TENTATIVE LECTURE SCHEDULE

		Date	Topic
1.	Wed	07.09.	Course Introduction & Short Review of the Elements
2.	Fri	09.09.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Mon	12.09.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Fri	16.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
5.	Mon	19.09.	Transition Metals: General Aspects & Pigments
6.	Wed	21.09.	Redox Chemistry
7.	Fri	23.09.	Crystal Field Theory (Linda Sederholm)
8.	Mon	26.09.	V, Nb, Ta & Metal Complexes & MOFs
9.	Wed	28.09.	Cr, Mo, W & 2D materials
10.	Fri	30.09.	Mn, Fe, Co, Ni, Cu & Magnetism & Superconductivity
10.	Mon	03.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
11.	Fri	07.10.	Lanthanoids + Actinoids & Luminescence
12.	Mon	10.10.	EXTRA
14.	Wed	12.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
15.	Fri	14.10.	Inorganic Materials Chemistry Research

EXAM: Oct. 18, 9:00-12:00

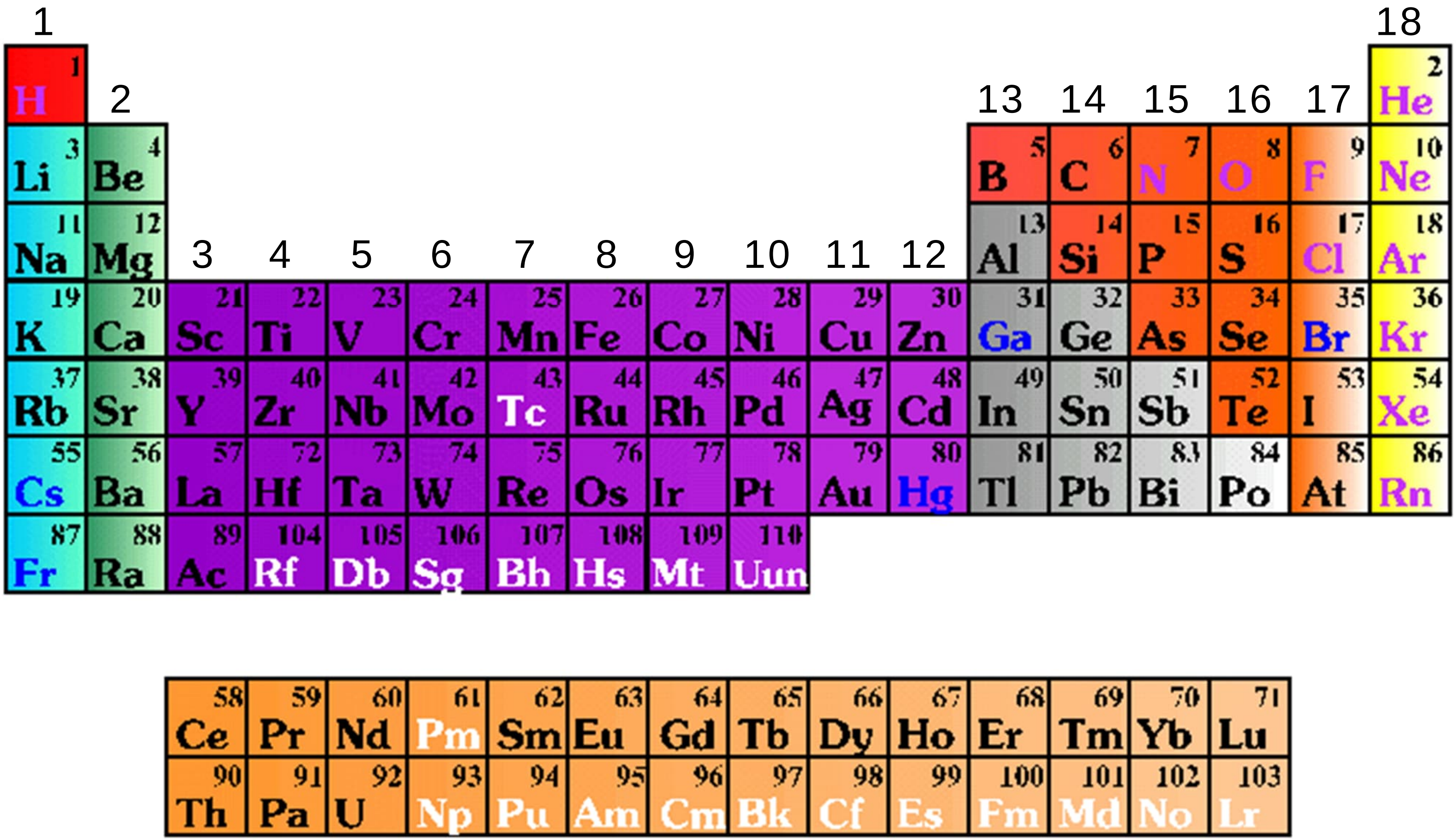
QUESTIONS: Lecture 2

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

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

2. How many unpaired electrons the following ions have **(please explain shortly !)**: Mn^{2+}, Fe^{3+}, Ni^{2+}

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)

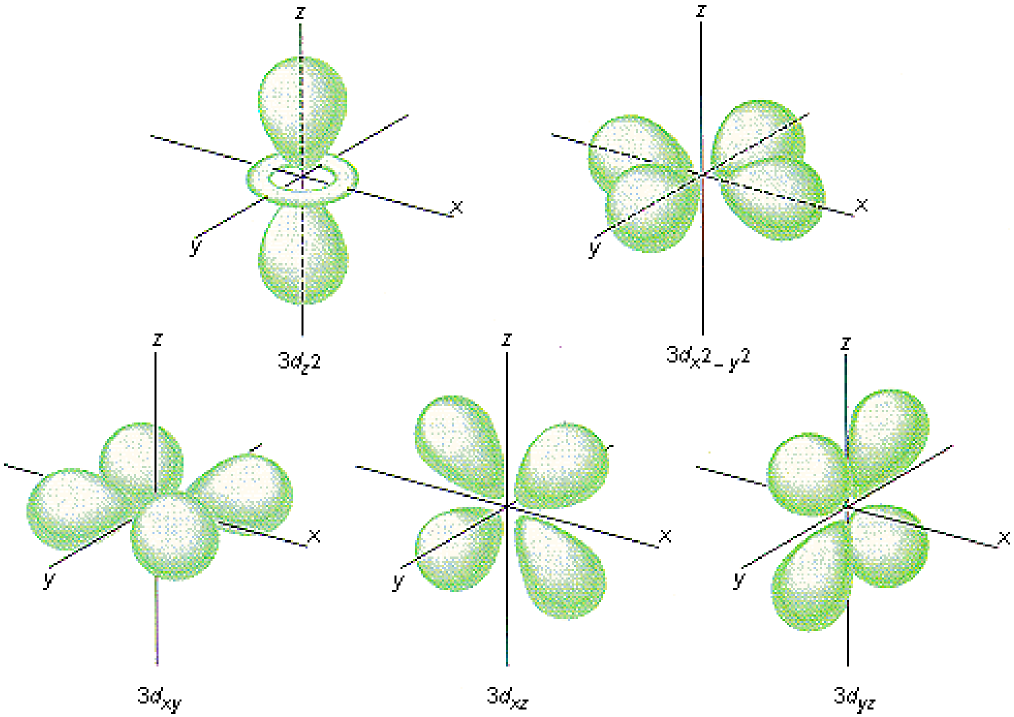
All orbitals in a subshell are first occupied with one electron before two electrons start to occupy the same orbital
(to minimize the electron-electron repulsions)

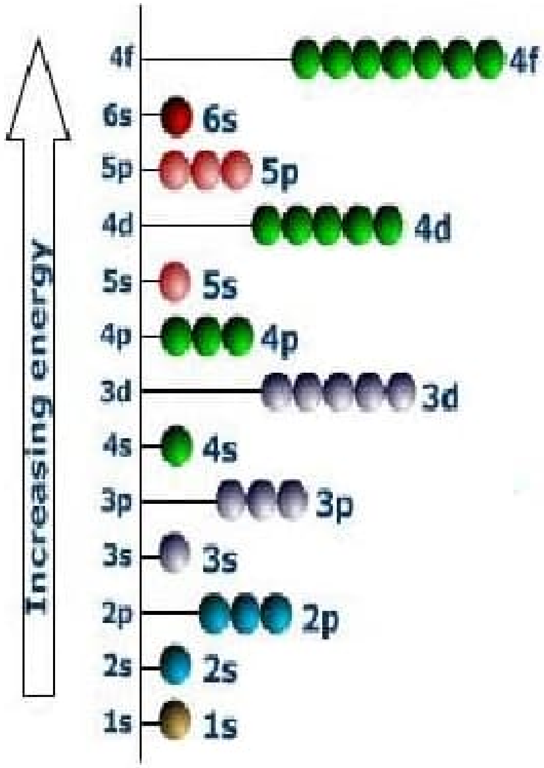
Atom orbitals

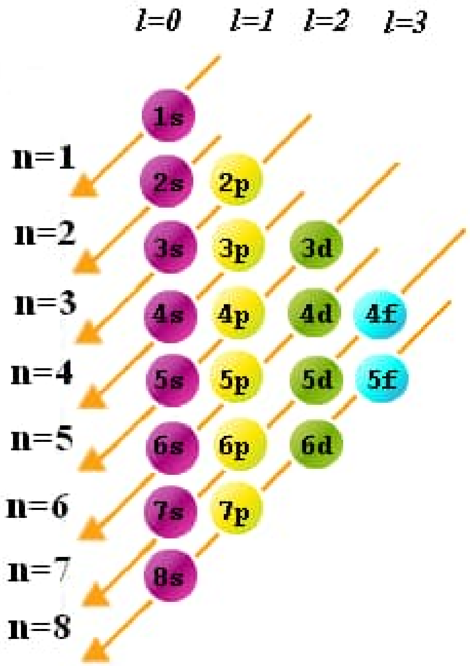
- ψ (wave function):
  does not tell the location or path of electron
  (c.f. Heisenberg uncertainty principle)

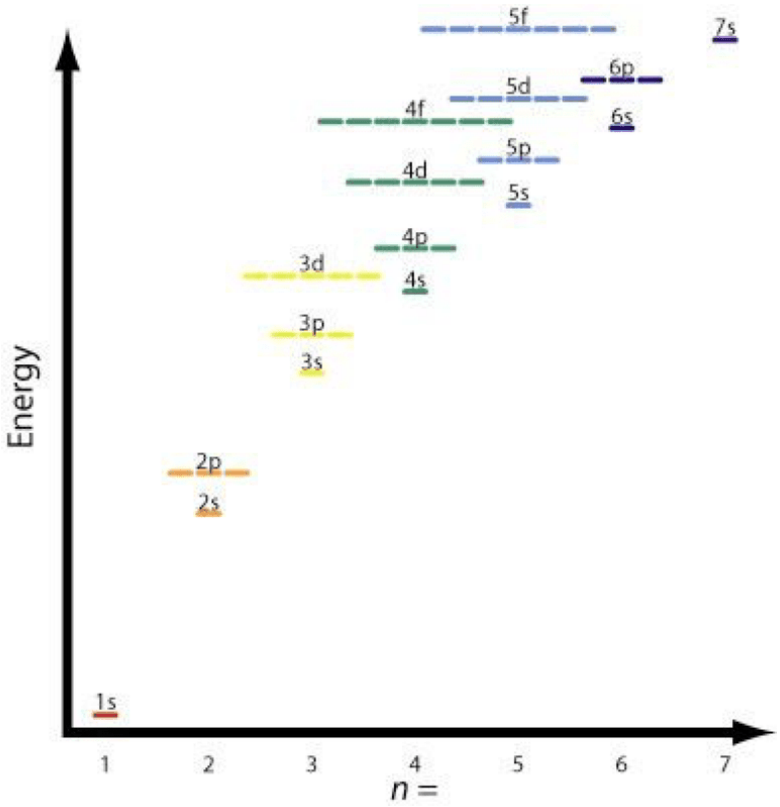
- ψ^2 (square of wave function):
  probability of electron to be located in a certain location

  → PROBABILITY DENSITY / ELECTRON DENSITY MAP
  → ”shape” of the orbital



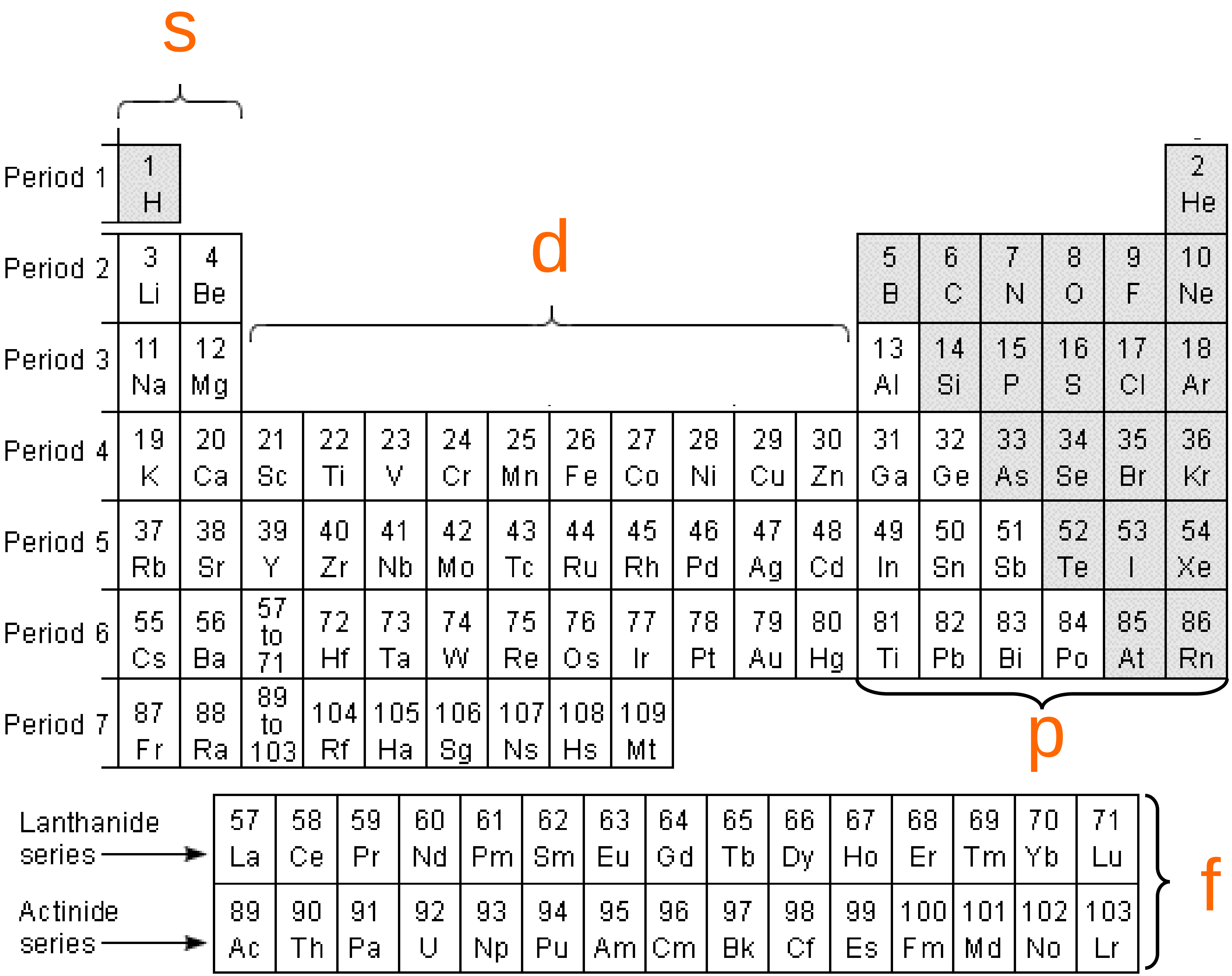






Relative Orbital Energies

- These diagrams show situation: - for empty orbitals
  - in a single isolated 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
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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

(to be discussed later in this course)

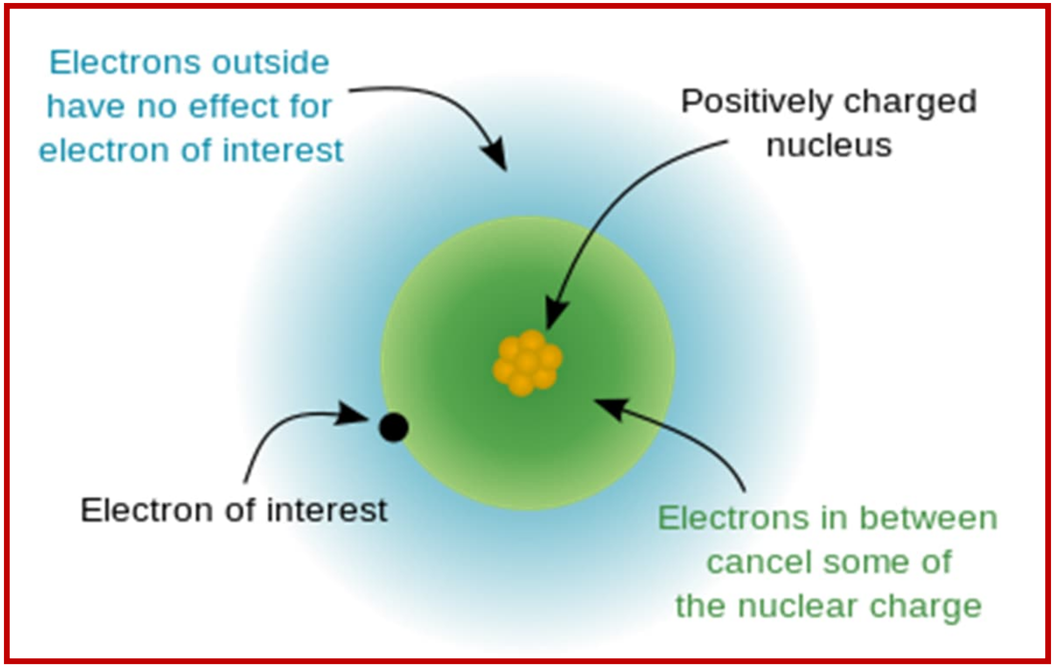
Z	Element	Electronic configuration	Oxidation states
57	Lanthanum (La)	$4f^{0}5d^{1}6s^{2}$	+III
58	Cerium (Ce)	$4f^{1}5d^{1}6s^{2}$	+III, +IV
59	Praseodymium (Pr)	$4f^{2}5d^{1}6s^{2}$	+III
60	Neodymium (Nd)	$4f^{3}5d^{1}6s^{2}$	+III
61	Promethium (Pm)	$4f^{4}5d^{1}6s^{2}$	+III
62	Samarium (Sm)	$4f^{5}5d^{1}6s^{2}$	+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

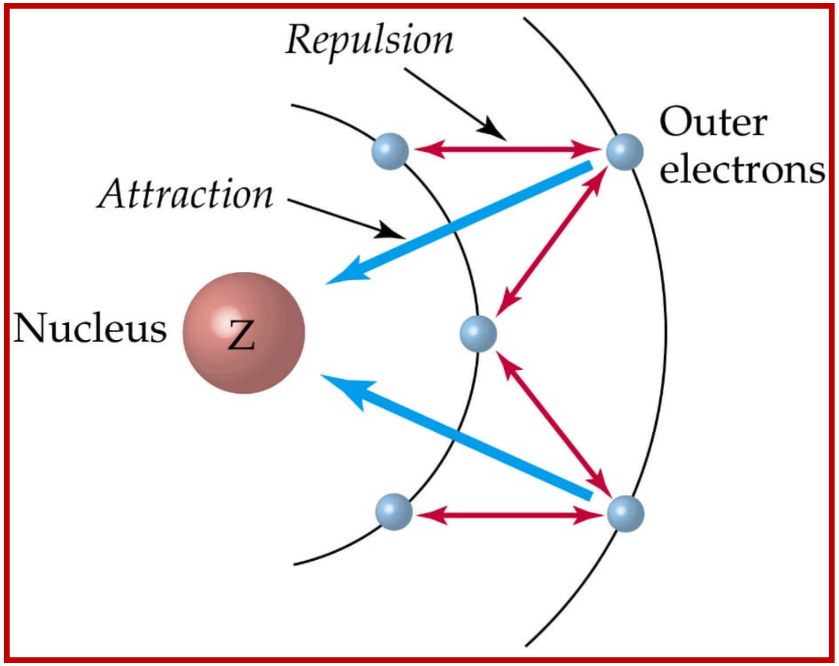
PERIODIC PROPERTIES

- 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)
- $+e < Z_{eff} < Z$

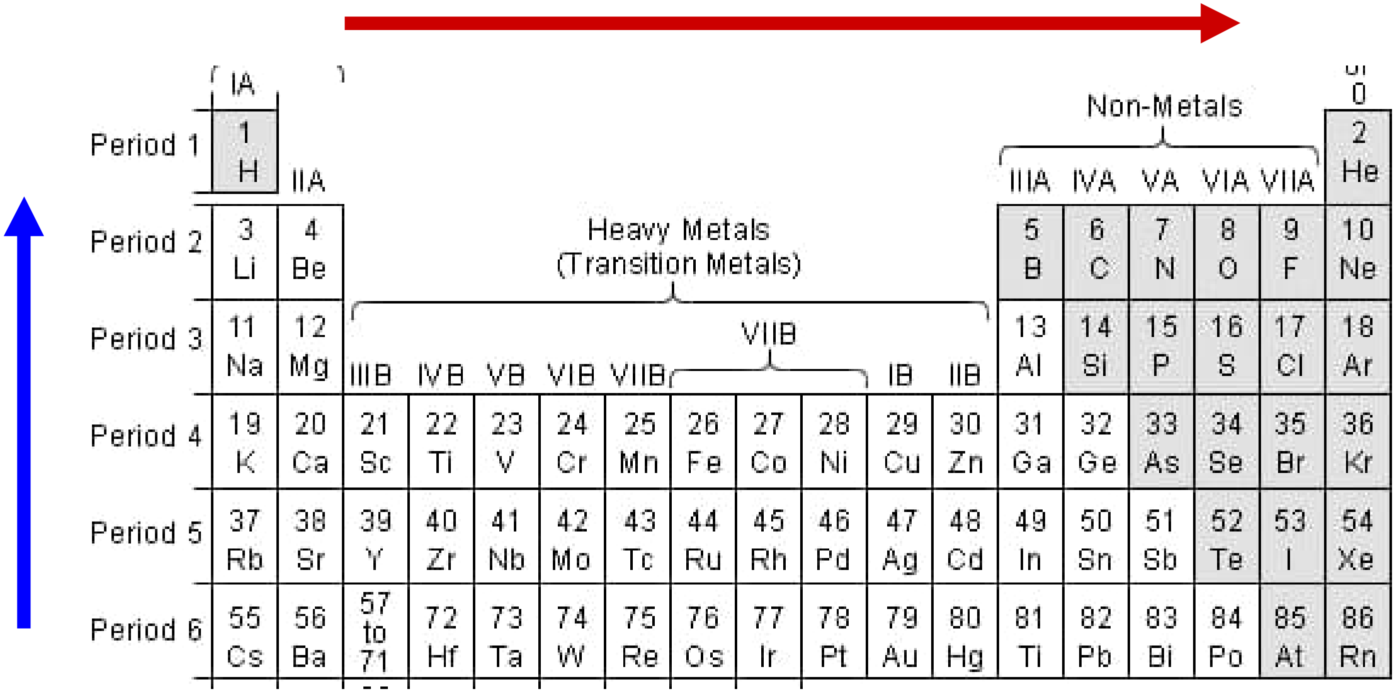




atomic radius (r_{atom})
ionization energy (IE)
electronegativity (EN)

Z_{eff} increases, r_{atom} decreases

→ IE and EN increase



			Heavy Metals (Transition Metals)										Non-Metals					
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
Period 1	1 H																	2 He
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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

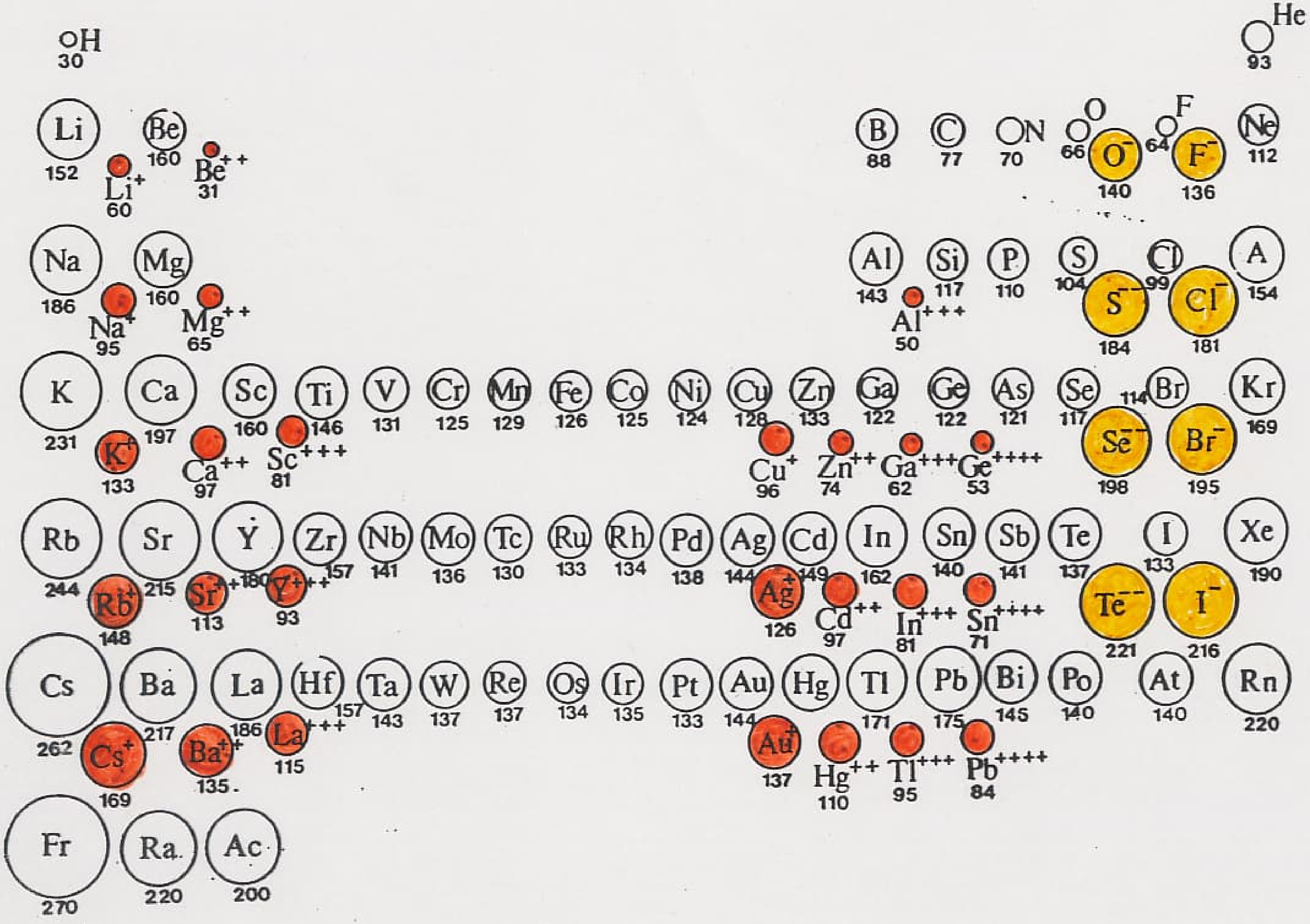
$Z_{eff} \approx$ constant:
IE and EN
increase, since
r_{atom} decreases

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

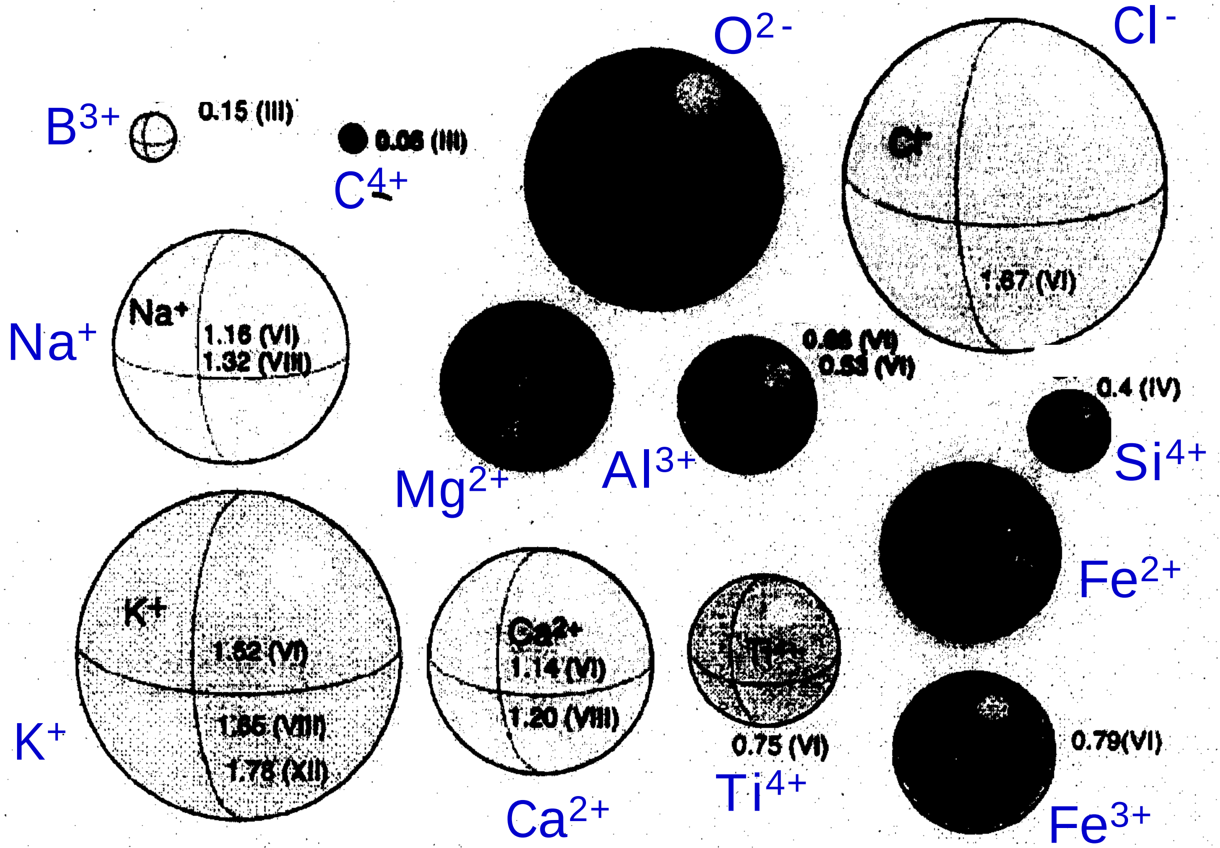
3d cations: CN = 6

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	-	-

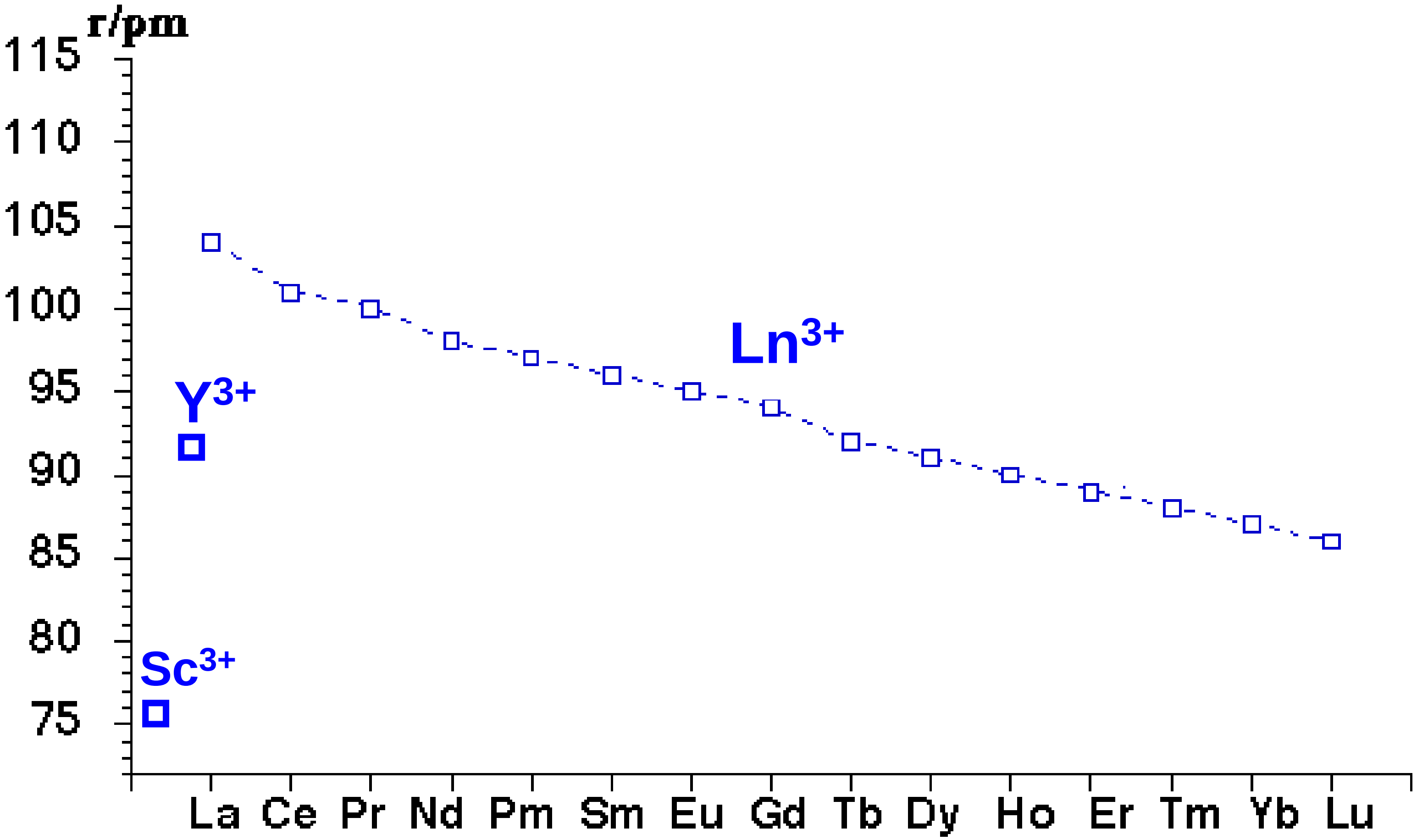
anions: CN = 6

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)



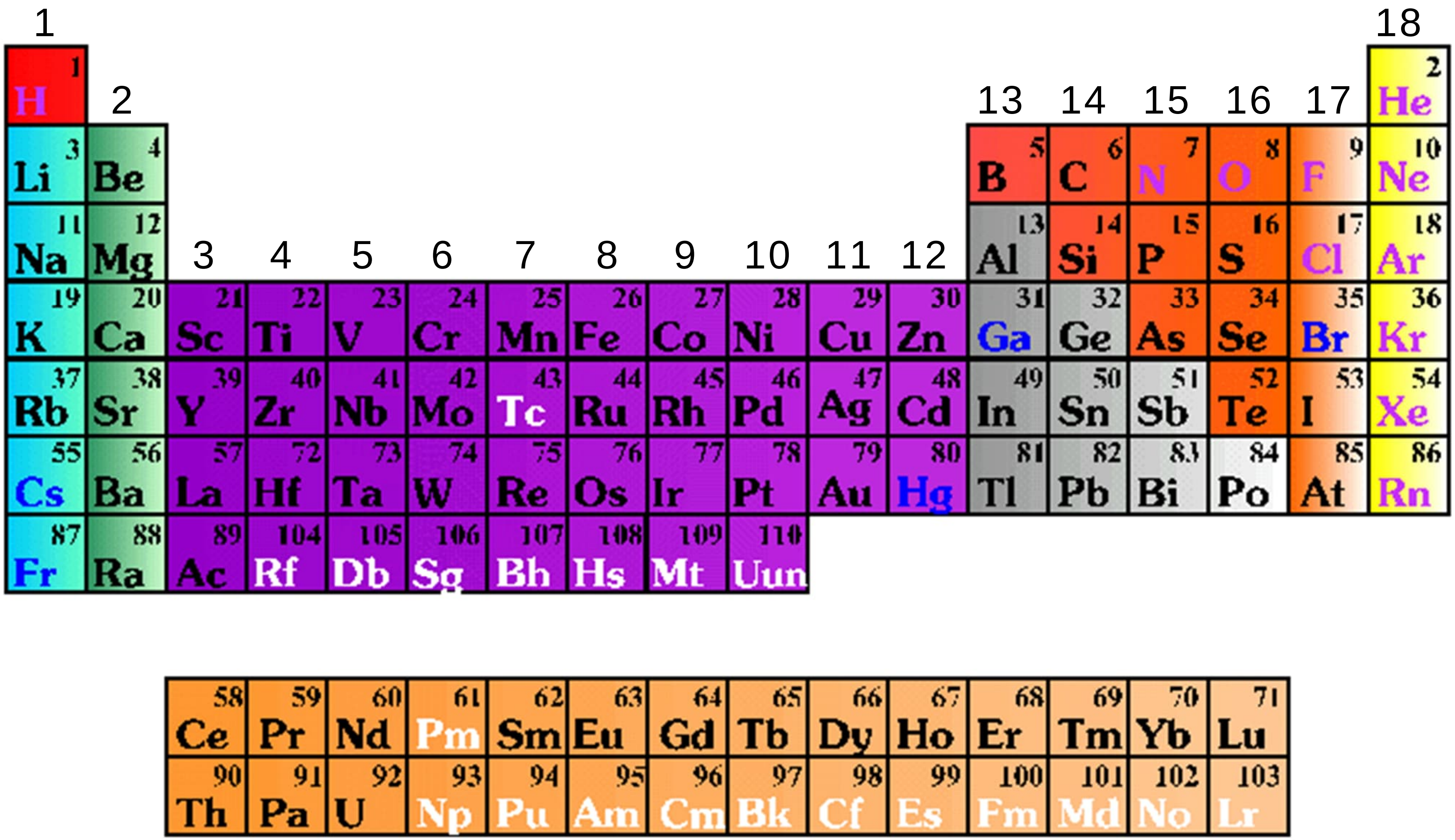
LANTHANIDE CONTRACTION



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 ?



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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

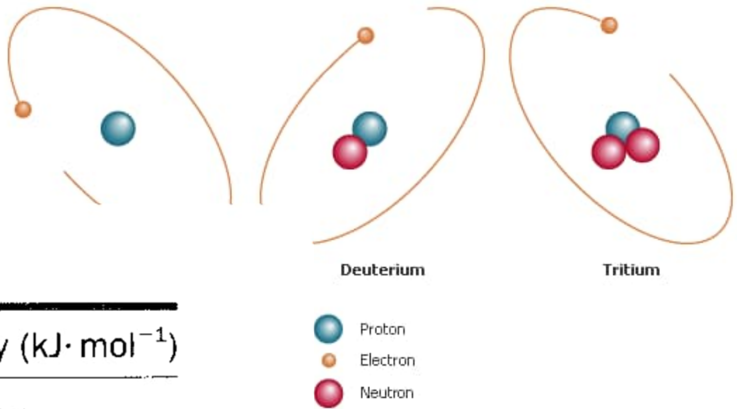
HYDROGEN in the Periodic Table:

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

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



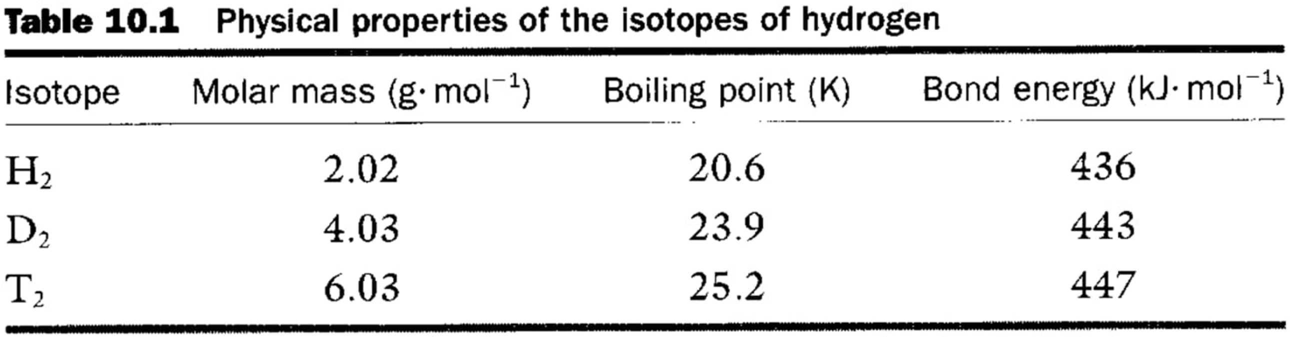


Table 10.1 Physical properties of the isotopes of hydrogen

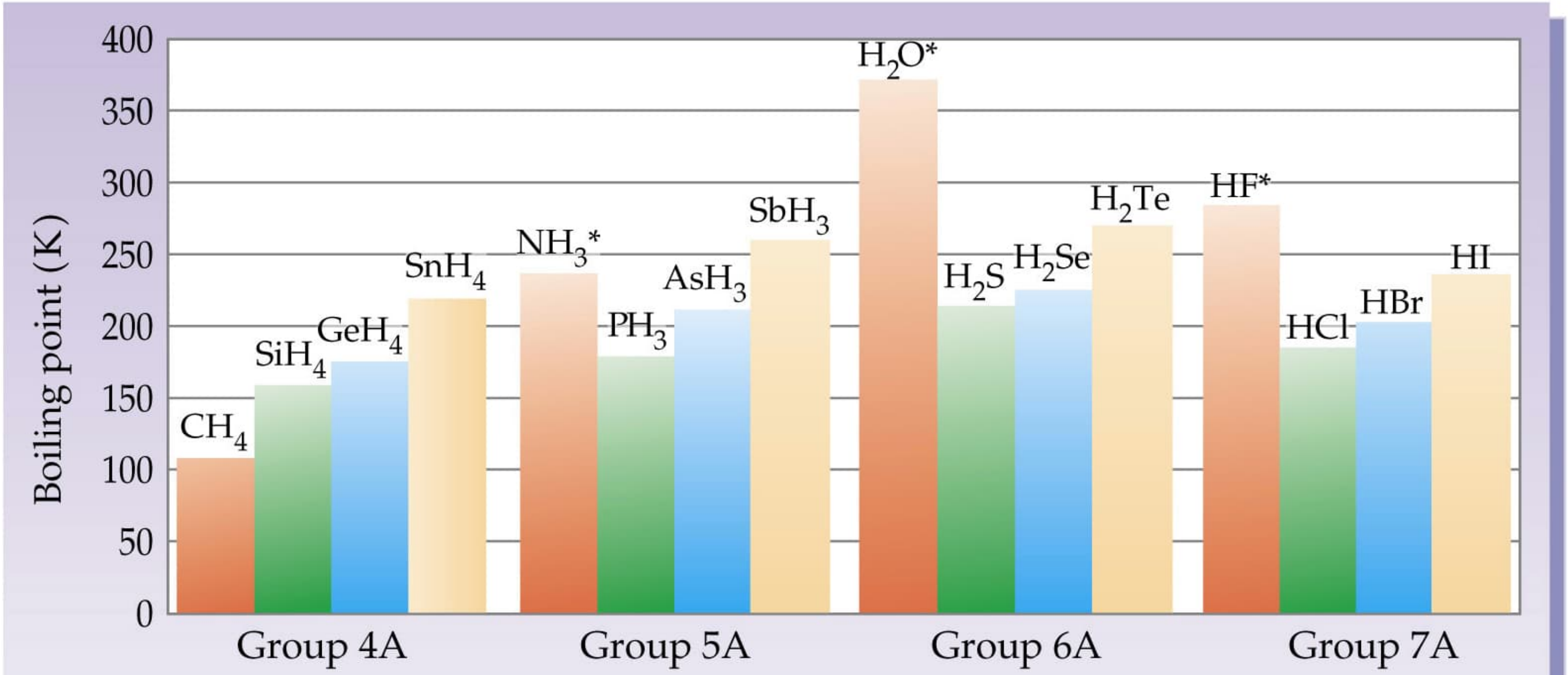
Isotope	Molar mass ($g \cdot mol^{-1}$)	Boiling point (K)	Bond energy ($kJ \cdot mol^{-1}$)
H_2	2.02	20.6	436
D_2	4.03	23.9	443
T_2	6.03	25.2	447

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)

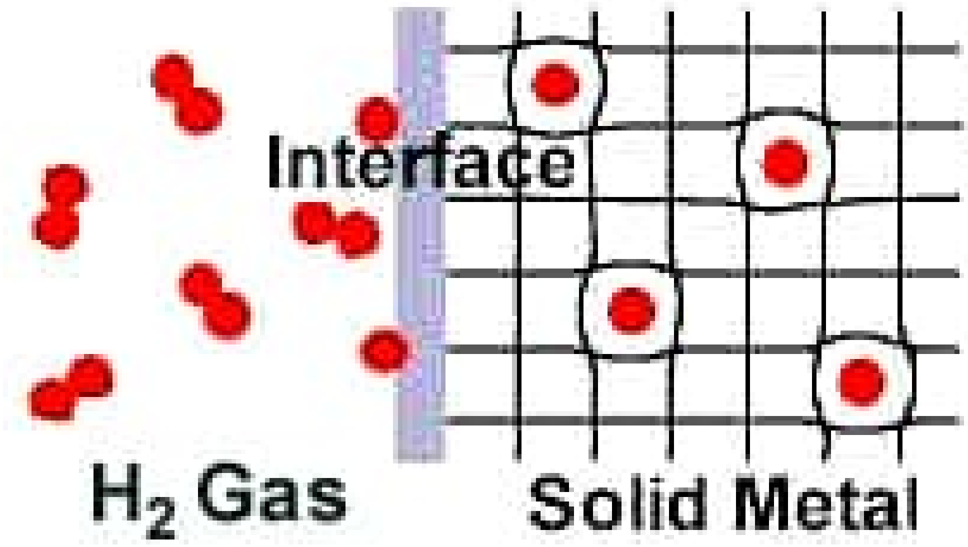
- **COVALENT HYDRIDES** **(not correct name for all these compounds)**
  - **with all nonmetals (except noble gases) and the most electronegative metals (Sn,Ga)**
  - **most of these hydrides are gaseous at room temperature**



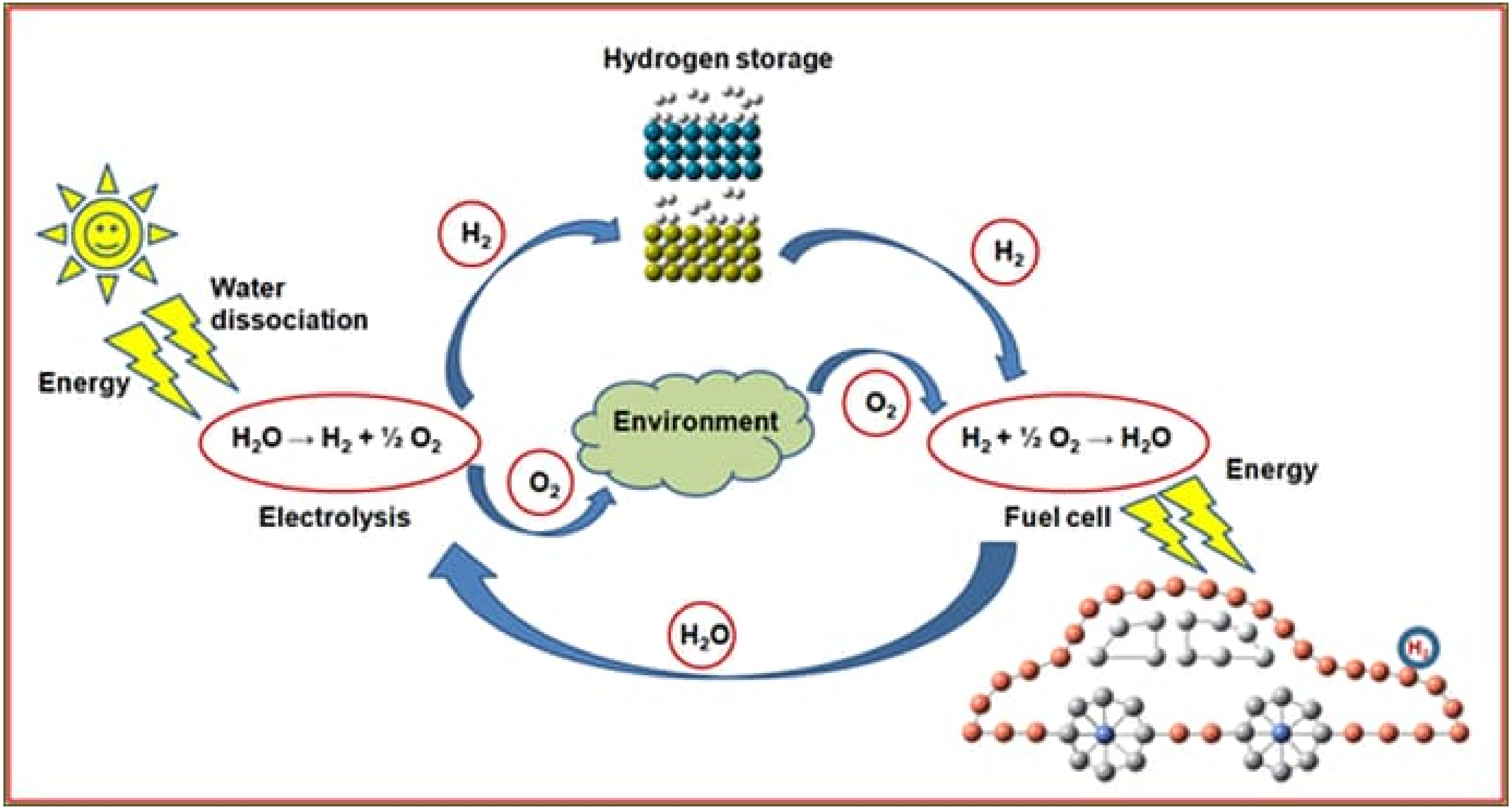
*The boiling points generally increase with increasing molecular mass down a group of the periodic table, but the hydrides of nitrogen (NH_3), oxygen (H_2O), and fluorine (HF) have abnormally high boiling points because these molecules form hydrogen bonds.

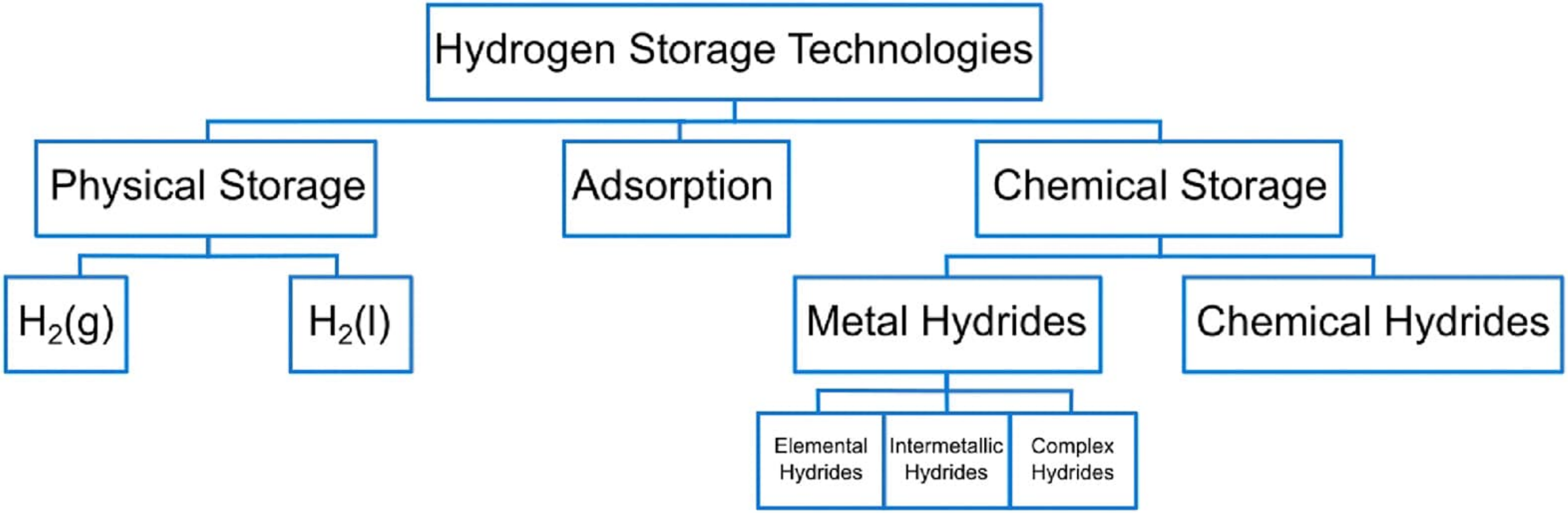
METALLIC (TRANSITION METAL) HYDRIDES

- 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. → $Ti + H_2$



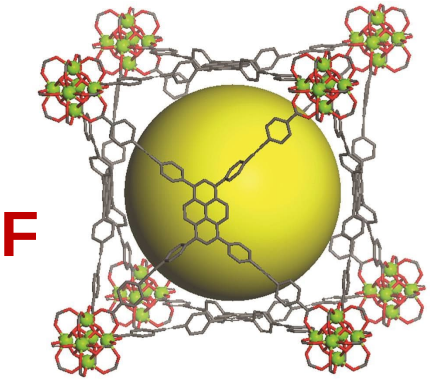
HYDROGEN STORAGE !!!



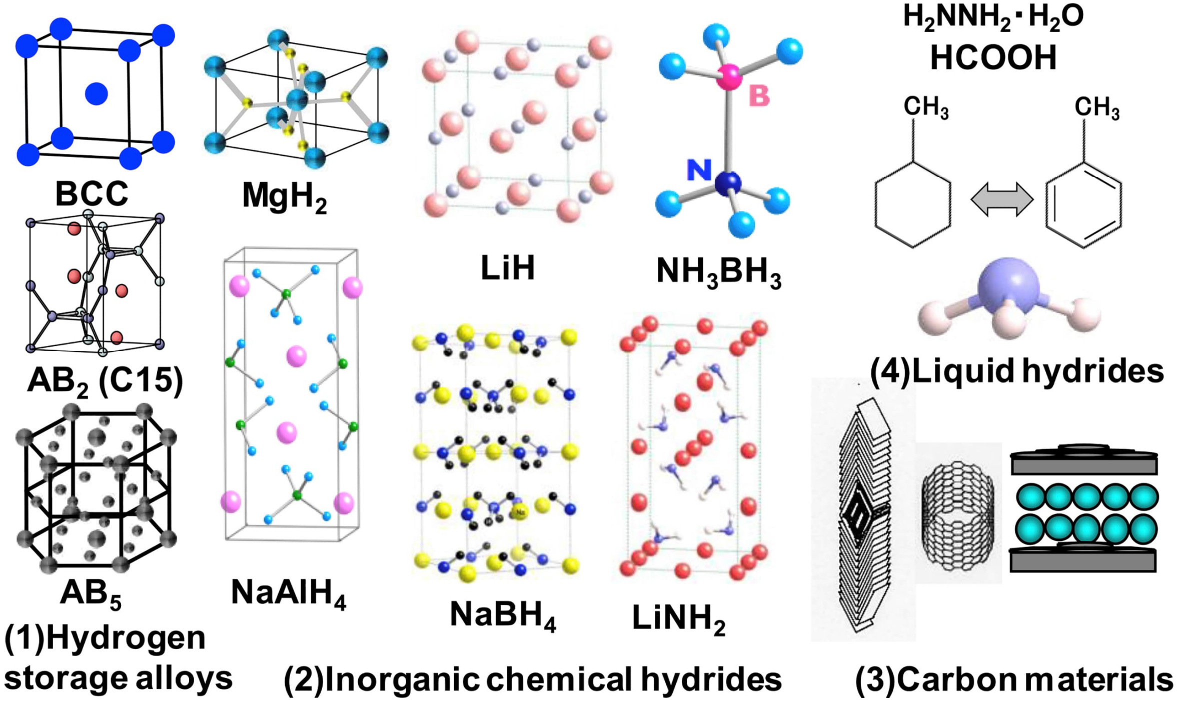


- Hydrogen Storage Technologies
  - Physical Storage
    - H_2(g)
    - H_2(l)
  - Adsorption
  - Chemical Storage
    - Metal Hydrides
      - Elemental Hydrides
      - Intermetallic Hydrides
      - Complex Hydrides
    - Chemical Hydrides

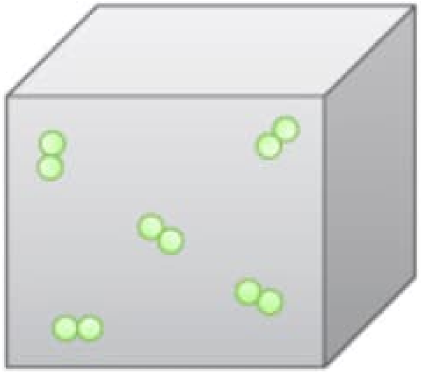
MOF



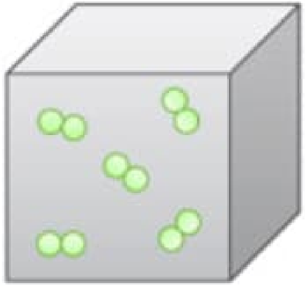
Metal Organic Framework



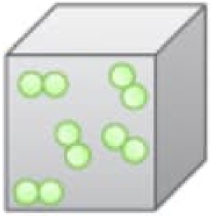
Physical Storage



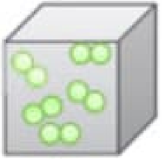
1 bar
normal
0.3 g/L



150 bar
lab cylinders
10 g/L



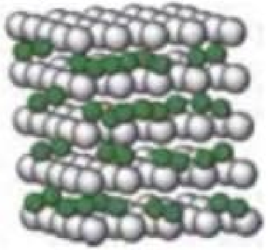
350 bar
Gen 1 vehicles
28 g/L



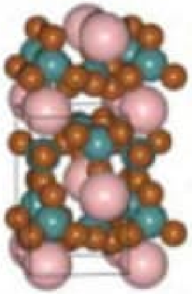
700 bar
Gen 2 vehicles
40g/L

liquid H_2
71 g H_2/L
@ 20 K

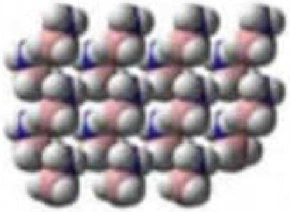
Materials -based Storage



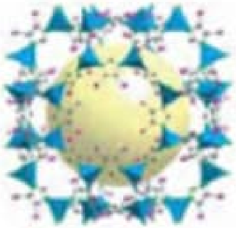
interstial hydrides
~100-150 g H_2/L



complex hydrides
~70-150 g H_2/L

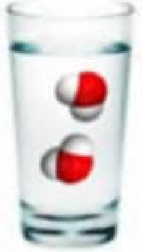


chemical storage
~70-150 g H_2/L

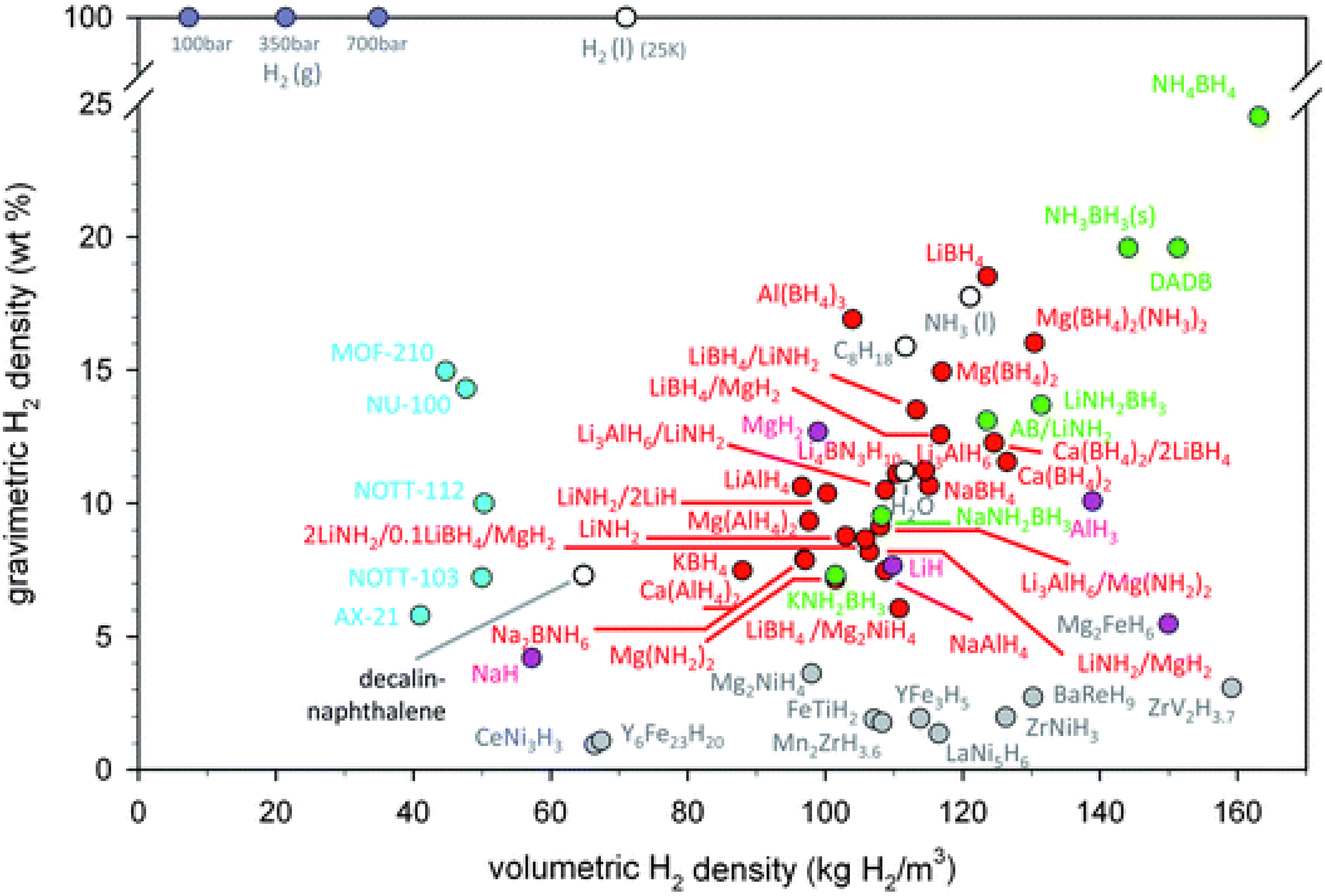


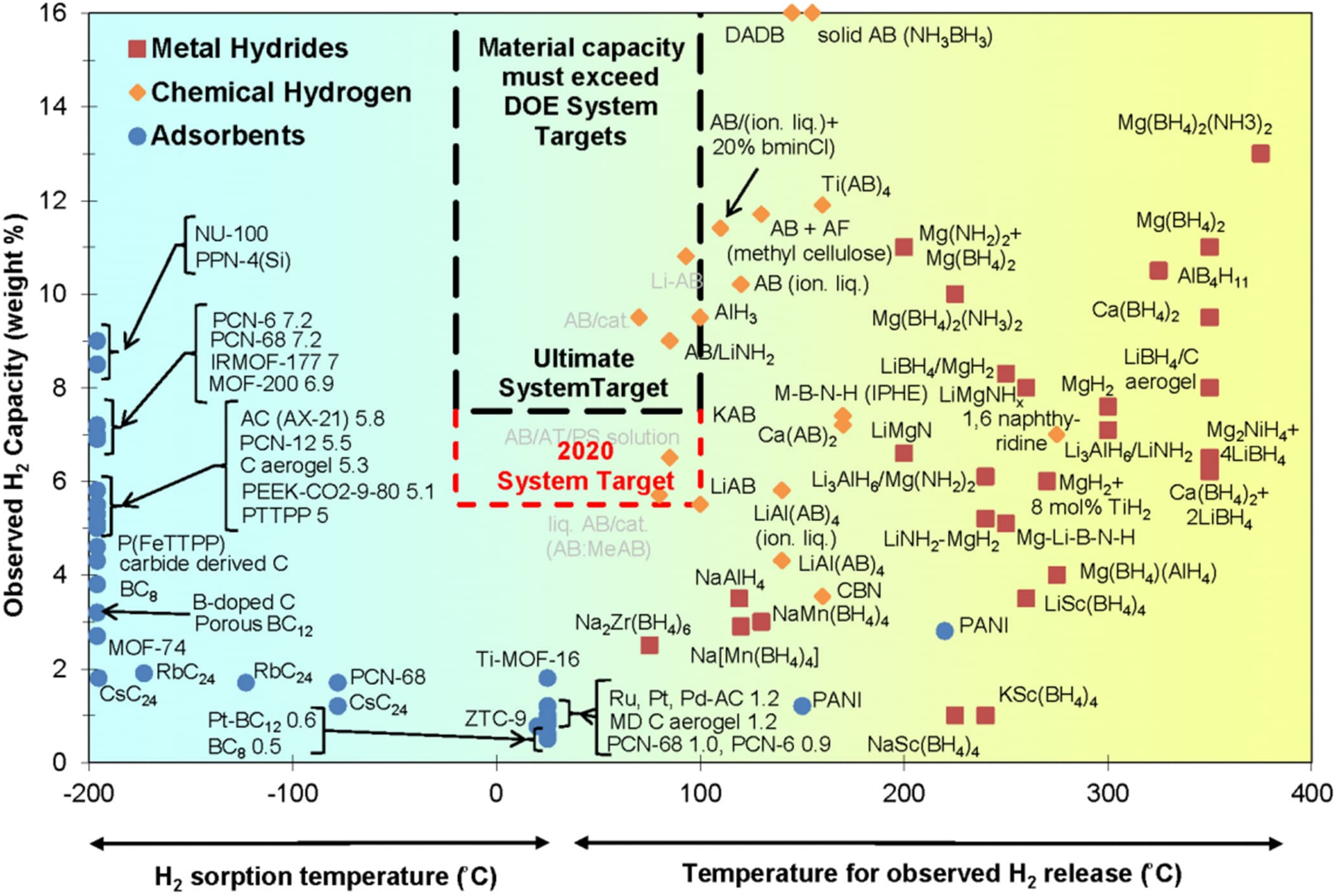
sorbents
≤ 70 g H_2/L

Reference



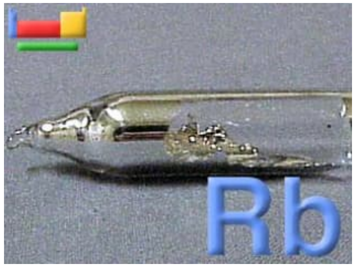
water
111 g H_2/L


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)
$Mg(BH_4)_2(NH_3)_2$
MOF-210
NU-100
C_8H_{18}
$LiBH_4/LiNH_2$
$Mg(BH_4)_2$
$LiBH_4/MgH_2$
$LiNH_2BH_3$
MgH_2
AB/$LiNH_2$
$Li_3AlH_6/LiNH_2$
$Li_4BN_3H_{10}$
Li_3AlH_6
$Ca(BH_4)_2/2LiBH_4$
$Ca(BH_4)_2$
NOTT-112
$LiAlH_4$
$NaBH_4$
$LiNH_2/2LiH$
H_2O
$Mg(AlH_4)_2$
$NaNH_2BH_3$
AlH_3
$2LiNH_2/0.1LiBH_4/MgH_2$
$LiNH_2$
$Li_3AlH_6/Mg(NH_2)_2$
KBH_4
LiH
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
$BaReH_9$
$ZrV_2H_{3.7}$
$FeTiH_2$
$ZrNiH_3$
$CeNi_3H_3$
$Y_6Fe_{23}H_{20}$
$Mn_2ZrH_{3.6}$
$LaNi_5H_6$
gravimetric H_2 density (wt %)
volumetric H_2 density (kg H_2/m^3)
0
5
10
15
20
25
100
0
20
40
60
80
100
120
140
160


■ Metal Hydrides
◆ Chemical Hydrogen
● Adsorbents
Material capacity must exceed DOE System Targets
Ultimate SystemTarget
2020 System Target
DADB
solid AB (NH_3BH_3)
AB/(ion. liq.)+ 20% bminCl)
$Mg(BH_4)_2(NH3)_2$
$Ti(AB)_4$
AB + AF (methyl cellulose)
$Mg(NH_2)_2$+ $Mg(BH_4)_2$
$Mg(BH_4)_2$
AlB_4H_{11}
Li-AB
AB (ion. liq.)
$Mg(BH_4)_2(NH_3)_2$
$Ca(BH_4)_2$
AB/cat.
AlH_3
$AB/LiNH_2$
$LiBH_4/MgH_2$
$LiBH_4$/C aerogel
M-B-N-H (IPHE)
$LiMgNH_x$
MgH_2
KAB
1,6 naphthy-ridine
AB/AT/PS solution
$Ca(AB)_2$
LiMgN
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
$LiAl(AB)_4$
$NaAlH_4$
$Mg(BH_4)(AlH_4)$
CBN
$LiSc(BH_4)_4$
$Na_2Zr(BH_4)_6$
$NaMn(BH_4)_4$
PANI
$Na[Mn(BH_4)_4]$
$KSc(BH_4)_4$
PANI
$NaSc(BH_4)_4$
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
CsC_{24}
RbC_{24}
RbC_{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
Observed H_2 Capacity (weight %)
0
2
4
6
8
10
12
14
16
-200
-100
0
100
200
300
400
H_2 sorption temperature (°C)
Temperature for observed H_2 release (°C)

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 (°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

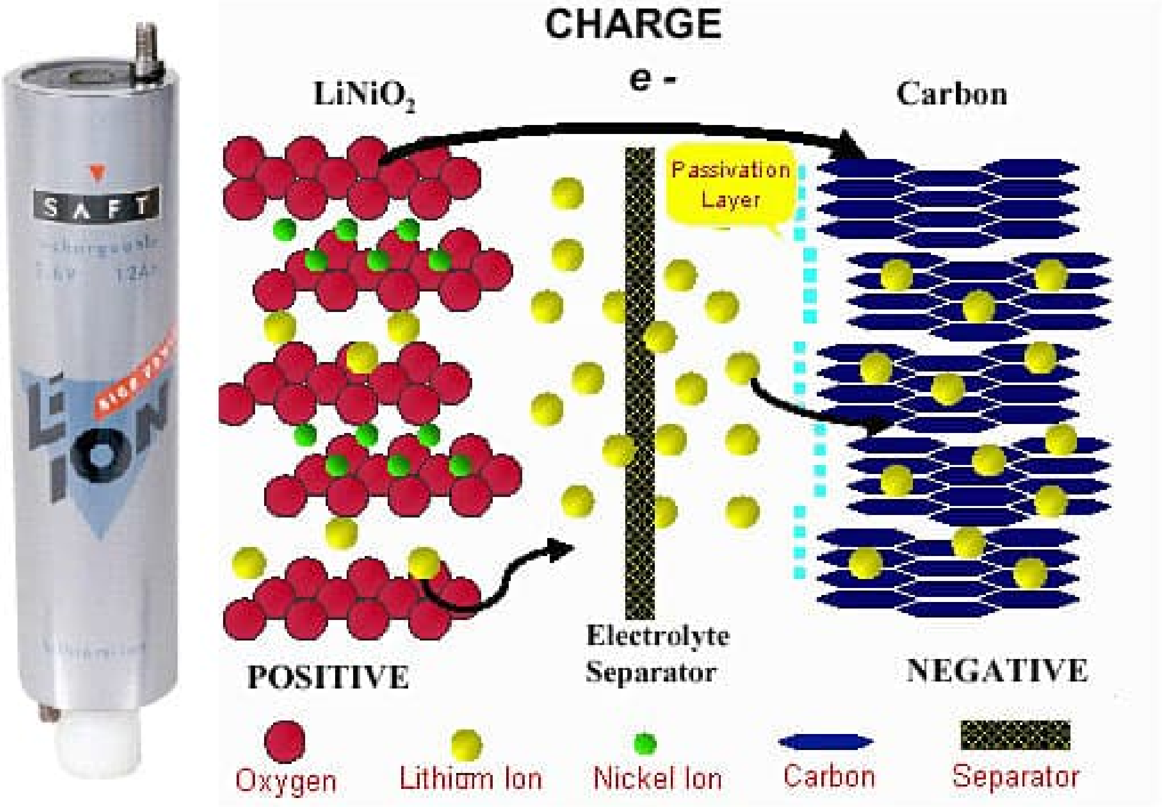
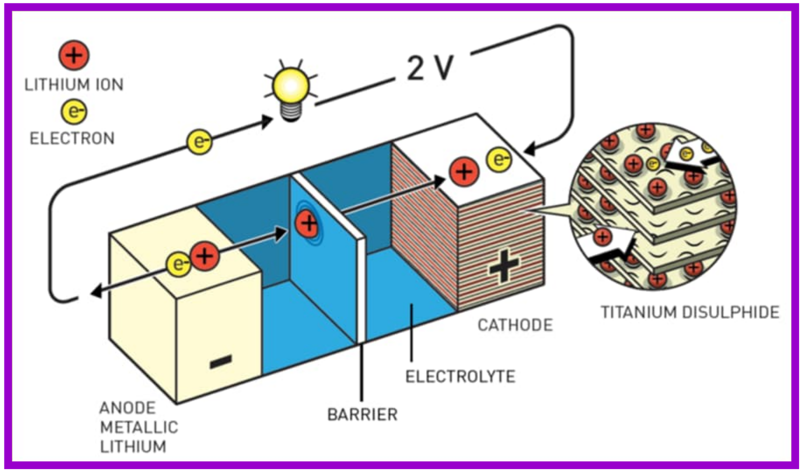
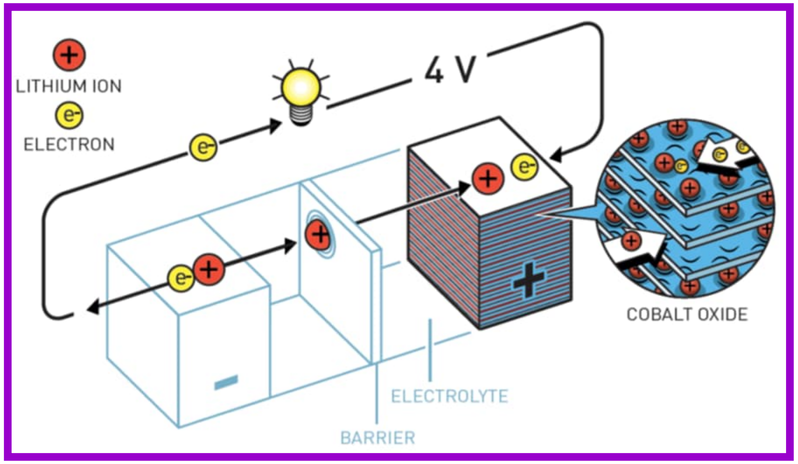
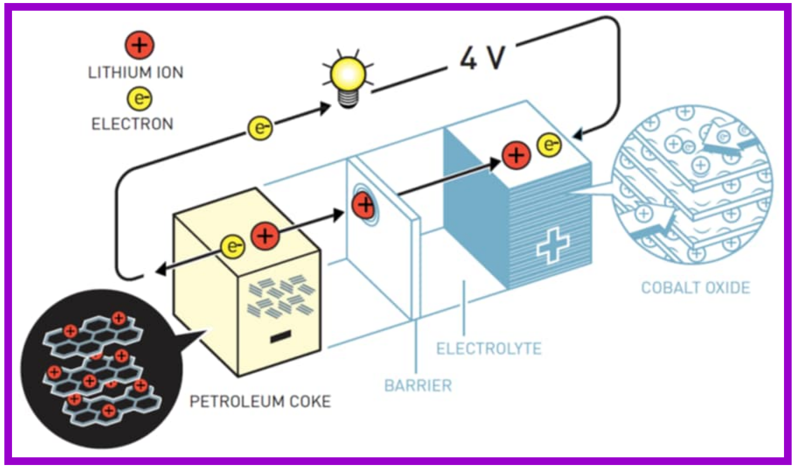
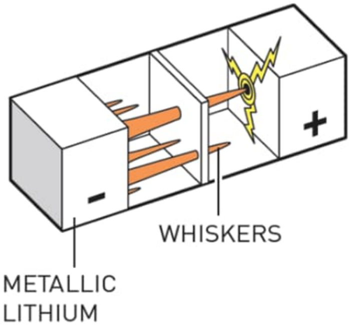


Photo Courtesy of SAFT America









Chemistry Nobel 2019

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

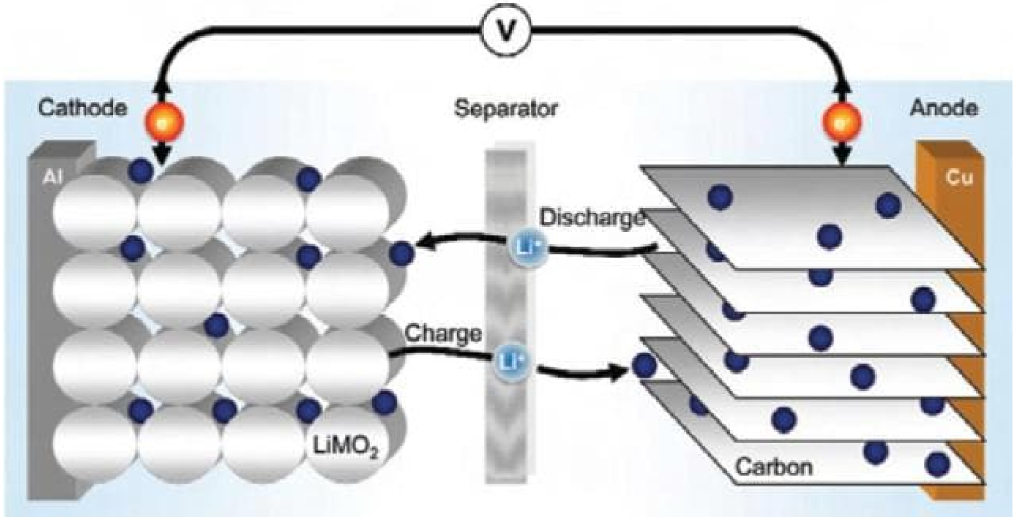
John Goodenough (born 1922 USA):
- Univ. Oxford: $LiCoO_2$ cathode 1980

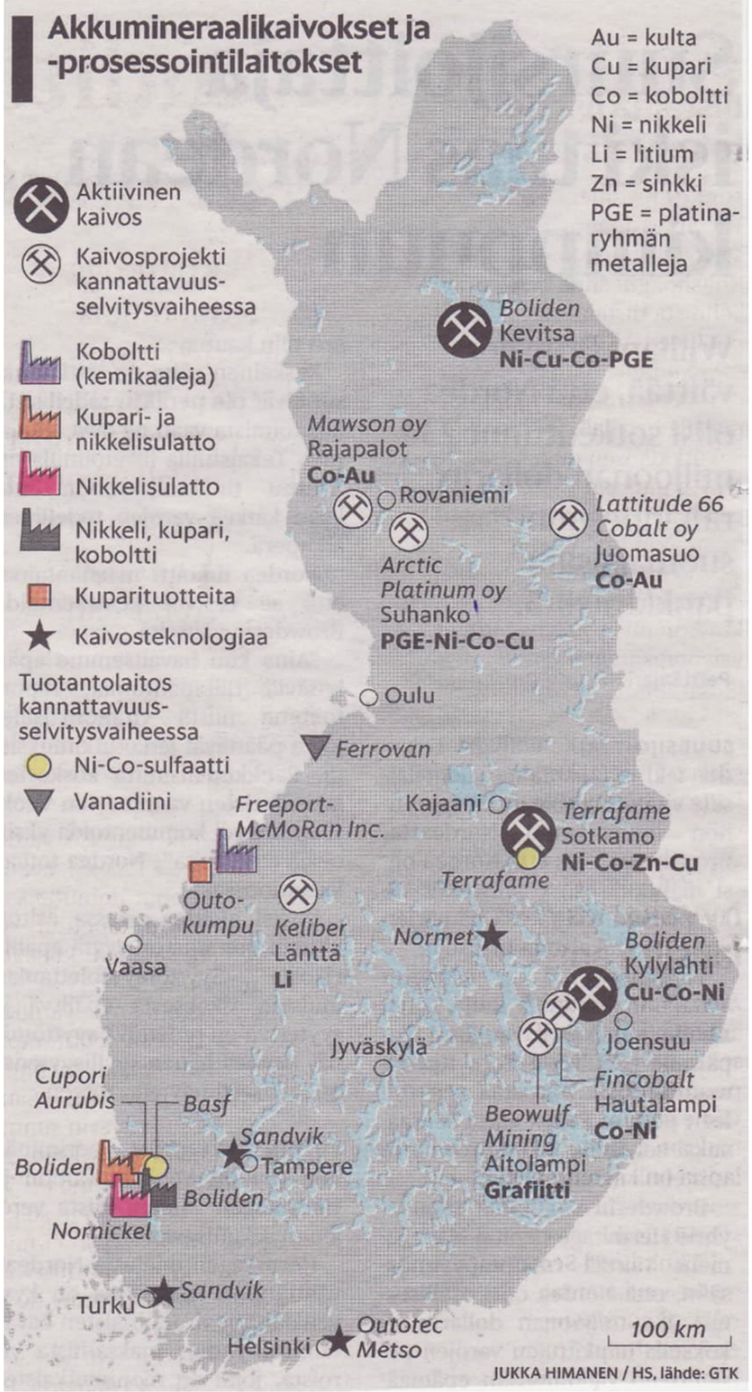
Akira Yoshino (born 1948 Jpn):
- Asahi Kasei: carbon-based anode 1985

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