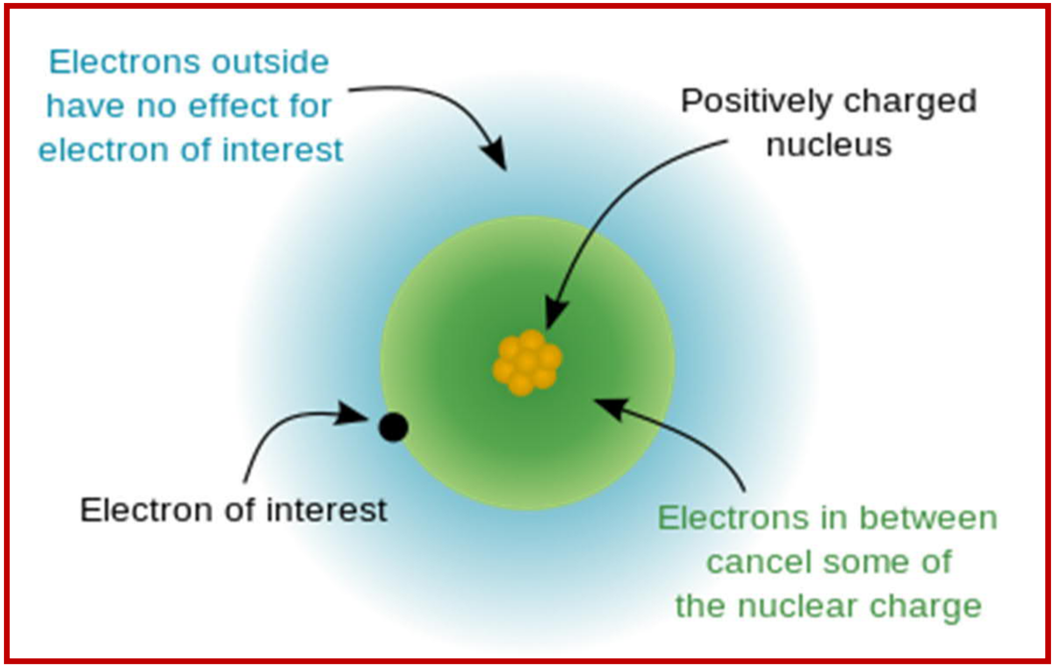
Z	Element	Electronic configuration	Oxidation states
57	Lanthanum (La)	$4f^{0}5d^{1}6s^{2}$	+III
58	Cerium (Ce)	$4f^{1}5d^{1}6s^{2}$	+III, +IV
59	Praseodymium (Pr)	$4f^{2}5d^{1}6s^{2}$	+III
60	Neodymium (Nd)	$4f^{3}5d^{1}6s^{2}$	+III
61	Promethium (Pm)	$4f^{4}5d^{1}6s^{2}$	+III
62	Samarium (Sm)	$4f^{5}5d^{1}6s^{2}$	+III
63	Europium (Eu)	$4f^{7}5d^{0}6s^{2}$	+II, +III
64	Gadolinium (Gd)	$4f^{7}5d^{1}6s^{2}$	+III
65	Terbium (Tb)	$4f^{7}5d^{2}6s^{2}$	+III, +IV
66	Dysprosium (Dy)	$4f^{9}5d^{1}6s^{2}$	+III
67	Holmium (Ho)	$4f^{10}5d^{1}6s^{2}$	+III
68	Erbium (Er)	$4f^{11}5d^{1}6s^{2}$	+III
69	Thulium (Tm)	$4f^{12}5d^{1}6s^{2}$	+III
70	Ytterbium (Yb)	$4f^{14}5d^{0}6s^{2}$	+II, +III
71	Lutetium (Lu)	$4f^{14}5d^{1}6s^{2}$	+III

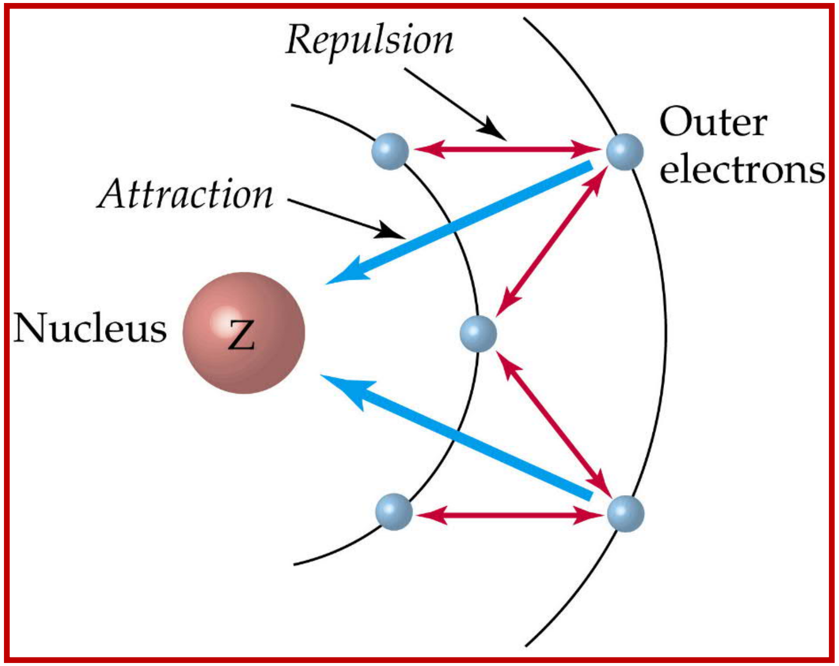
PERIODIC PROPERTIES

- effective nuclear charge
- atomic radius and ionic radius
- ionization energy
- electron affinity
- electronegativity
- oxidation numbers
- density
- melting and boiling points
- reactivity and stoichiometries of compounds
- properties of compounds
- etc.

EFFECTIVE NUCLEAR CHARGE (Z_{eff})

- Atomic number (Z) = number of protons = (true) positive nuclear charge
- Z_{eff}: positive charge experienced by an electron in a multi-electron atom
- Z_{eff} is smaller than Z due to the shielding effect of the other (inner) electrons in the same atom
- Only the electrons that are closer to the nucleus contribute to the shielding effect (not electrons on the same orbitals)
- $+e < Z_{eff} < Z$



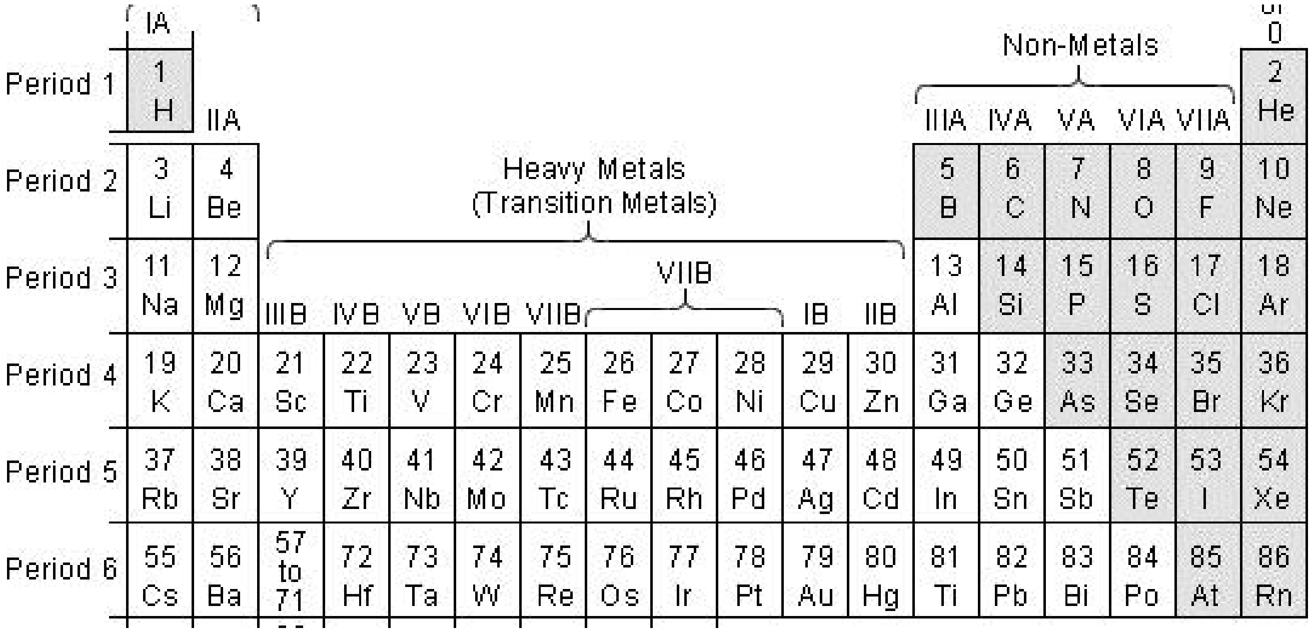


atomic radius (r_{atom})
ionization energy (IE)
electronegativity (EN)

Z_{eff} increases, r_{atom} decreases

→ IE and EN increase

$Z_{eff} \approx$ constant:
IE and EN increase, since r_{atom} decreases



Non-Metals

Heavy Metals (Transition Metals)

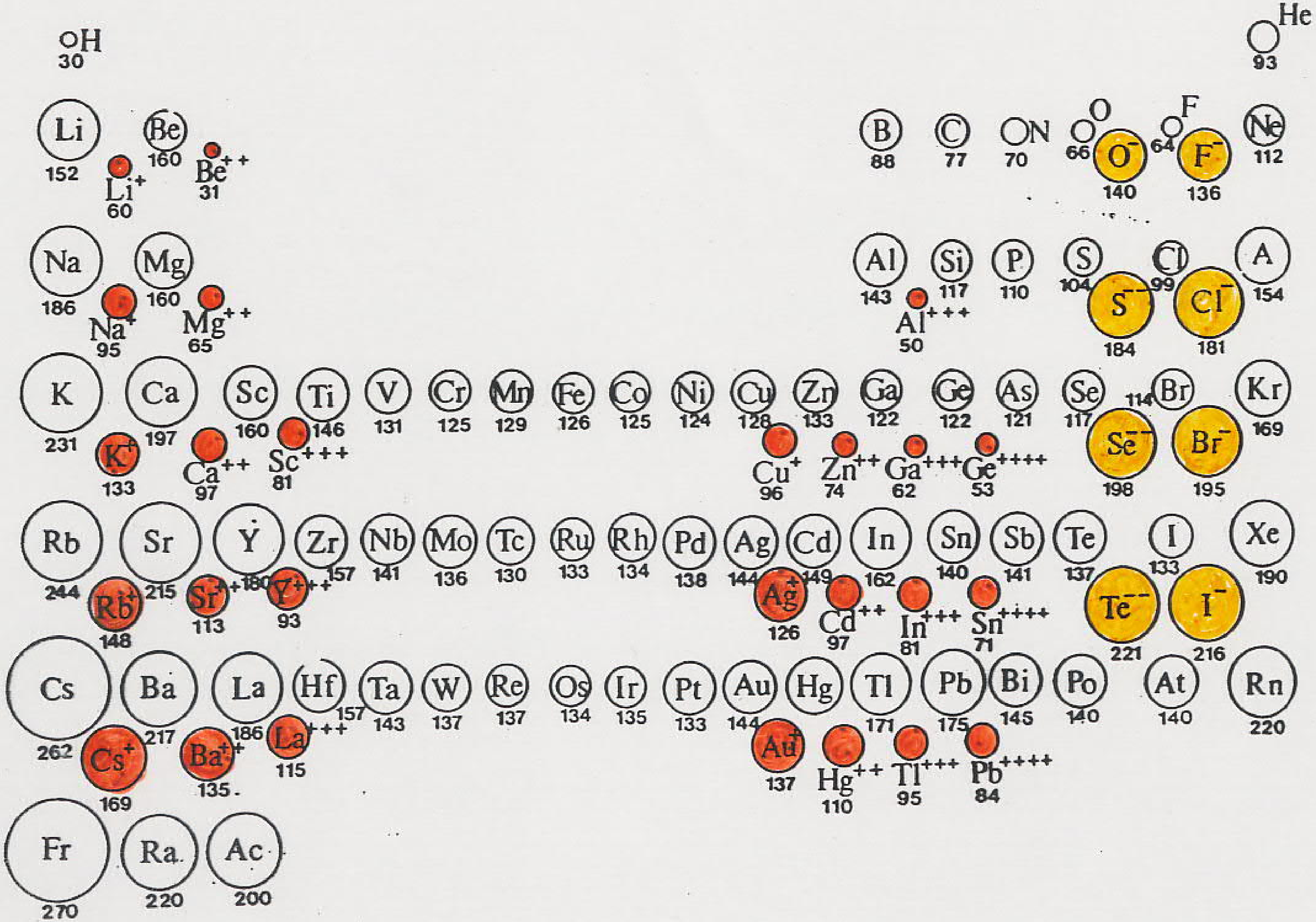
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
Period 1	1 H																	2 He
Period 2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
Period 3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
Period 4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
Period 5	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
Period 6	55 Cs	56 Ba	57 to 71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Ti	82 Pb	83 Bi	84 Po	85 At	86 Rn

IONIC RADIUS

- **Ionic radius values can not be measured directly**
- **The values are estimated (using statistical techniques) for each ion from a large data set for experimentally determined bond lengths in different ionic compounds**
- **The values are tabulated (originally) in:**

R.D. Shannon, Acta Cryst. A 32, 751 (1976)

You can find ionic radius values at: http://abulafia.mt.ic.ac.uk/shannon/ptable.php


H 30
He 93
Li 152
Be 160
Li^{+} 60
Be^{++} 31
B 88
C 77
N 70
O 66
F 64
Ne 112
O^{-} 140
F^{-} 136
Na 186
Mg 160
Na^{+} 95
Mg^{++} 65
Al 143
Si 117
P 110
S 104
Cl 99
A 154
Al^{+++} 50
S^{--} 184
Cl^{-} 181
K 231
Ca 197
Sc 160
Ti 146
V 131
Cr 125
Mn 129
Fe 126
Co 125
Ni 124
Cu 128
Zn 133
Ga 122
Ge 122
As 121
Se 117
Br 114
Kr 169
K^{+} 133
Ca^{++} 97
Sc^{+++} 81
Cu^{+} 96
Zn^{++} 74
Ga^{+++} 62
Ge^{++++} 53
Se^{--} 198
Br^{-} 195
Rb 244
Sr 215
Y 180
Zr 157
Nb 141
Mo 136
Tc 130
Ru 133
Rh 134
Pd 138
Ag 144
Cd 149
In 162
Sn 140
Sb 141
Te 137
I 133
Xe 190
Rb^{+} 148
Sr^{++} 113
Y^{+++} 93
Ag^{+} 126
Cd^{++} 97
In^{+++} 81
Sn^{++++} 71
Te^{--} 221
I^{-} 216
Cs 262
Ba 217
La 186
Hf 157
Ta 143
W 137
Re 137
Os 134
Ir 135
Pt 133
Au 144
Hg
Tl 171
Pb 175
Bi 145
Po 140
At 140
Rn 220
Cs^{+} 169
Ba^{++} 135
La^{+++} 115
Au^{+} 137
Hg^{++} 110
Tl^{+++} 95
Pb^{++++} 84
Fr 270
Ra 220
Ac 200

Ionic radius [Å]

earth-alkaline metals: oxidation state +II

CN	4	6	8	9	10	12
Be	0.27	0.45	-	-	-	-
Mg	0.57	0.72	0.89	-	-	-
Ca	-	1.00	1.12	1.18	1.23	1.34
Sr	-	1.18	1.26	1.31	1.36	1.44
Ba	-	1.35	1.42	1.47	1.52	1.66

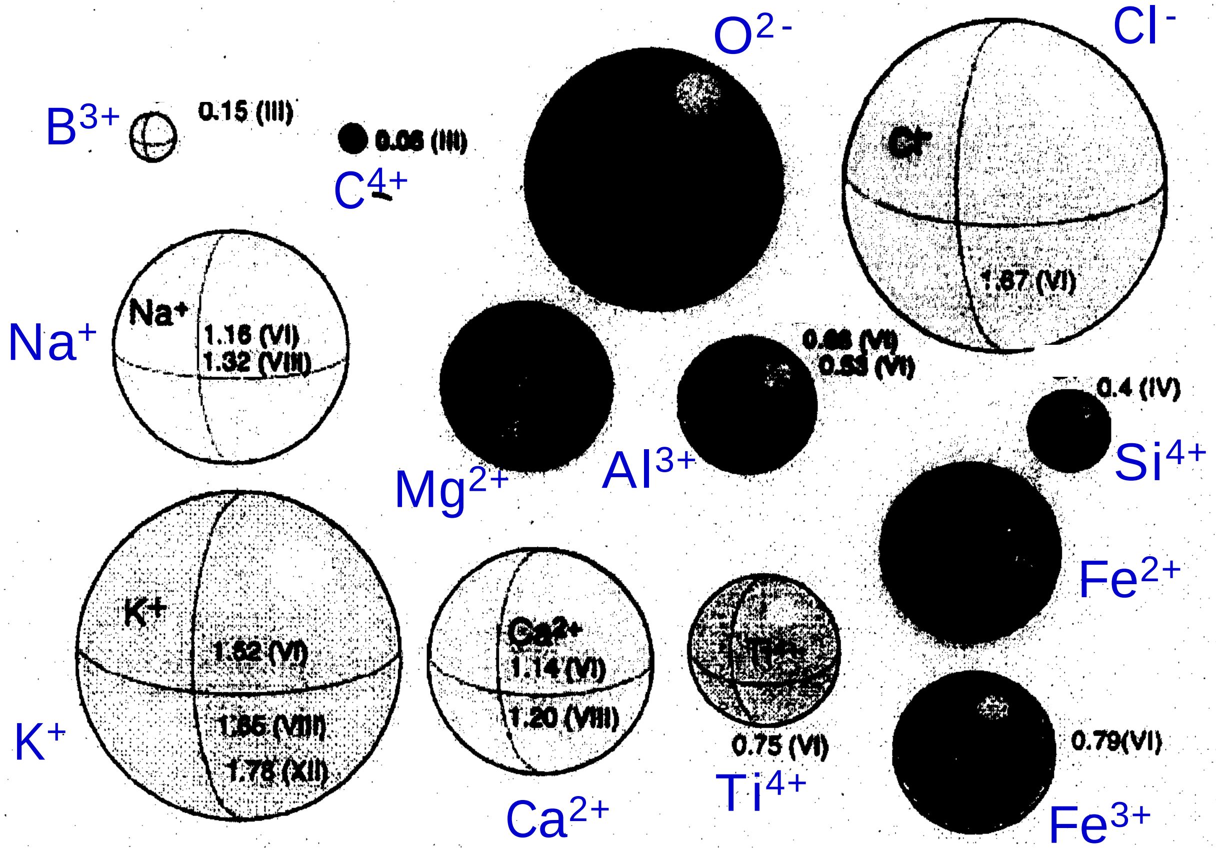
3d cations: CN = 6

Ox. state	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+II	0.86	0.79	0.80	0.83	0.78	0.75	0.69	0.73	0.74
+III	0.67	0.64	0.62	0.65	0.65	0.61	0.60	0.54	-
+IV	0.61	0.58	0.55	0.53	0.59	0.53	0.48	-	-

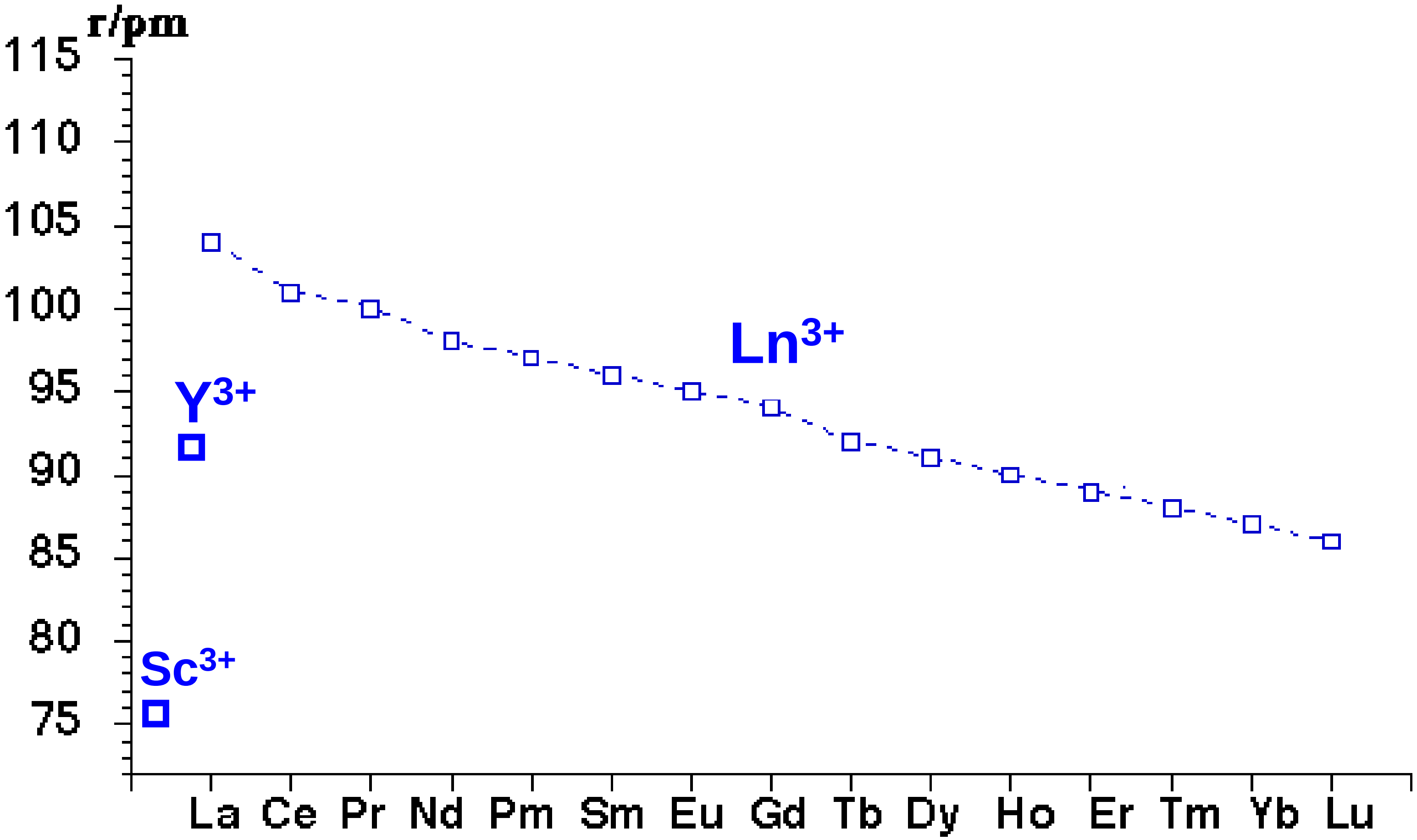
anions: CN = 6

OH^- 1.37	H^- 1.67
O^{2-} 1.40	F^- 1.33
S^{2-} 1.84	Cl^- 1.81
Se^{2-} 1.98	Br^- 1.96
Te^{2-} 2.21	I^- 2.20

Ionic Radii (Shannon, 1976)



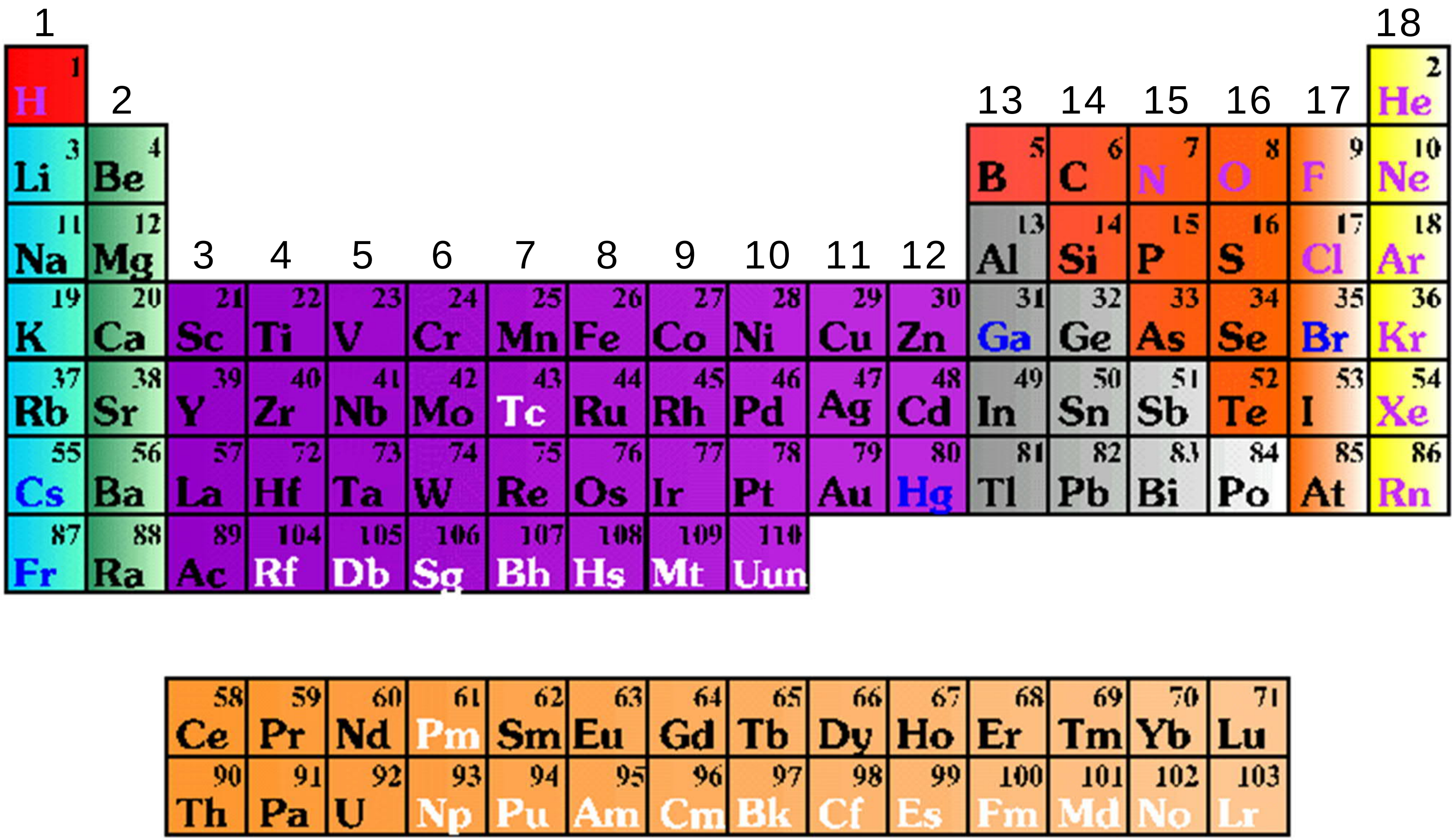
LANTHANIDE CONTRACTION



MAIN GROUP ELEMENTS

- **Hydrogen: position in Periodic Table, isotopes, hydrides, hydrogen storage**
- **Alkali metals: group trends, Li-ion battery**
- **Alkaline earth metals *versus* alkali metals**
- **Boron group: crystal structures & melting points, boranes, borides, BNCT**
- **Isoelectronic: C-C ja B-N**
- **Nitrogen group: metal character and basicity of oxides (N < P < As < Sb < Bi)**
- **Multitude of sulphur compounds**
- **Lightest element *versus* other group members: F – Cl, Br, I**
- **Ionization energies and compounds of noble gases**

Where would you place **hydrogen** in Periodic Table ?



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
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	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	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun								

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

HYDROGEN in the Periodic Table:

Group 1: **PRO:**
- one s electron
- monovalent cation

CONTRA:
- not a metal
- does not react with water

Group 17: **PRO:**
- one electron to the full shell
- non-metal
- two-atom molecule

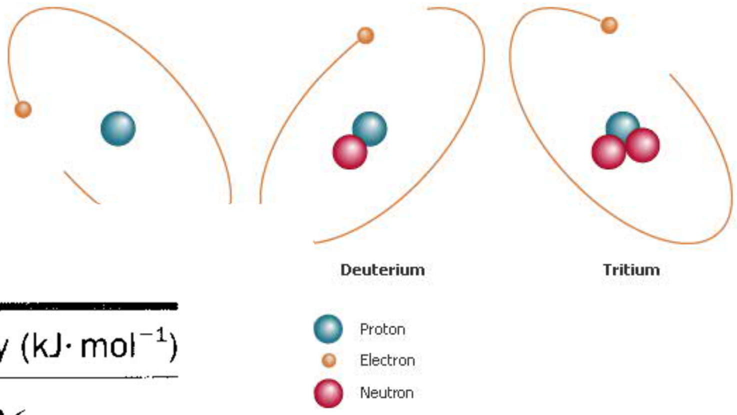
CONTRA:
- anion not common
- relatively inert

Group 14: **PRO:**
- half-filled electron shell
- electronegativity 2.2

Hydrogen, Deuterium & Tritium

- H_2 99.985%, D_2 0.015 %, T_2 10^{-15} %
- Tritium is radioactive (half-life-time 12 years) but found in atmosphere upon cosmic radiation
- Industrial preparation: in nuclear reactors from ^{6}Li; bound into metals, e.g. UT_3
- Uses: medical application as a radioactive tracer, hydrogen bombs, fusion reactors
- H, D & T: all physical properties different, e.g. boiling point
- H, D & T: also chemical properties slightly different, e.g. covalent bond strength
- H-O bond weaker than the D-O bond (gets broken more easily)
  → electrolysis of water is utilized for the separation of D_2O from H_2O

$${}^{6}_{3}\mathrm{Li} + {}^{1}_{0}\mathrm{n} \text{ --> } {}^{4}_{2}\mathrm{He} + {}^{3}_{1}\mathrm{H}$$



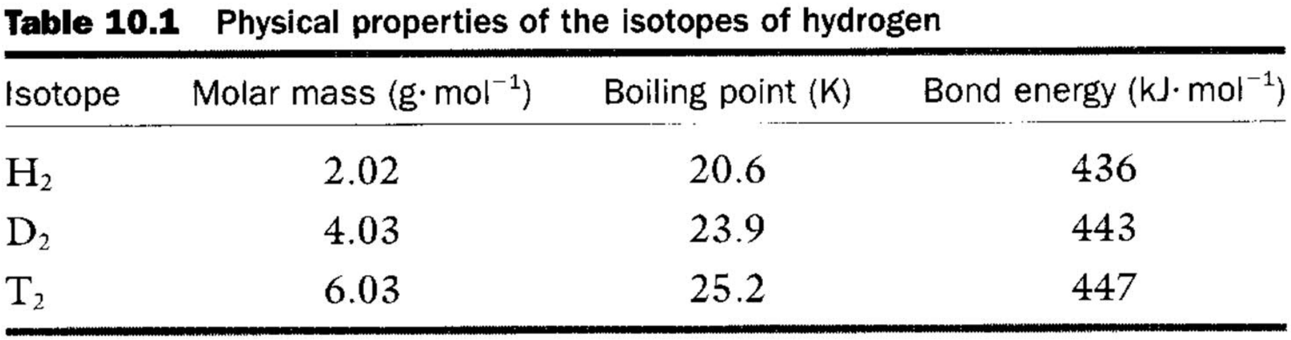


Table 10.1 Physical properties of the isotopes of hydrogen

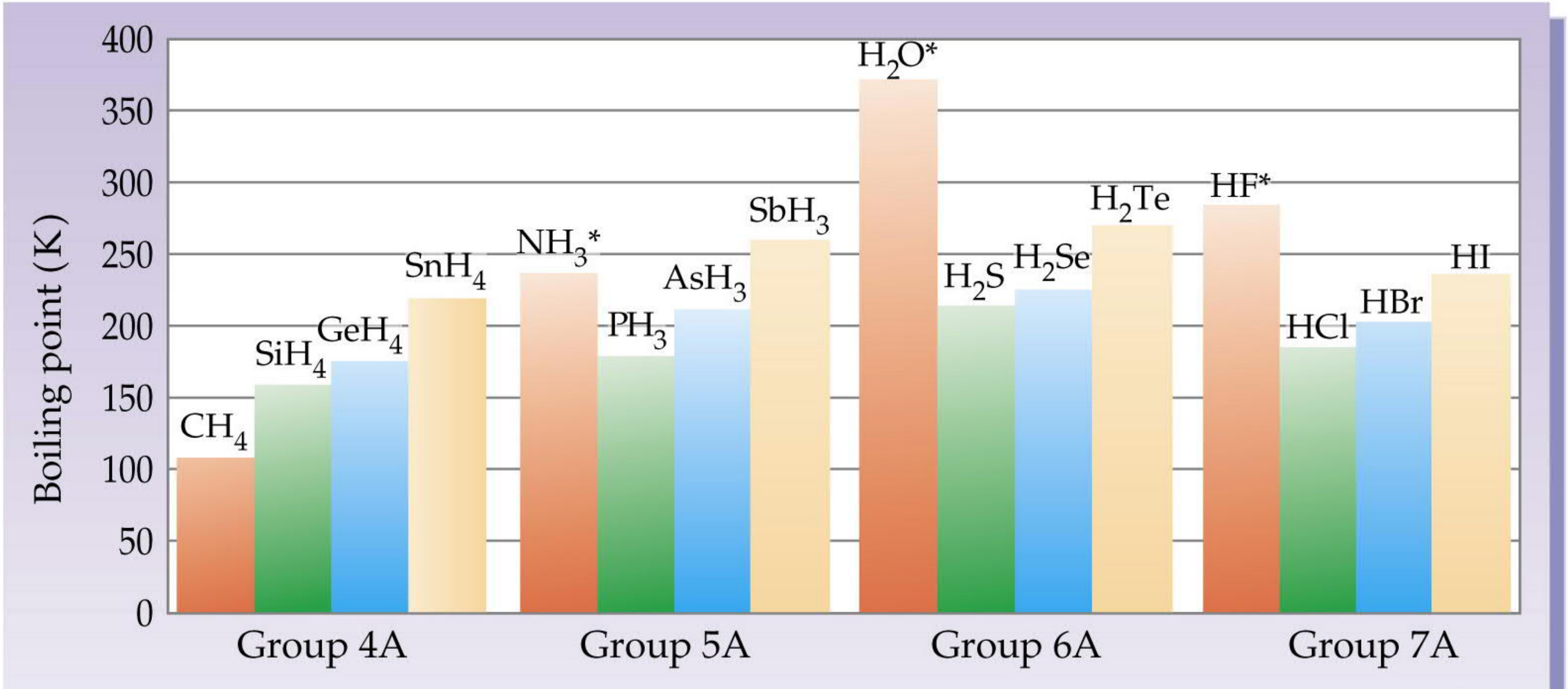
Isotope	Molar mass ($g \cdot mol^{-1}$)	Boiling point (K)	Bond energy ($kJ \cdot mol^{-1}$)
H_2	2.02	20.6	436
D_2	4.03	23.9	443
T_2	6.03	25.2	447

HYDRIDES

- Binary compounds of hydrogen
- Hydrogen forms hydrides with most of the elements
- Electronegativity of hydrogen only little higher than the average electronegativity of elements → many of the ”hydrides” do not contain the H^- hydride ion
- Hydrides are categorized according to the type of bonding: ionic, covalent or metallic

- IONIC HYDRIDES
  - with alkali and alkaline earth metals (except Be, Mg)
  - metal cation and H^- ion
  - crystal structures similar to those of halides (Cl replaced by H)
  - very reactive, e.g.: $LiH + H_2O \rightarrow LiOH + H_2$
    (used as reductants)

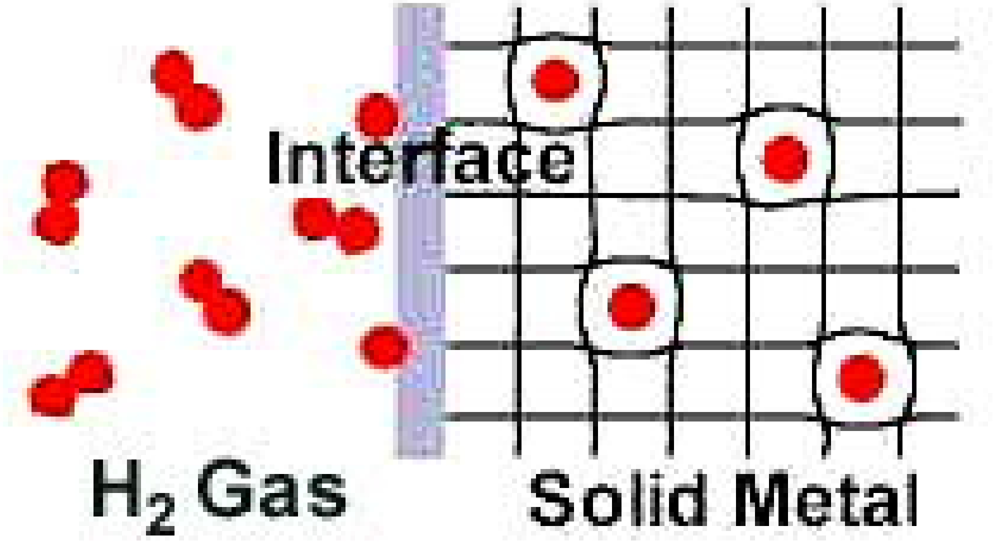
- **COVALENT HYDRIDES (not correct name for all these compounds)**
  - with all nonmetals (except noble gases) and the most electro-negative metals (Sn,Ga)
  - most of these hydrides are gaseous at room temperature



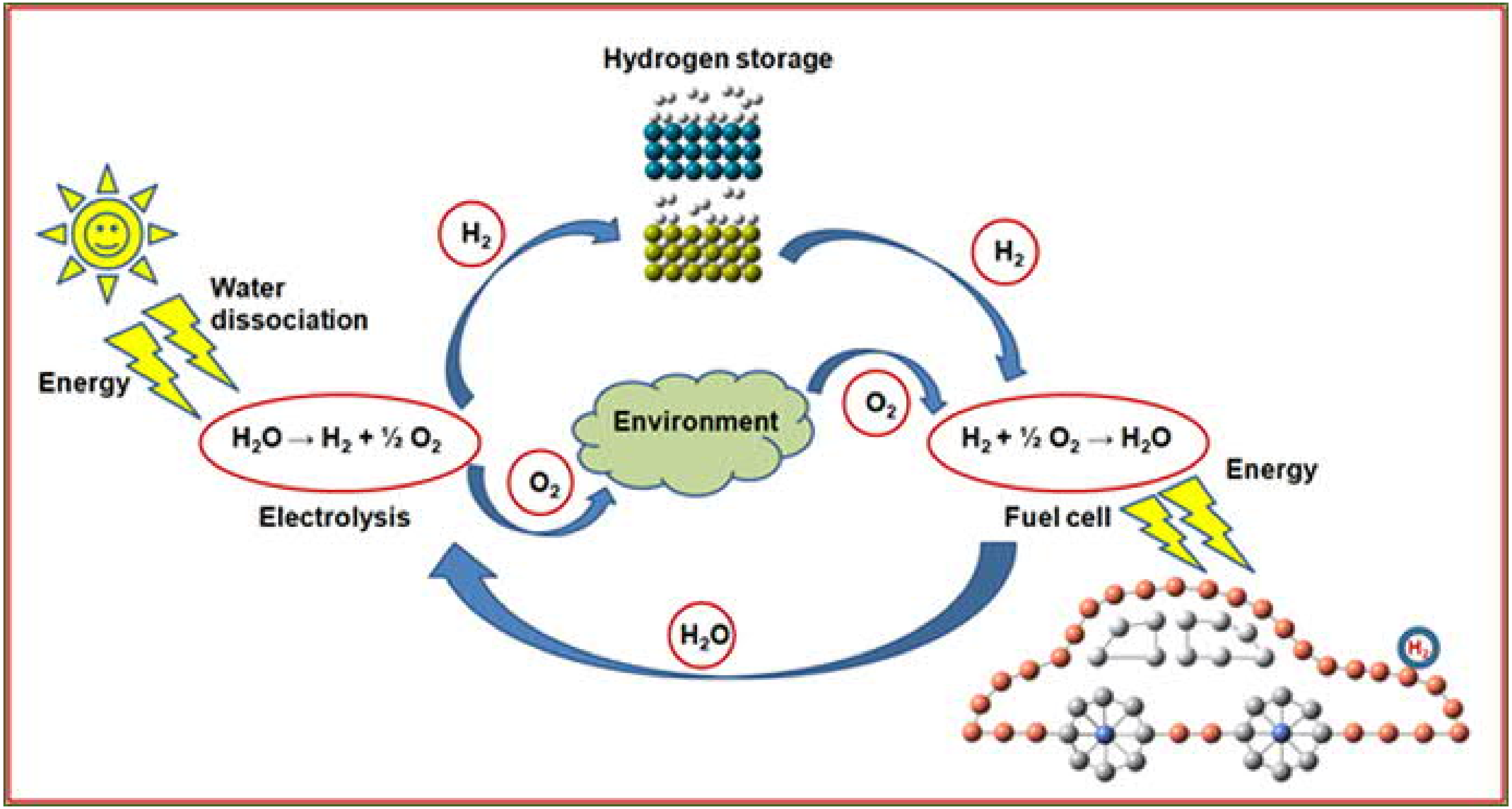
*The boiling points generally increase with increasing molecular mass down a group of the periodic table, but the hydrides of nitrogen (NH_3), oxygen (H_2O), and fluorine (HF) have abnormally high boiling points because these molecules form hydrogen bonds.

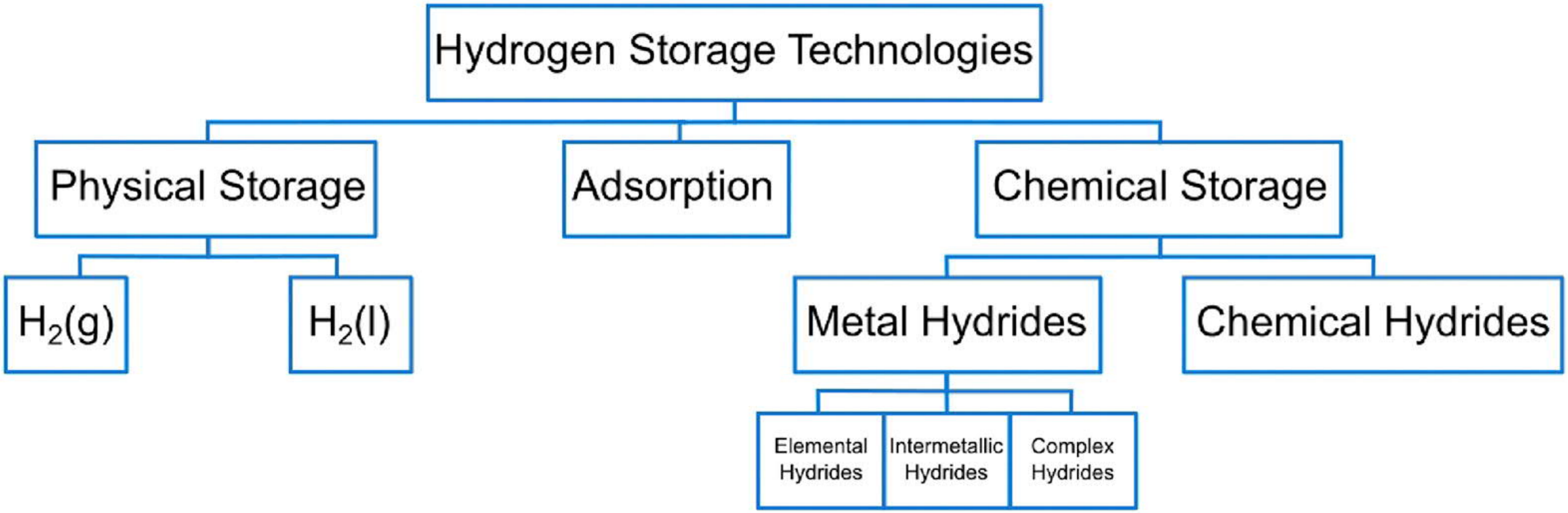
METALLIC (TRANSITION METAL) HYDRIDES

- solid materials
- hydrogen in interstitial positions
- often nontoichiometric, e.g. $TiH_{1.9}$
- volume increases upon hydrogen intercalation
  → no strong bonding (attraction)
- used for **HYDROGEN STORAGE**
  - $Ti + H_2$ + little heating/pressure → $TiH_{1.9}$
  - $TiH_{1.9}$ + higher temp. → $Ti + H_2$

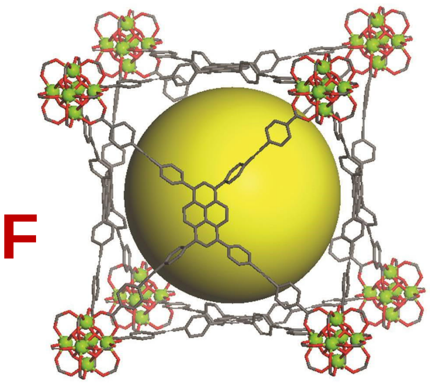


HYDROGEN STORAGE !!!



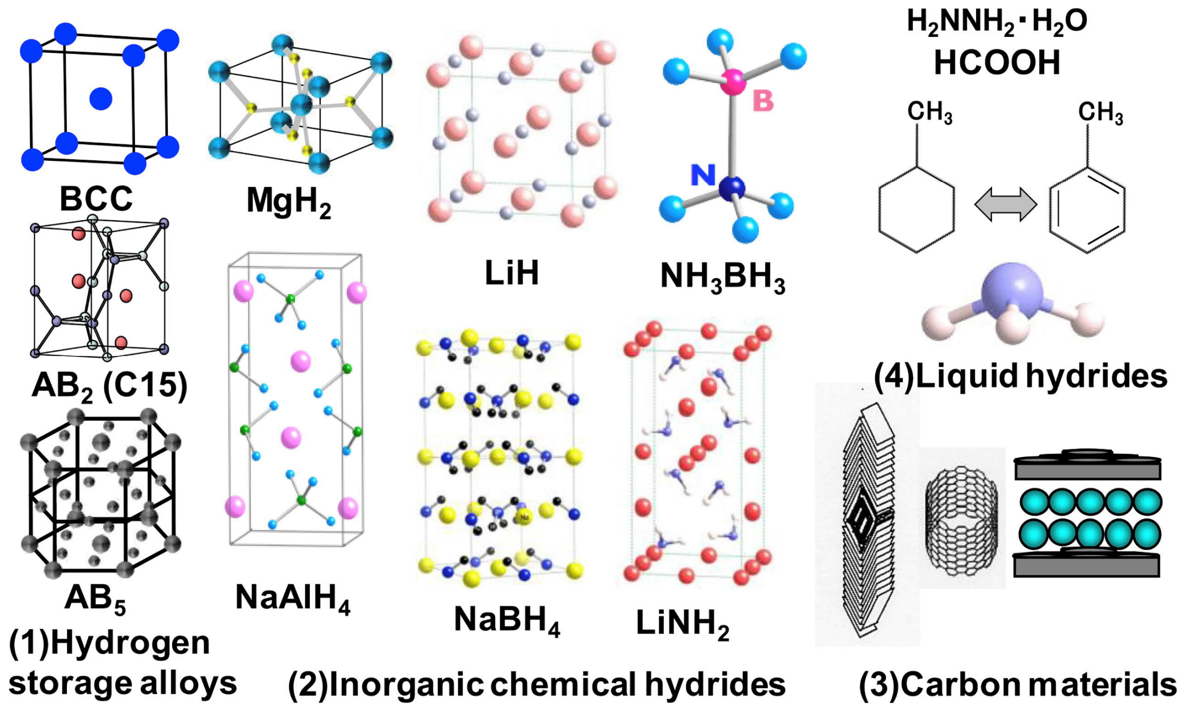


- Hydrogen Storage Technologies
  - Physical Storage
    - $H_2(g)$
    - $H_2(l)$
  - Adsorption
  - Chemical Storage
    - Metal Hydrides
      - Elemental Hydrides
      - Intermetallic Hydrides
      - Complex Hydrides
    - Chemical Hydrides

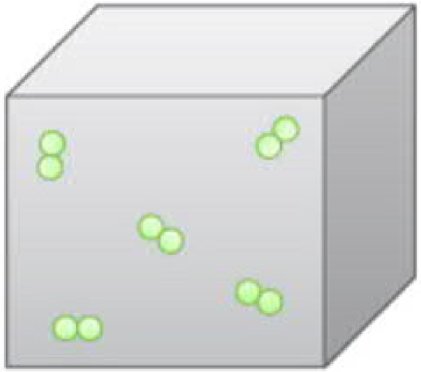


MOF

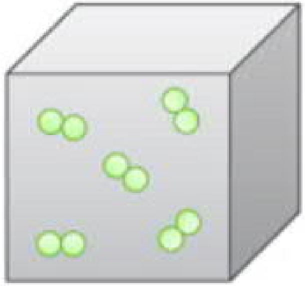
Metal Organic Framework



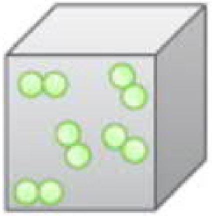
Physical Storage



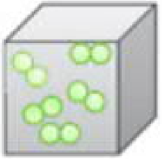
1 bar
normal
0.3 g/L



150 bar
lab cylinders
10 g/L



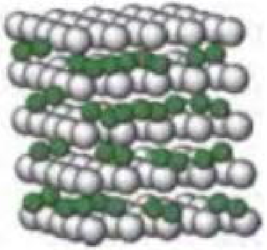
350 bar
Gen 1 vehicles
28 g/L



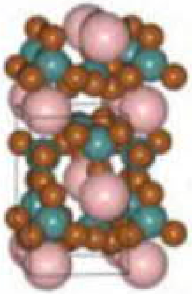
700 bar
Gen 2 vehicles
40g/L

liquid H_2
71 g H_2/L
@ 20 K

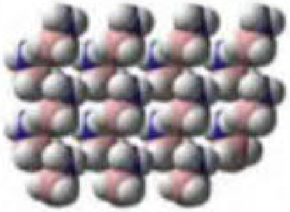
Materials -based Storage



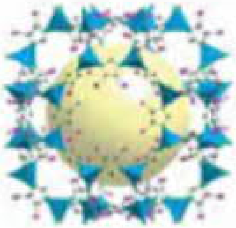
interstial hydrides
~100-150 g H_2/L



complex hydrides
~70-150 g H_2/L

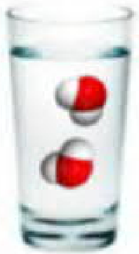


chemical storage
~70-150 g H_2/L

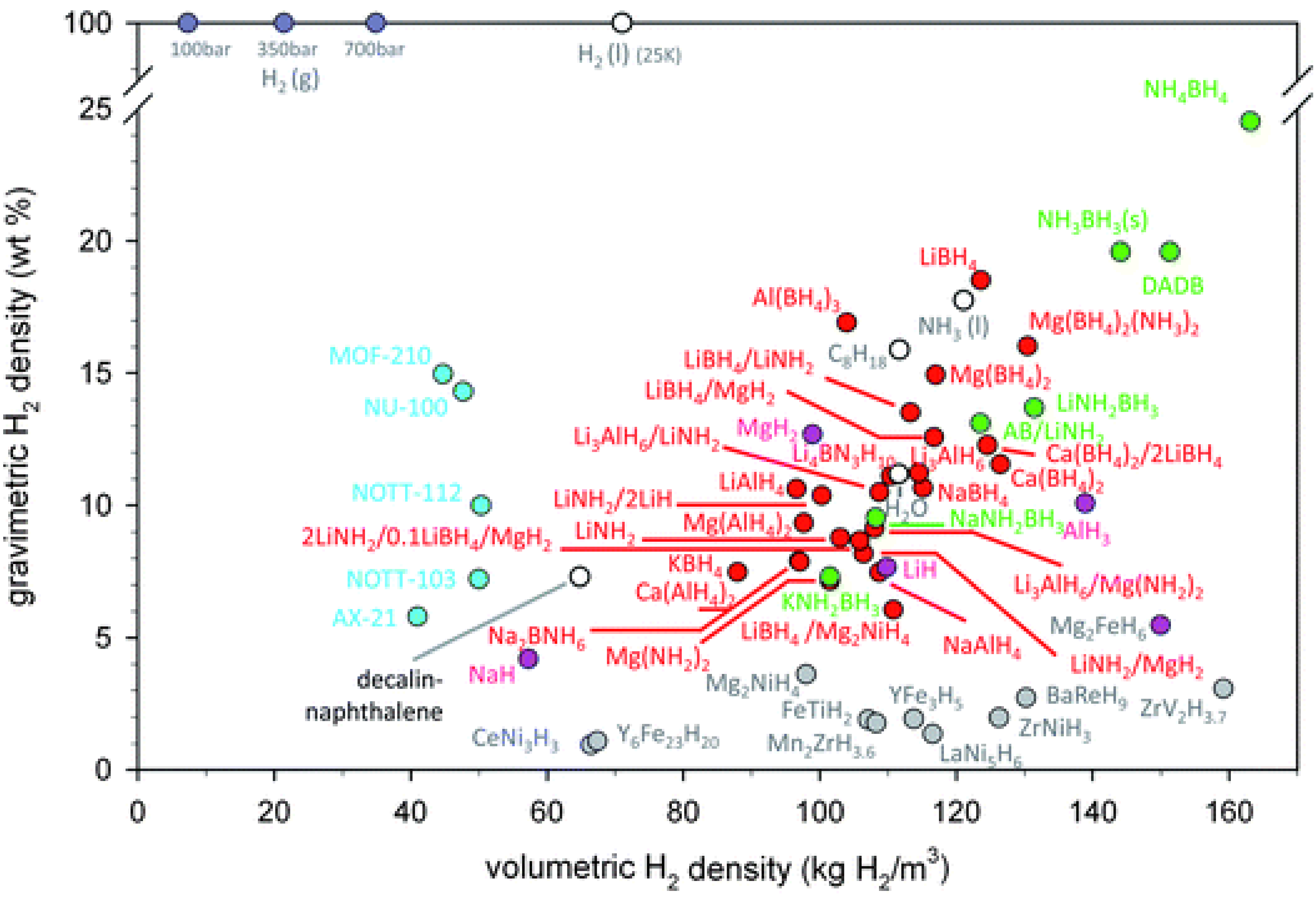


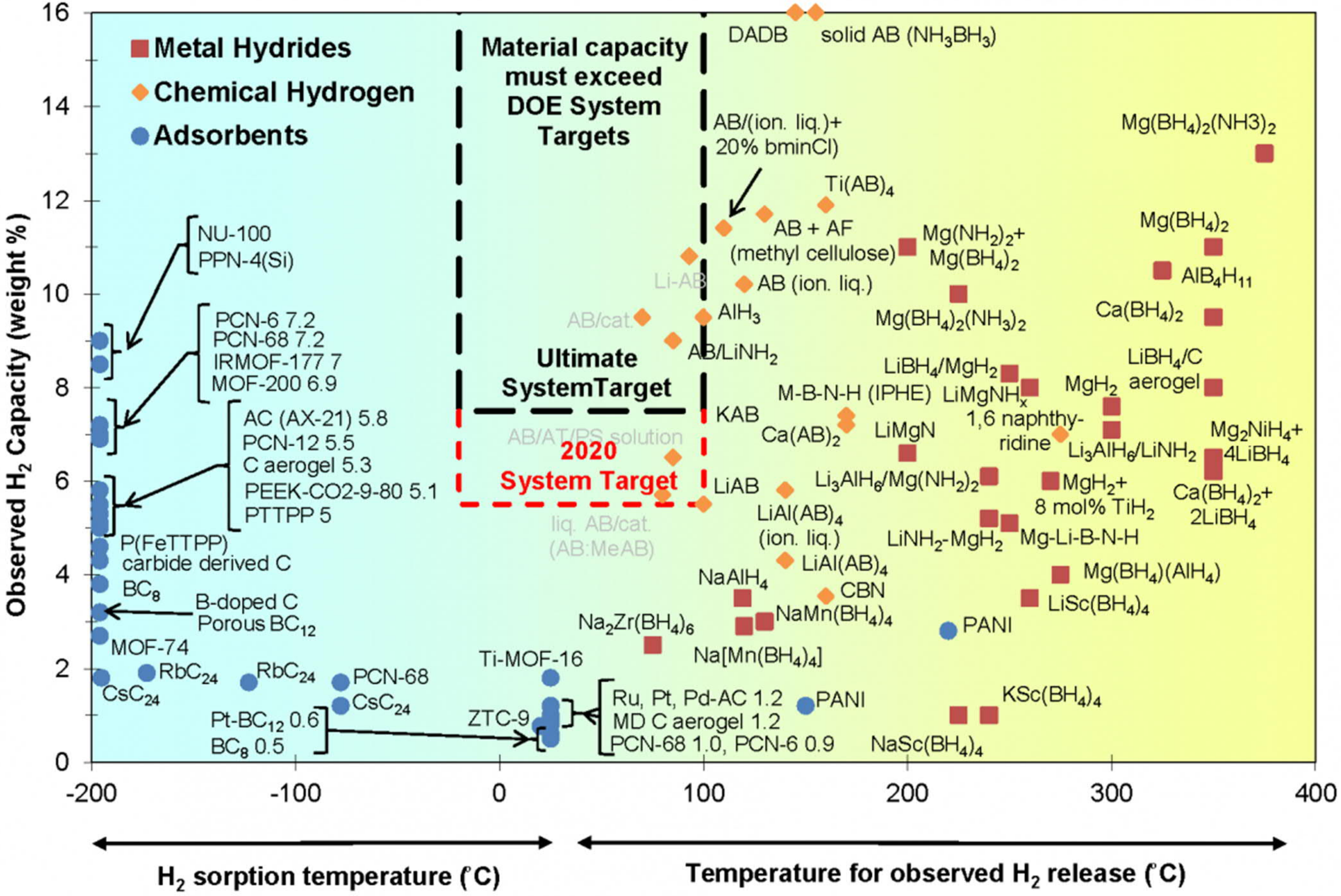
sorbents
≤ 70 g H_2/L

Reference



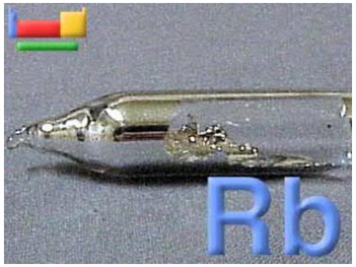
water
111 g H_2/L

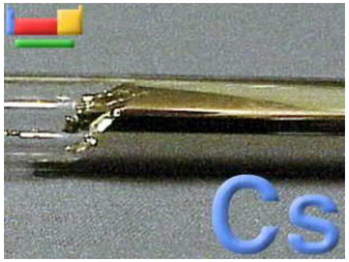

100
25
20
15
10
5
0
100bar
350bar
700bar
H_2 (g)
H_2 (l) (25K)
NH_4BH_4
NH_3BH_3(s)
DADB
$LiBH_4$
$Al(BH_4)_3$
NH_3 (l)
$Mg(BH_4)_2(NH_3)_2$
C_8H_{18}
$LiBH_4/LiNH_2$
$Mg(BH_4)_2$
MOF-210
NU-100
$LiBH_4/MgH_2$
$LiNH_2BH_3$
MgH_2
$AB/LiNH_2$
$Li_3AlH_6/LiNH_2$
$Li_4BN_3H_{10}$
Li_3AlH_6
$Ca(BH_4)_2/2LiBH_4$
$Ca(BH_4)_2$
$LiAlH_4$
NOTT-112
$LiNH_2/2LiH$
$NaBH_4$
H_2O
$Mg(AlH_4)_2$
$NaNH_2BH_3$
AlH_3
$LiNH_2$
$2LiNH_2/0.1LiBH_4/MgH_2$
KBH_4
LiH
$Li_3AlH_6/Mg(NH_2)_2$
NOTT-103
$Ca(AlH_4)_2$
KNH_2BH_3
AX-21
Mg_2FeH_6
Na_2BNH_6
$LiBH_4$ $/Mg_2NiH_4$
$NaAlH_4$
$Mg(NH_2)_2$
$LiNH_2/MgH_2$
NaH
decalin-
naphthalene
Mg_2NiH_4
YFe_3H_5
$BaReH_9$
$ZrV_2H_{3.7}$
$FeTiH_2$
$ZrNiH_3$
$CeNi_3H_3$
$Y_6Fe_{23}H_{20}$
$Mn_2ZrH_{3.6}$
$LaNi_5H_6$
0
20
40
60
80
100
120
140
160
gravimetric H_2 density (wt %)
volumetric H_2 density (kg H_2/m^3)


Metal Hydrides
Chemical Hydrogen
Adsorbents
Material capacity must exceed DOE System Targets
Ultimate SystemTarget
2020 System Target
Observed H_2 Capacity (weight %)
16
14
12
10
8
6
4
2
0
-200
-100
0
100
200
300
400
H_2 sorption temperature (°C)
Temperature for observed H_2 release (°C)
DADB
solid AB (NH_3BH_3)
$Mg(BH_4)_2(NH3)_2$
AB/(ion. liq.)+ 20% bminCl)
$Ti(AB)_4$
AB + AF (methyl cellulose)
$Mg(NH_2)_2$+ $Mg(BH_4)_2$
$Mg(BH_4)_2$
AlB_4H_{11}
Li-AB
AB (ion. liq.)
$Ca(BH_4)_2$
AB/cat.
AlH_3
$Mg(BH_4)_2(NH_3)_2$
AB/$LiNH_2$
$LiBH_4/MgH_2$
$LiBH_4$/C aerogel
M-B-N-H (IPHE)
$LiMgNH_x$
MgH_2
KAB
AB/AT/PS solution
$Ca(AB)_2$
LiMgN
1,6 naphthy-ridine
Mg_2NiH_4+ $4LiBH_4$
$Li_3AlH_6/LiNH_2$
LiAB
$Li_3AlH_6/Mg(NH_2)_2$
MgH_2+ 8 mol% TiH_2
$Ca(BH_4)_2$+ $2LiBH_4$
$LiAl(AB)_4$ (ion. liq.)
liq. AB/cat. (AB:MeAB)
$LiNH_2$-MgH_2
Mg-Li-B-N-H
$LiAl(AB)_4$
$Mg(BH_4)(AlH_4)$
$NaAlH_4$
CBN
$LiSc(BH_4)_4$
$Na_2Zr(BH_4)_6$
$NaMn(BH_4)_4$
$Na[Mn(BH_4)_4]$
PANI
NU-100
PPN-4(Si)
PCN-6 7.2
PCN-68 7.2
IRMOF-177 7
MOF-200 6.9
AC (AX-21) 5.8
PCN-12 5.5
C aerogel 5.3
PEEK-CO2-9-80 5.1
PTTPP 5
P(FeTTPP)
carbide derived C
BC_8
B-doped C
Porous BC_{12}
MOF-74
RbC_{24}
RbC_{24}
CsC_{24}
PCN-68
CsC_{24}
Ti-MOF-16
ZTC-9
Pt-BC_{12} 0.6
BC_8 0.5
Ru, Pt, Pd-AC 1.2
MD C aerogel 1.2
PCN-68 1.0, PCN-6 0.9
PANI
$KSc(BH_4)_4$
$NaSc(BH_4)_4$

ALKALI METALS

- **Chemically highly coherent group, but lithium somewhat more different (diagonal relationship Li-Mg)**
- **Metal radius (Å):**
  Li 1.52 (Mg 1.60), Na 1.86, K 2.27, Rb 2.48, Cs 2.65
- **Ionic radius (Å):**
  Li 0.76 (Mg 0.72), Na 1.02, K 1.38, Rb 1.52, Cs 1.67
- **Charge/ionic radius:**
  Li 1.40, Na 0.88, K 0.66, Rb 0.60, Cs 0.55
- **Melting point (^{o}C): Li 180, Na 98, K 64, Rb 39, Cs 29**
- **Oxidation product: Li_2O, Na_2O/Na_2O_2, K_2O_2, KO_2, RbO_2, CsO_2**
- **Li compounds more covalent than others**
- **Li compounds dissolve more easily into nonpolar solvents, and less into water**
- **Only Li forms the nitride, Li_3N (ref. Mg_3N_2)**
- **Li salts often contain water of crystallization, e.g. $LiClO_4{\bullet}3H_2O$ (ref. $MgClO_4{\bullet}6H_2O$)**





ALKALI *VERSUS* ALKALINE EARTH METALS

- **Alkaline earth metals have larger Z_{eff} than alkali metals**
  - **→ smaller**
  - **→ denser**
  - **→ harder**
- **Alkaline earth metals have two valence electrons per atom**
  - **→ metal bonds stronger**
  - **→ better electrical conductivity**
  - **→ higher melting and boiling points**

	Li/Be	Na/Mg	K/Ca	Rb/Sr	Cs/Ba
Electronegativity	1.0/1.5	0.9/1.2	0.8/1.0	0.8/1.0	0.7/0.9
Metal radius (Å)	1.52/1.12	1.86/1.60	2.27/1.97	2.48/2.15	2.65/2.22
Density (g/cm^3)	0.53/1.85	0.97/1.74	0.86/1.55	1.53/2.63	1.87/3.59
Melting point (^{o}C)	181/1289	98/650	64/842	40/769	28/729
RT-resistivity (μohm cm)	9.47/3.70	4.89/4.48	7.39/3.42	13.1/13.4	

LITHIUM-ION BATTERY

- **WHY Lithium:** the lightest of all metals & the greatest electrochemical potential & the largest energy density per weight & small and easy/fast to move
- Charging: Li-ions from cathode to anode; Discharging: Li-ions from anode to cathode
- Commercialization: Sony 1991
- Used: portable electronics

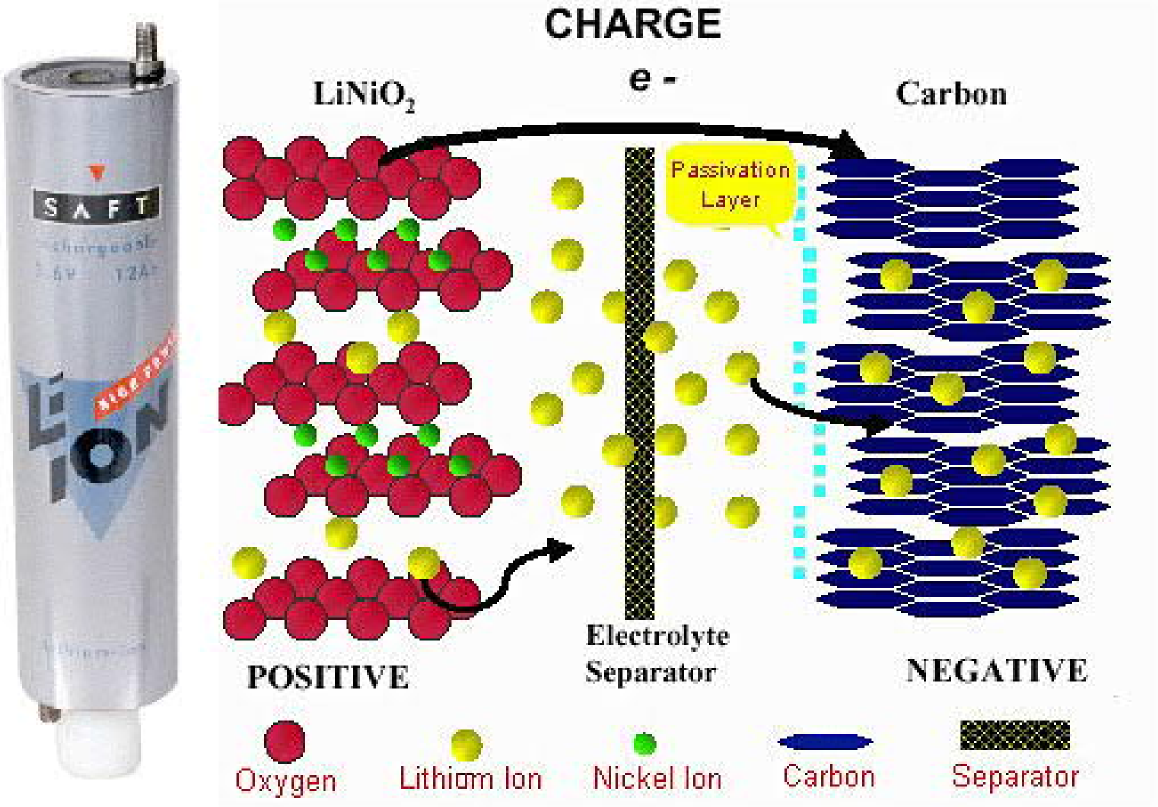
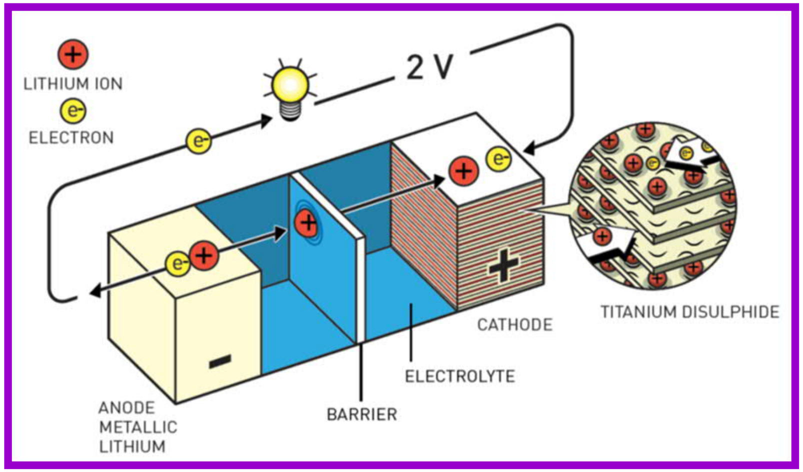
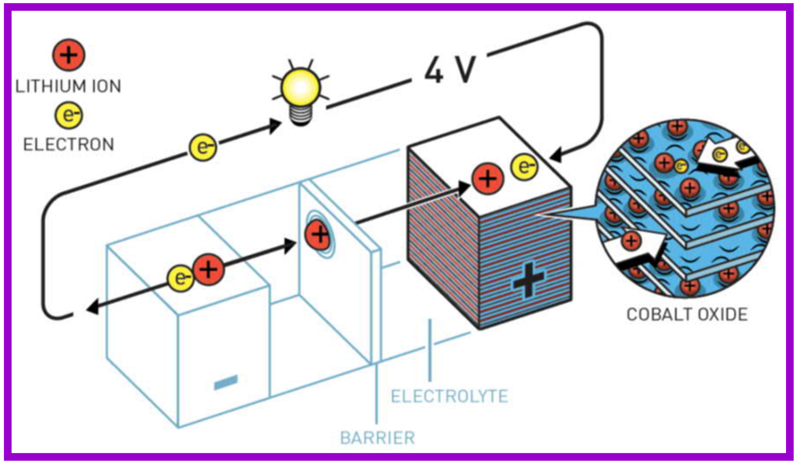
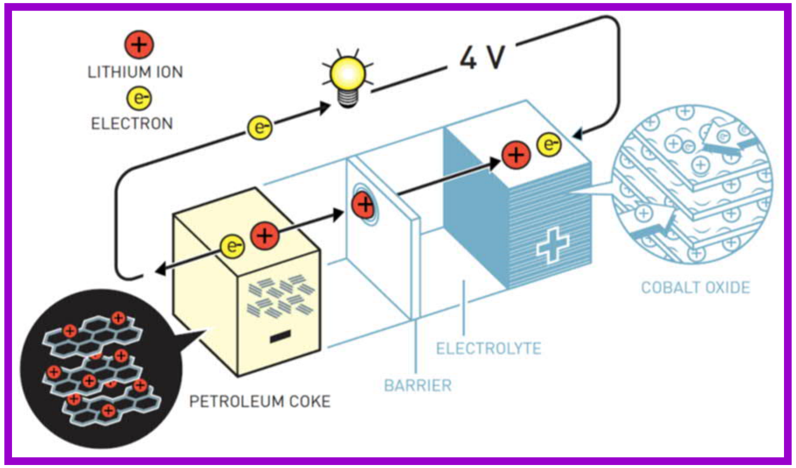
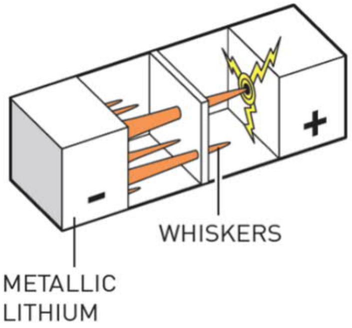


Photo Courtesy of SAFT America









Chemistry Nobel 2019

Stanley Whittingham (born 1941 UK):
- Exxon: TiS_2 cathode 1976

John Goodenough (born 1922 USA):
- Univ. Oxford: $LiCoO_2$ cathode 1980

Akira Yoshino (born 1948 Jpn):
- Asahi Kasei: carbon-based anode 1985

Commercialization: Sony 1991

Current Li-ion battery materials / new alternatives

CATHODE: $LiCoO_2$

$Li(Co_{1/3}Mn_{1/3}Ni_{1/3})O_2$, $LiMn_2O_4$, $LiFePO_4$

ANODE: Grafite

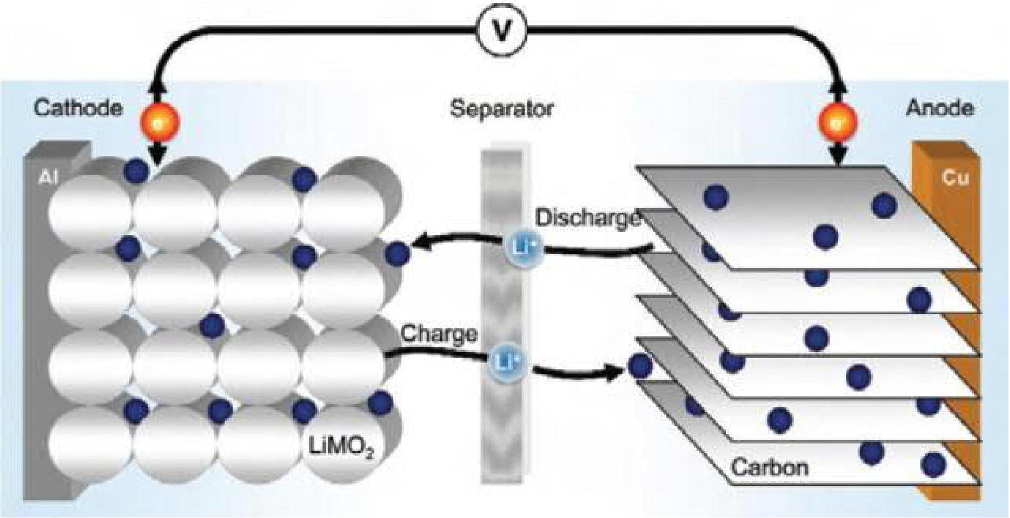
Si, $Li_4Ti_5O_{12}$

ELECTROLYTE: $LiPF_6$ + ethylene carbonate solvent

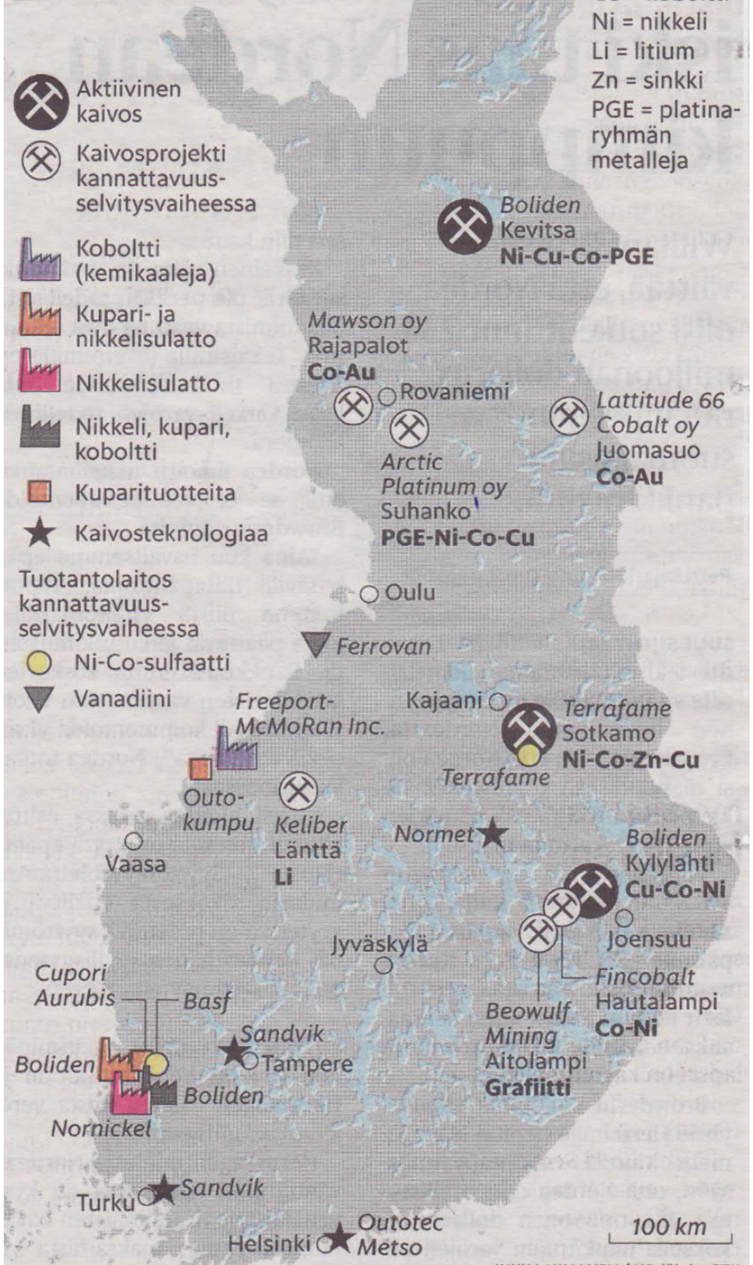
Solid electrolyte materials

BINDERS: PVDF (polyvinyldifluoride) + NMP (N-methylpyrrolidone)

Water-soluble binders



Akkumineraalikaivokset ja -prosessointilaitokset



JUKKA HIMANEN / HS, lähde: GTK