Inorganic Chemistry III

C4010

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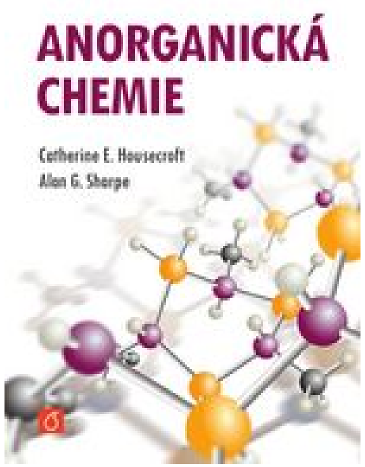
Syllabus

Část I. Prof. Příhoda

1. **Koordinační chemie**
2. **Chelatující ligandy**
3. **Ionty v roztoku**
4. **Makroseparační metody kovů**
5. **Transurany**

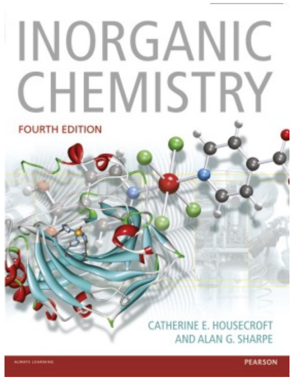
Část II. Prof. Pinkas

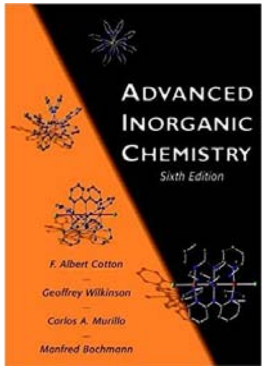
6. Periodic Table
7. + 8. Chemical Bonding
9. Acid-base Chemistry
10. + 11. Rings and Polyhedra
12. + 13. Magnetochemistry, Moessbauer spectroscopy

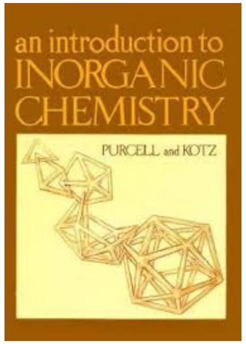


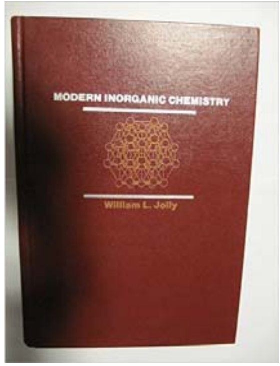
Textbooks

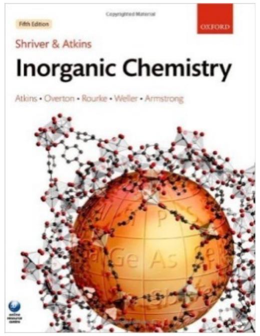
Reading assignments = FIND ERRORS

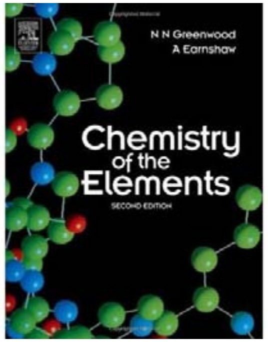


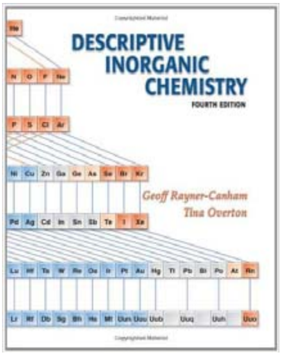


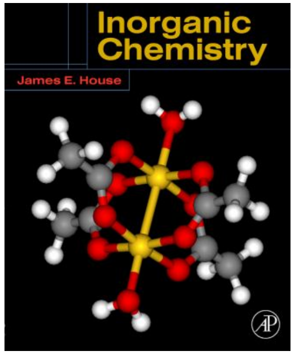


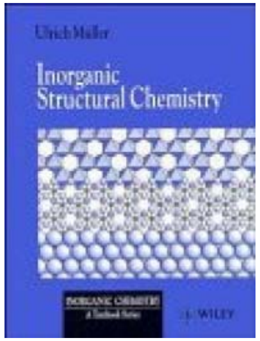


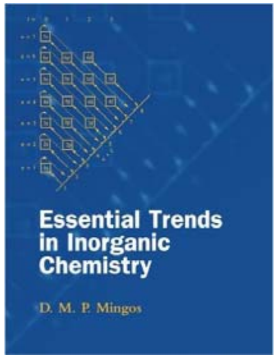


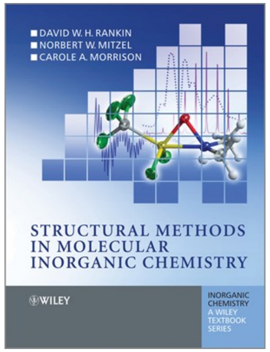


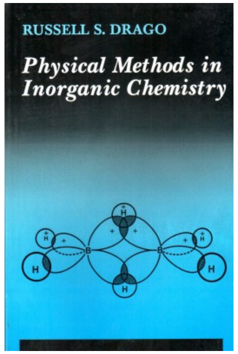






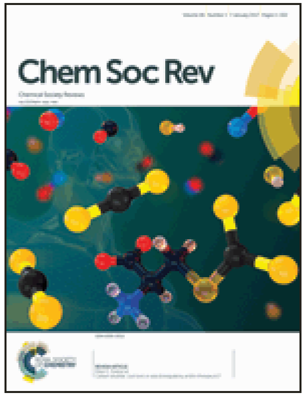


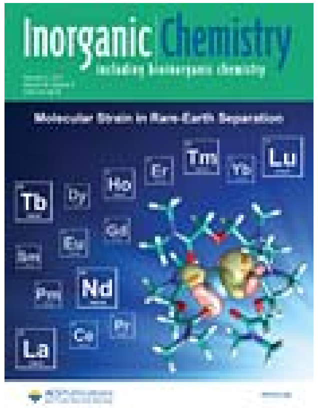


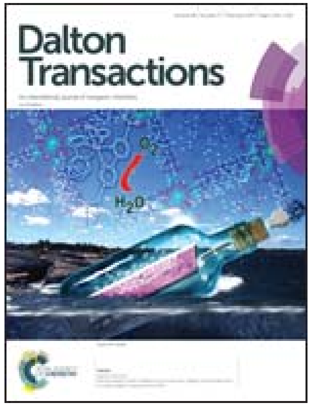


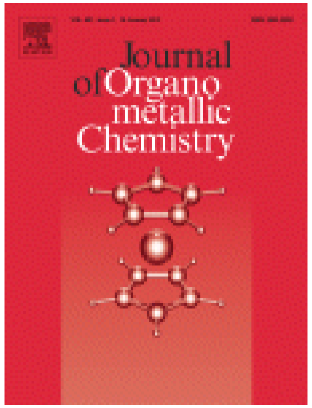
Journals

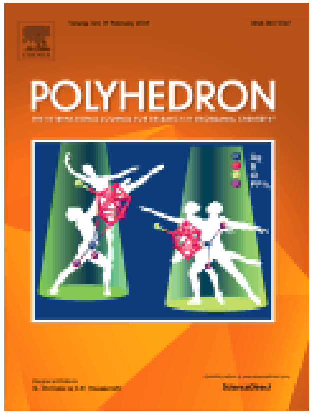
Reading assignments

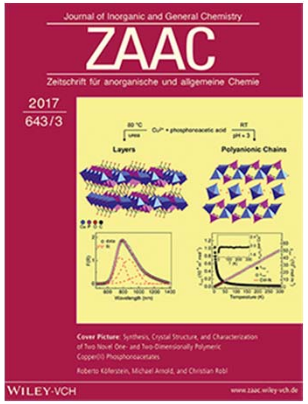


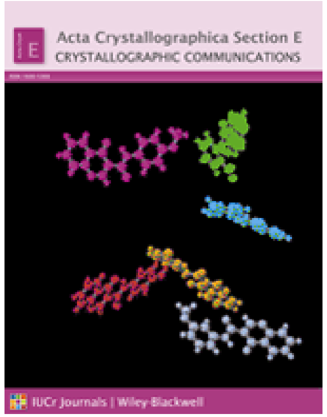












IUPAC Periodic Table of the Elements

Key:

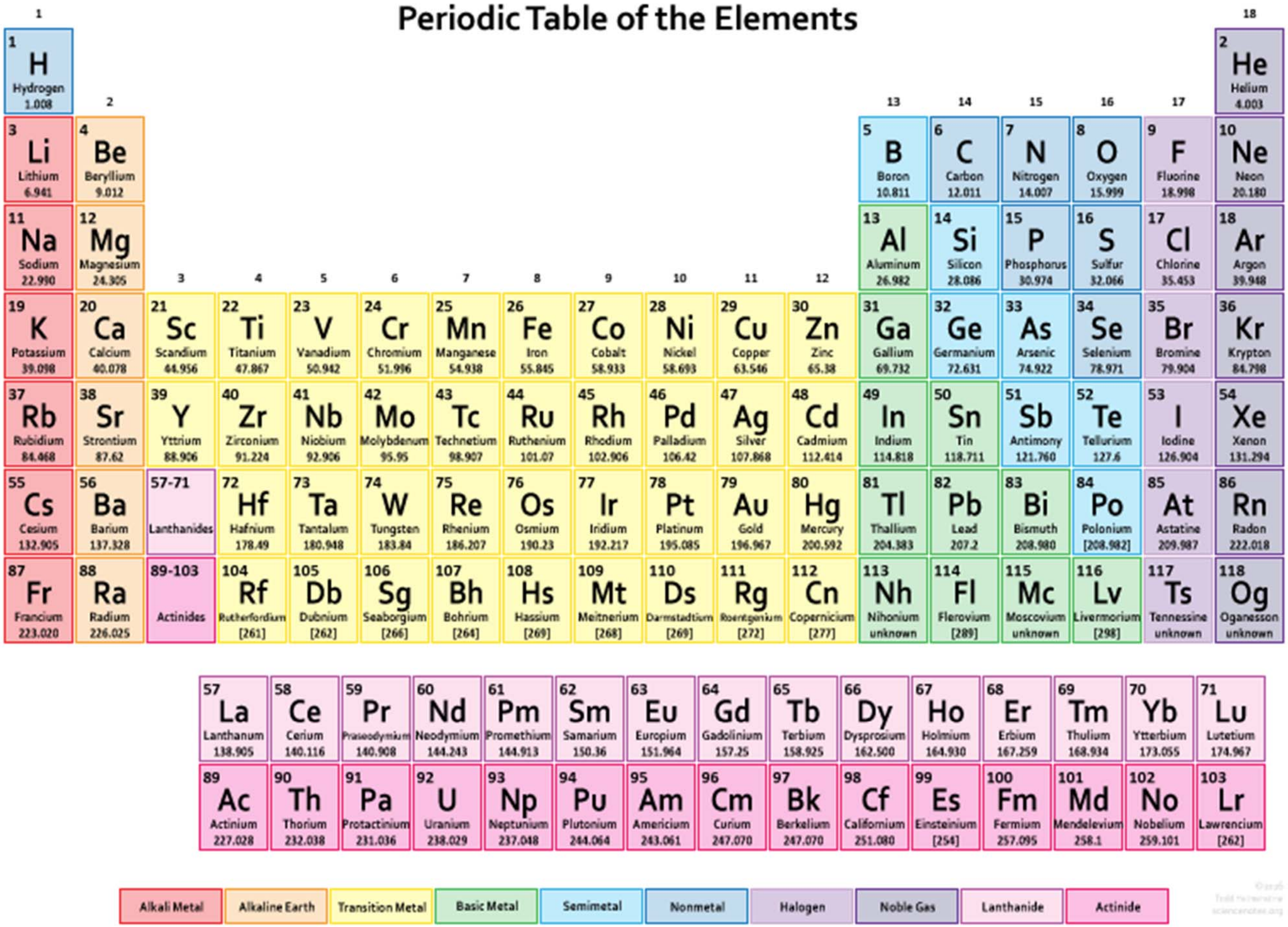
atomic number
Symbol
name
conventional atomic weight
standard atomic weight

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** hydrogen 1.008 [1.0078, 1.0082]																	2 **He** helium 4.0026
3 **Li** lithium 6.94 [6.938, 6.997]	4 **Be** beryllium 9.0122											5 **B** boron 10.81 [10.806, 10.821]	6 **C** carbon 12.011 [12.009, 12.012]	7 **N** nitrogen 14.007 [14.006, 14.008]	8 **O** oxygen 15.999 [15.999, 16.000]	9 **F** fluorine 18.998	10 **Ne** neon 20.180
11 **Na** sodium 22.990	12 **Mg** magnesium 24.305 [24.304, 24.307]											13 **Al** aluminium 26.982	14 **Si** silicon 28.085 [28.084, 28.086]	15 **P** phosphorus 30.974	16 **S** sulfur 32.06 [32.059, 32.076]	17 **Cl** chlorine 35.45 [35.446, 35.457]	18 **Ar** argon 39.948
19 **K** potassium 39.098	20 **Ca** calcium 40.078(4)	21 **Sc** scandium 44.956	22 **Ti** titanium 47.867	23 **V** vanadium 50.942	24 **Cr** chromium 51.996	25 **Mn** manganese 54.938	26 **Fe** iron 55.845(2)	27 **Co** cobalt 58.933	28 **Ni** nickel 58.693	29 **Cu** copper 63.546(3)	30 **Zn** zinc 65.38(2)	31 **Ga** gallium 69.723	32 **Ge** germanium 72.630(8)	33 **As** arsenic 74.922	34 **Se** selenium 78.971(8)	35 **Br** bromine 79.904 [79.901, 79.907]	36 **Kr** krypton 83.798(2)
37 **Rb** rubidium 85.468	38 **Sr** strontium 87.62	39 **Y** yttrium 88.906	40 **Zr** zirconium 91.224(2)	41 **Nb** niobium 92.906	42 **Mo** molybdenum 95.95	43 **Tc** technetium	44 **Ru** ruthenium 101.07(2)	45 **Rh** rhodium 102.91	46 **Pd** palladium 106.42	47 **Ag** silver 107.87	48 **Cd** cadmium 112.41	49 **In** indium 114.82	50 **Sn** tin 118.71	51 **Sb** antimony 121.76	52 **Te** tellurium 127.60(3)	53 **I** iodine 126.90	54 **Xe** xenon 131.29
55 **Cs** caesium 132.91	56 **Ba** barium 137.33	57-71 lanthanoids	72 **Hf** hafnium 178.49(2)	73 **Ta** tantalum 180.95	74 **W** tungsten 183.84	75 **Re** rhenium 186.21	76 **Os** osmium 190.23(3)	77 **Ir** iridium 192.22	78 **Pt** platinum 195.08	79 **Au** gold 196.97	80 **Hg** mercury 200.59	81 **Tl** thallium 204.38 [204.38, 204.39]	82 **Pb** lead 207.2	83 **Bi** bismuth 208.98	84 **Po** polonium	85 **At** astatine	86 **Rn** radon
87 **Fr** francium	88 **Ra** radium	89-103 actinoids	104 **Rf** rutherfordium	105 **Db** dubnium	106 **Sg** seaborgium	107 **Bh** bohrium	108 **Hs** hassium	109 **Mt** meitnerium	110 **Ds** darmstadtium	111 **Rg** roentgenium	112 **Cn** copernicium	113 **Nh** nihonium	114 **Fl** flerovium	115 **Mc** moscovium	116 **Lv** livermorium	117 **Ts** tennessine	118 **Og** oganesson

57 **La** lanthanum 138.91	58 **Ce** cerium 140.12	59 **Pr** praseodymium 140.91	60 **Nd** neodymium 144.24	61 **Pm** promethium	62 **Sm** samarium 150.36(2)	63 **Eu** europium 151.96	64 **Gd** gadolinium 157.25(3)	65 **Tb** terbium 158.93	66 **Dy** dysprosium 162.50	67 **Ho** holmium 164.93	68 **Er** erbium 167.26	69 **Tm** thulium 168.93	70 **Yb** ytterbium 173.05	71 **Lu** lutetium 174.97
89 **Ac** actinium	90 **Th** thorium 232.04	91 **Pa** protactinium 231.04	92 **U** uranium 238.03	93 **Np** neptunium	94 **Pu** plutonium	95 **Am** americium	96 **Cm** curium	97 **Bk** berkelium	98 **Cf** californium	99 **Es** einsteinium	100 **Fm** fermium	101 **Md** mendelevium	102 **No** nobelium	103 **Lr** lawrencium

INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY

For notes and updates to this table, see www.iupac.org. This version is dated 28 November 2016.



Periodic Table of the Elements

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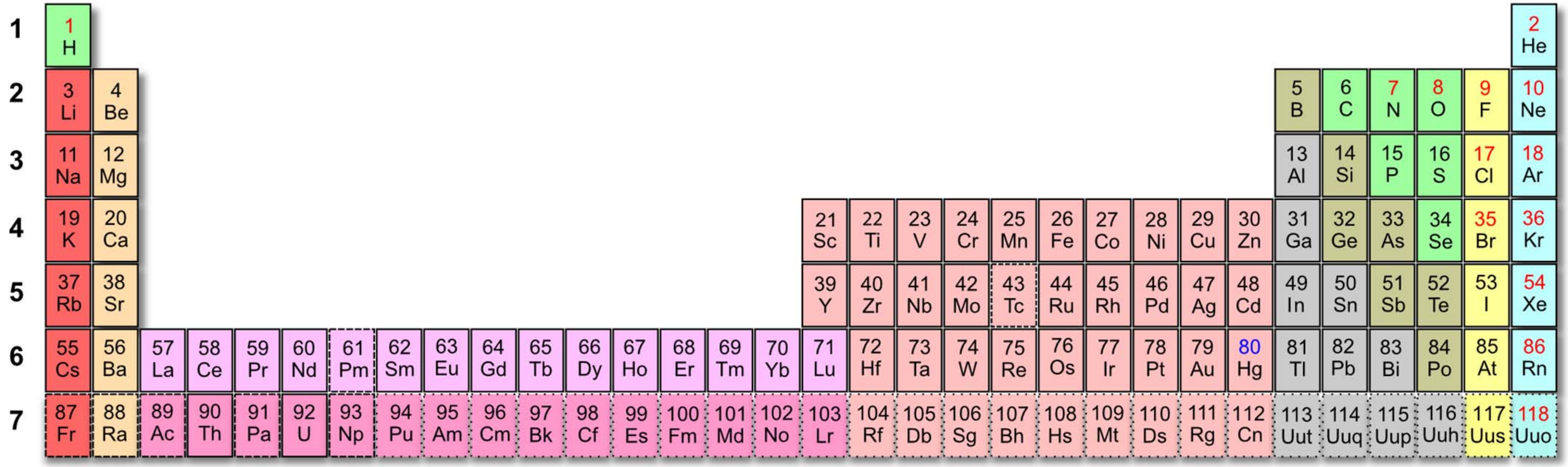
1 H Hydrogen 1.008																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.732	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 84.798
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71 Lanthanides	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103 Actinides	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Nh Nihonium unknown	114 Fl Flerovium [289]	115 Mc Moscovium unknown	116 Lv Livermorium [298]	117 Ts Tennessine unknown	118 Og Oganesson unknown

57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Alkali Metal	Alkaline Earth	Transition Metal	Basic Metal	Semimetal	Nonmetal	Halogen	Noble Gas	Lanthanide	Actinide

Periodic Table of the Elements



1	1 H																															2 He
2	3 Li	4 Be																									5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg																									13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
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
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
6	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
7	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 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

Alkali metals	Alkaline earth metals	Lanthanides	Actinides	Transition metals
Poor metals	Metalloids	Nonmetals	Halogens	Noble gases

State at standard tempurature and pressure

Atomic number in red: gas

Atomic number in blue: liquid

Atomic number in black: solid

solid border: at least one isotope is older than the Earth (Primordial elements)

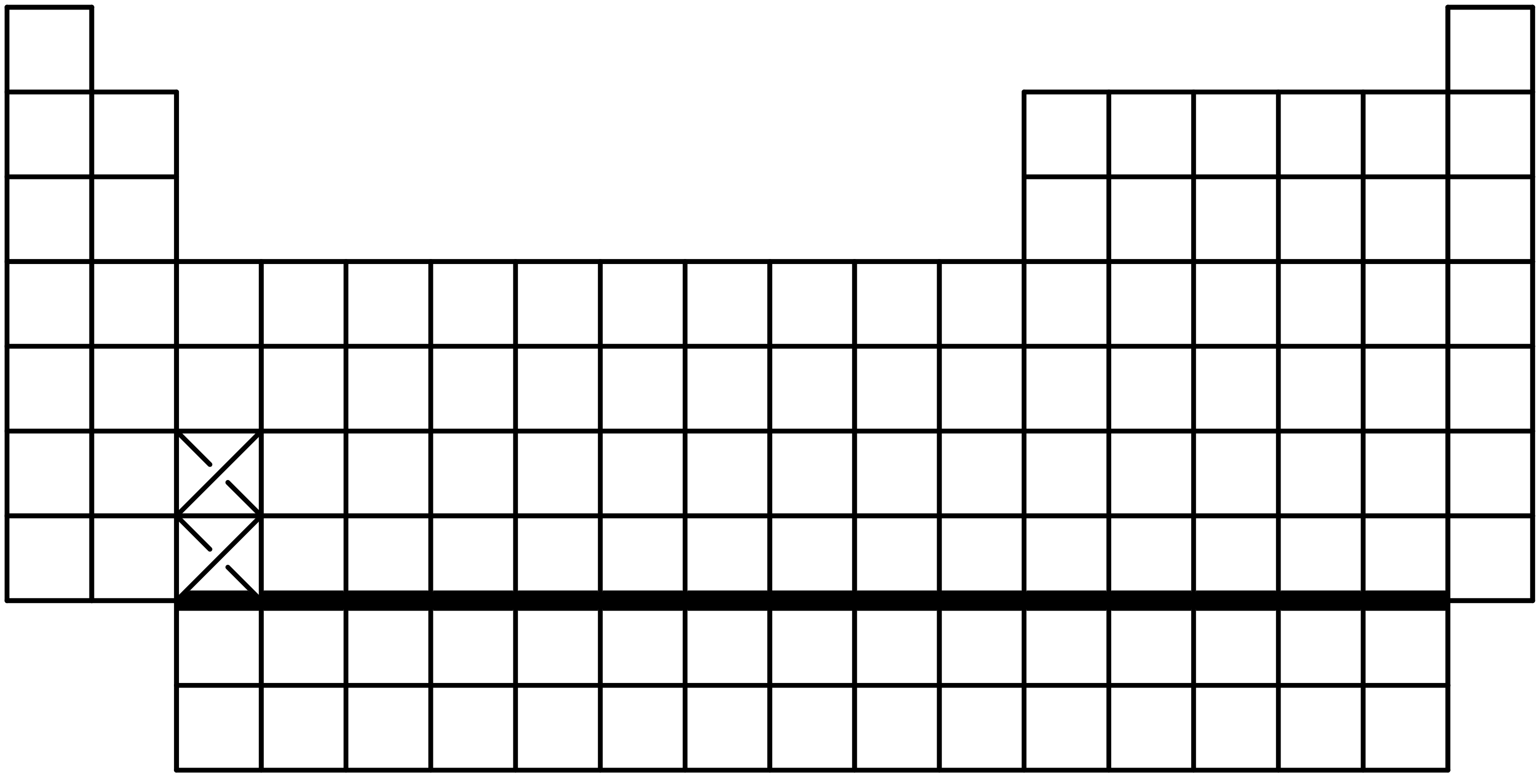
dashed border: at least one isotope naturally arise from decay of other chemical elements and no isotopes are older than the earth

dotted border: only artificially made isotopes (synthetic elements)

no border: undiscovered

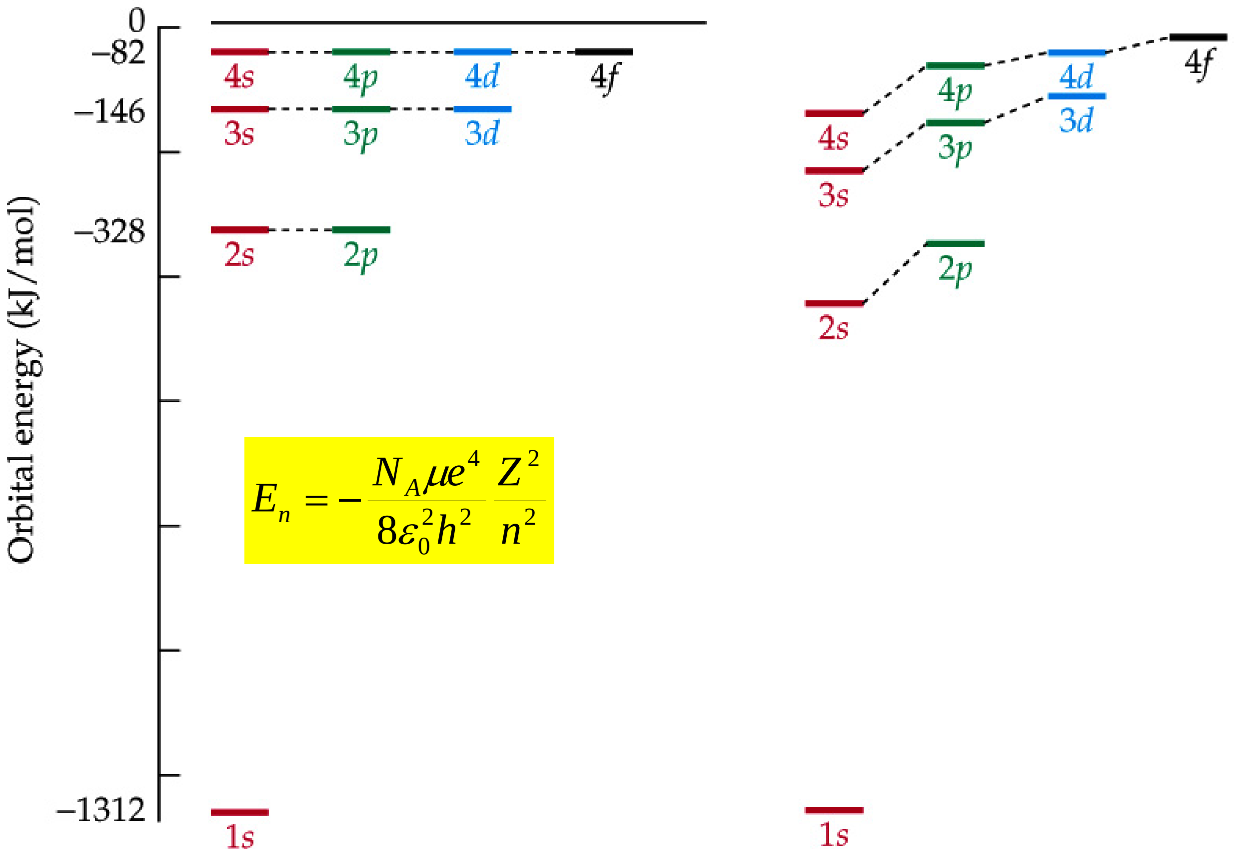
Periodic Table of the Elements

IUPAC 2017



Orbital Energies in Polyelectronic Atoms

$$\hat{H}\,\Psi = E\,\Psi$$

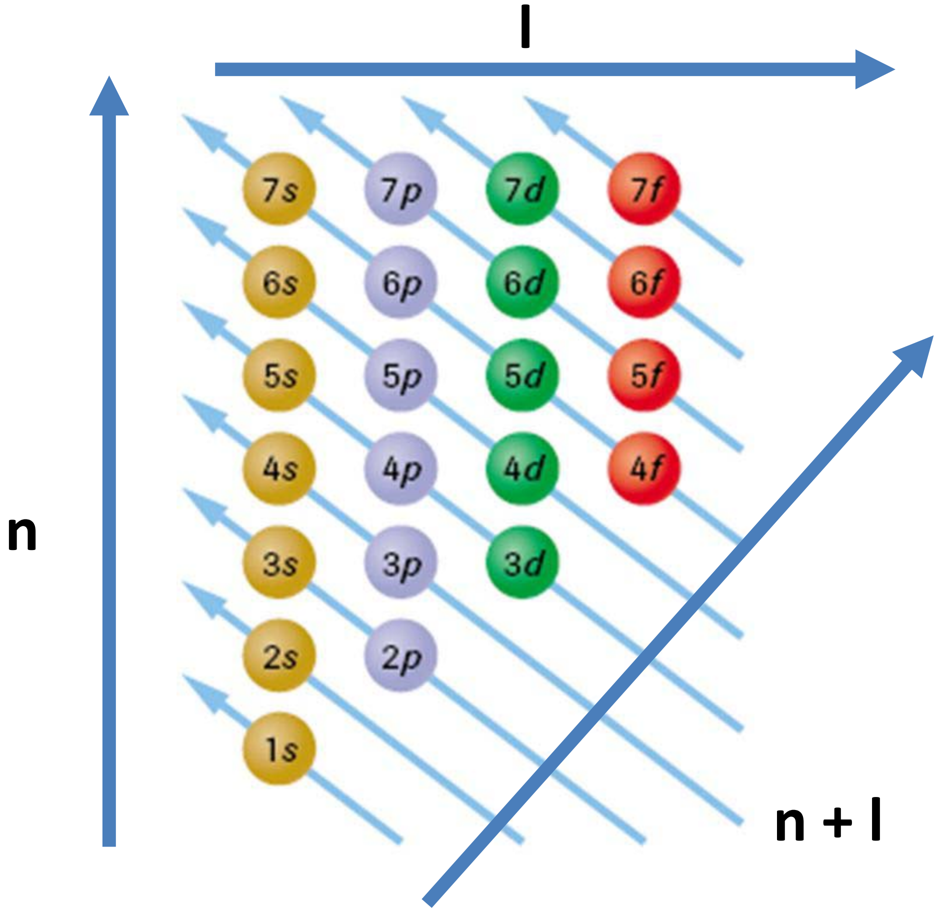


$$E_n = -\frac{N_A \mu e^4}{8\varepsilon_0^2 h^2}\,\frac{Z^2}{n^2}$$

(a) Hydrogen **(b)** Multielectron atoms

Aufbau Principle

The order of orbital filling – not the order of atomic energies



the Madelung rule:

Electrons (*e*) fill orbitals starting at the lowest available energy state before filling higher states.

The higher the total number of nodes in the atomic orbital, n + ℓ, the higher is its energy.

If n + ℓ is the same, then lower n

Hund’s Rules

State with **the largest value of S is most stable** and stability decreases with decreasing S = electrons always enter an empty orbital before they pair up.

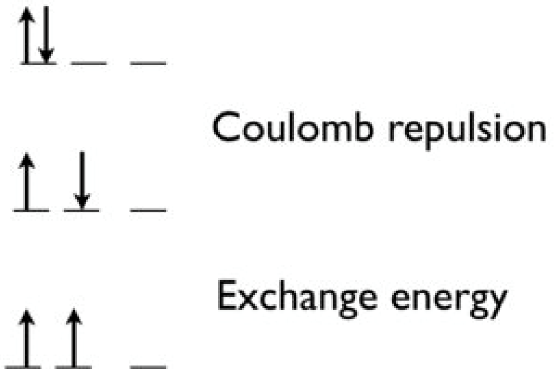
The ***e*** in singly occupied orbitals are less effectively screened or shielded from the nucleus = more tightly bound.

A Coulomb repulsion between two ***e*** in the same orbital = a spin pairing energy.

For states with same values of S, the state with the largest value of L is the most stable.

The total (scalar) angular momentum, the *relative* momentum vectors of the various ***e***.

If states have same values of L and S then, for a subshell that is less than half filled, state with smallest J is most stable; for subshells that are more than half filled, state with largest value of J is most stable.



Exchange Energy

Exchange energy (K) = the energy released when two or more ***e*** with the same spin exchange their positions in the degenerate orbitals of a subshell

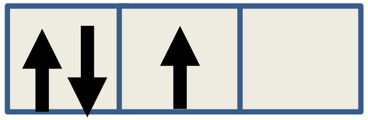
The result of spin correlation = ***e*** do not move independently

A pair of ***e*** with parallel spins ↑↑ has less repulsion than a pair with anti-parallel spins ↑↓

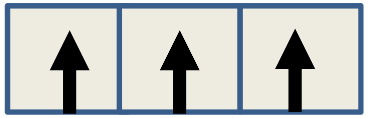
↑↓ occupy smaller volume than ↑↑ ⇒ ↑↓ experience more repulsion than ↑↑

Exchange energy decreases orbital energy - lower orbital energy = the orbital is closer to nucleus - electrons are more tightly bound which gives extra stability of electrons of valence shell

Relative exchange energy = number of pairs with parallel spins x K



1 K

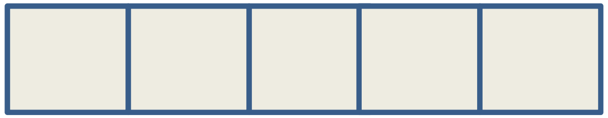


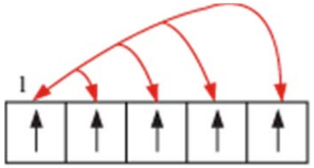
3 K

Exchange Energy

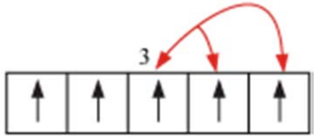
Calculate exchange energies for configurations p^1 to p^6

Calculate exchange energies for configurations d^1 to d^{10}

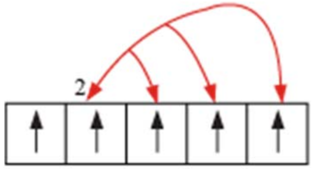




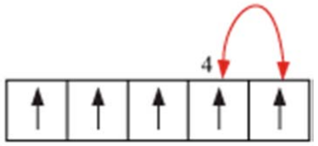
4 exchange by electron 1



2 exchange by electron 3



3 exchange by electron 2



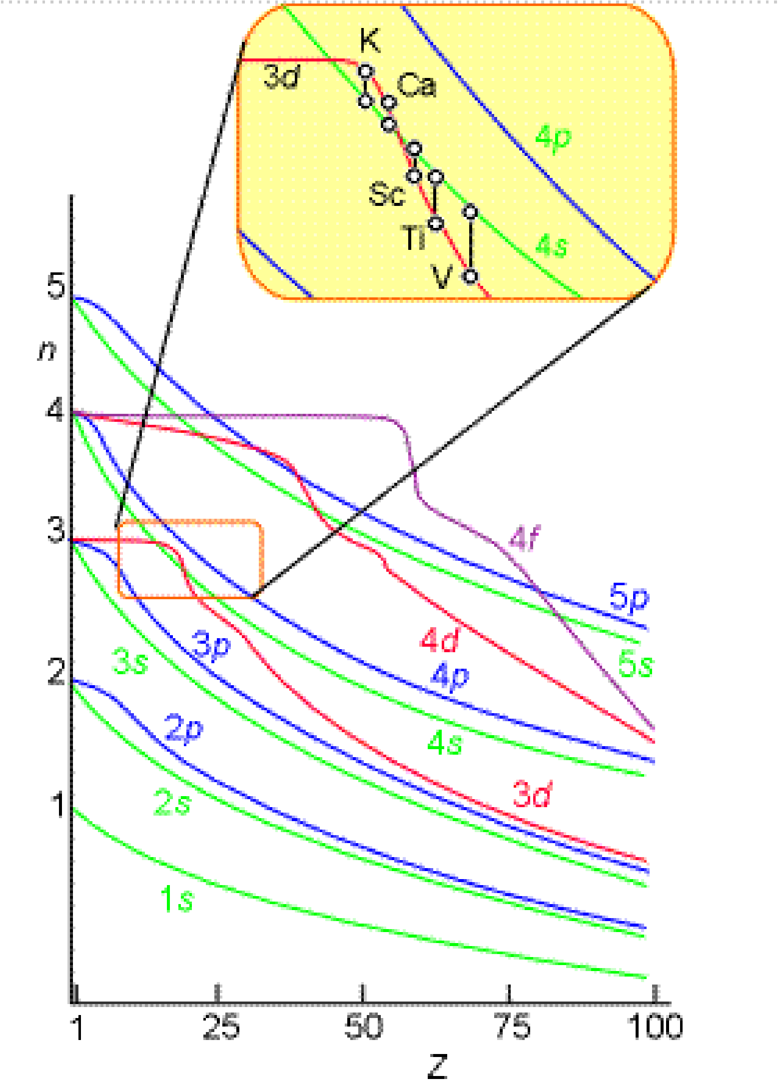
1 exchange by electron 4

exchange energy for d^5 = 10 K

For every pair of electrons with parallel spins, there is a corresponding exchange energy K that reduces the value of the orbital energy

Which configuration is the most stable Cr (Ar) $3d^4\ 4s^2$ or $3d^5\ 4s^1$

Orbital Energies



Cu Ag, Au
Cr, Mo, W
Ru, Rh, Pd
Nb
La, Ce, Pr, Gd
Cm, Th, Pa, Np

Ni [Ar] $3d^9\,4s^1\,(4p^0)$ free atom in vacuum

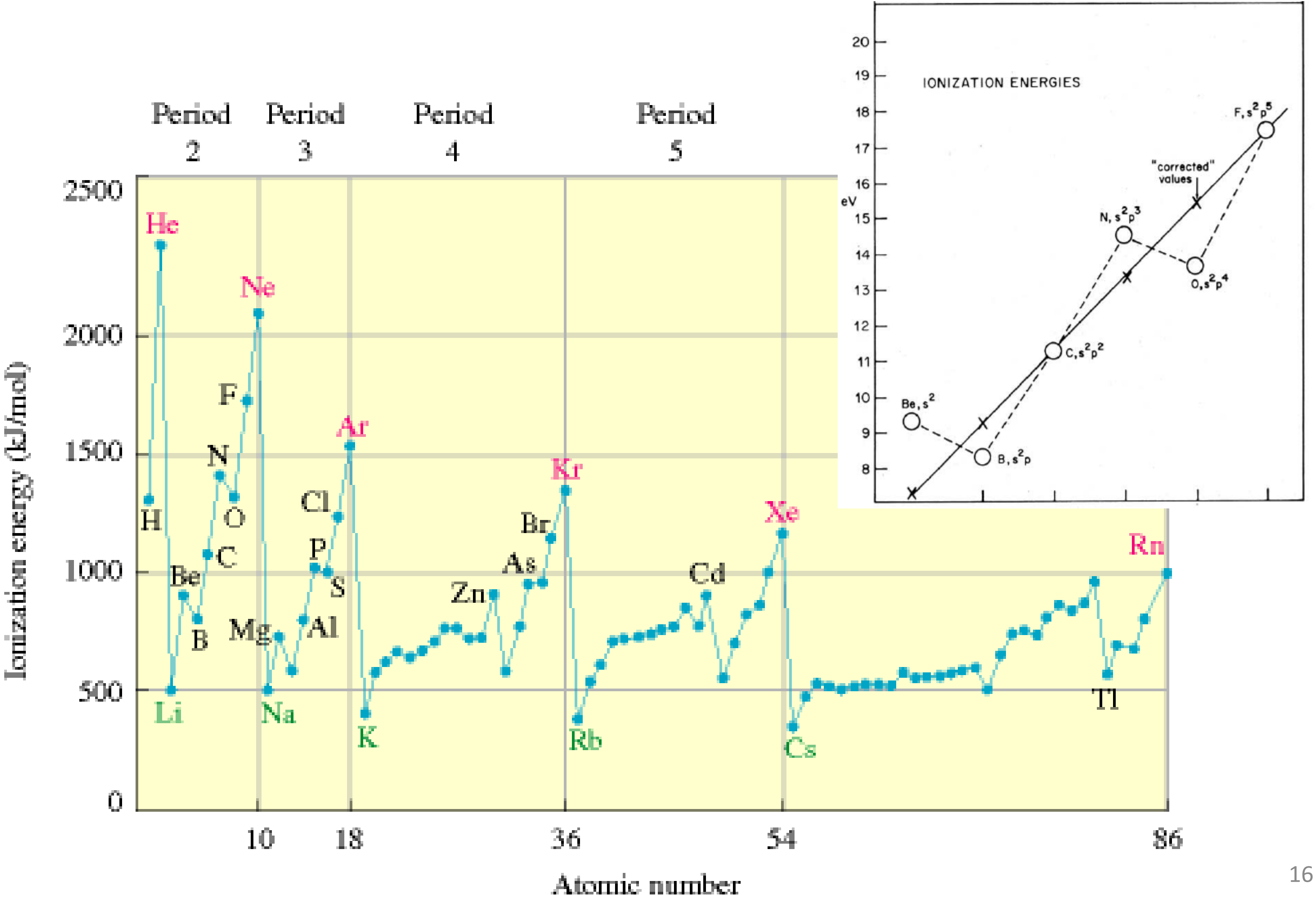
Ni [Ar] $3d^8\,4s^2\,(4p^0)$ very close in energy

Ni [Ar] $3d^{10}\,(4s^0\,4p^0)$ in molecules, $Ni(CO)_4$

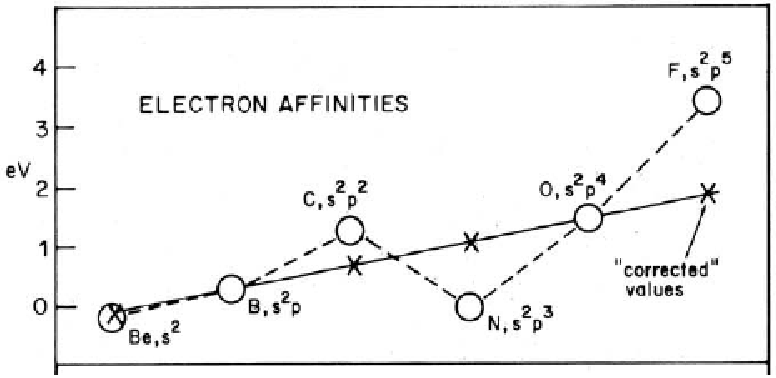
Lanthanides

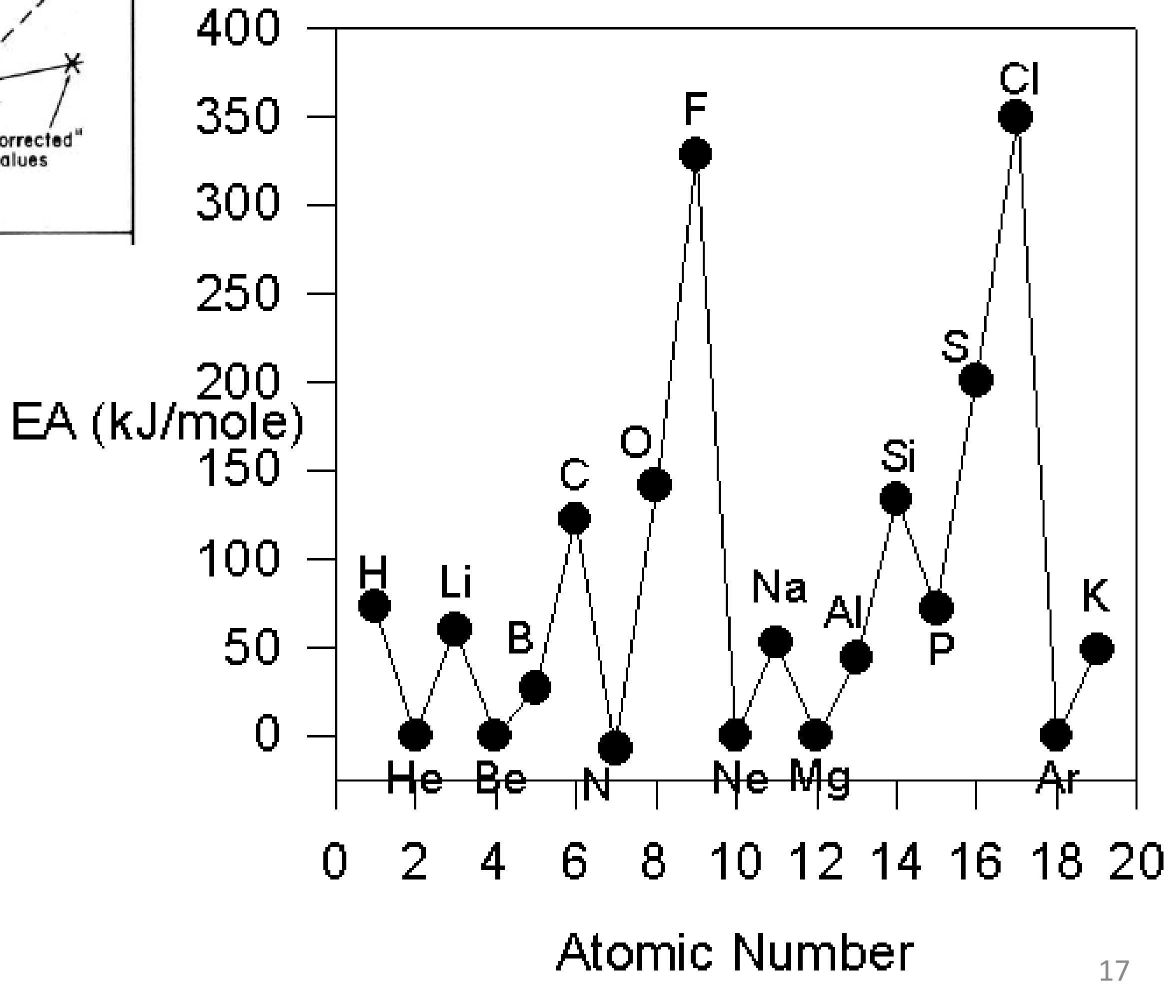
Xe	$[\mathrm{Kr}]\ 4d^{10}\ 5s^{2}\ 5p^{6}$	$E(4f) > E(6s)$
Cs	$[\mathrm{Xe}]\ 6s^{1}\ \ 4f^{0}\ 5d^{0}$	
Ba	$[\mathrm{Xe}]\ 6s^{2}\ 4f^{0}\ 5d^{0}$	
La	$[\mathrm{Xe}]\ 4f^{0}\ 5d^{1}\ 6s^{2}$	transition metal
Ce	$[\mathrm{Xe}]\ 4f^{1}\ 5d^{1}\ 6s^{2}$	$E(4f) < E(6s), E(5d)$
Pr	$[\mathrm{Xe}]\ 4f^{3}\ 6s^{2}$	
Eu	$[\mathrm{Xe}]\ 4f^{7}\ 5s^{2}\ 5p^{6}\ 5d^{0}\ 6s^{2}$	
Gd	$[\mathrm{Xe}]\ 4f^{8}\ 5s^{2}\ 5p^{6}\ 5d^{0}\ 6s^{2}$	
Gd	$[\mathrm{Xe}]\ 4f^{7}\ 5s^{2}\ 5p^{6}\ 5d^{1}\ 6s^{2}$	4f half-filled
Lu	$[\mathrm{Xe}]\ 4f^{14}\ 5d^{1}\ 6s^{2}$	4f full

Ionization Energies

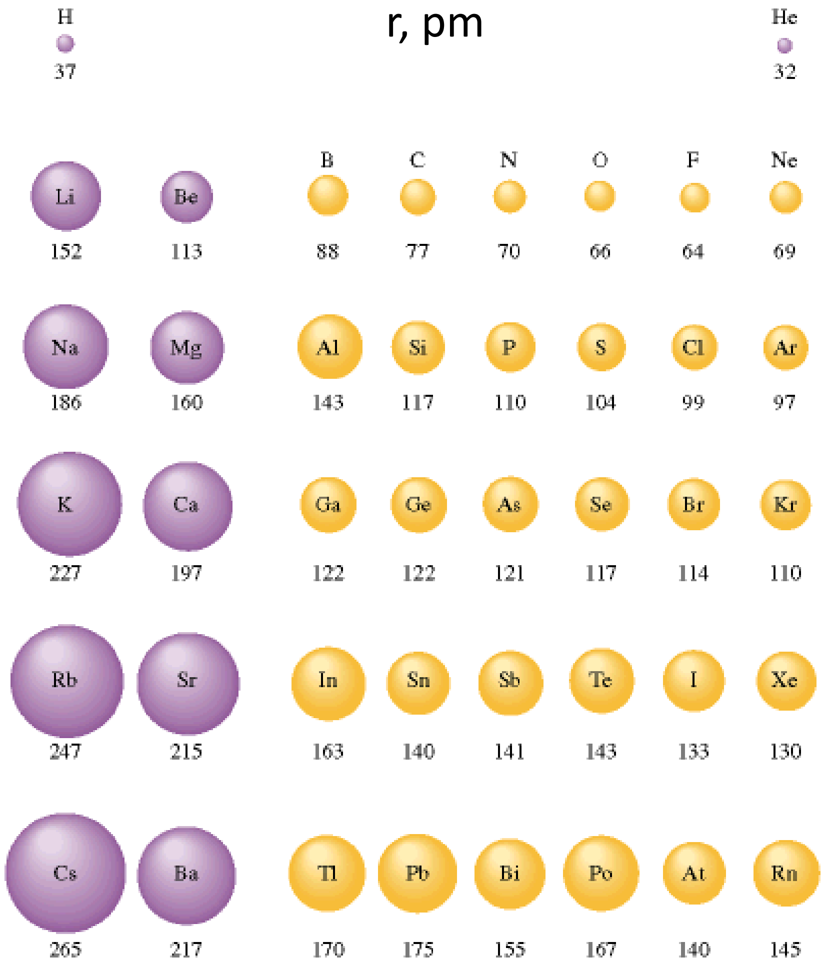


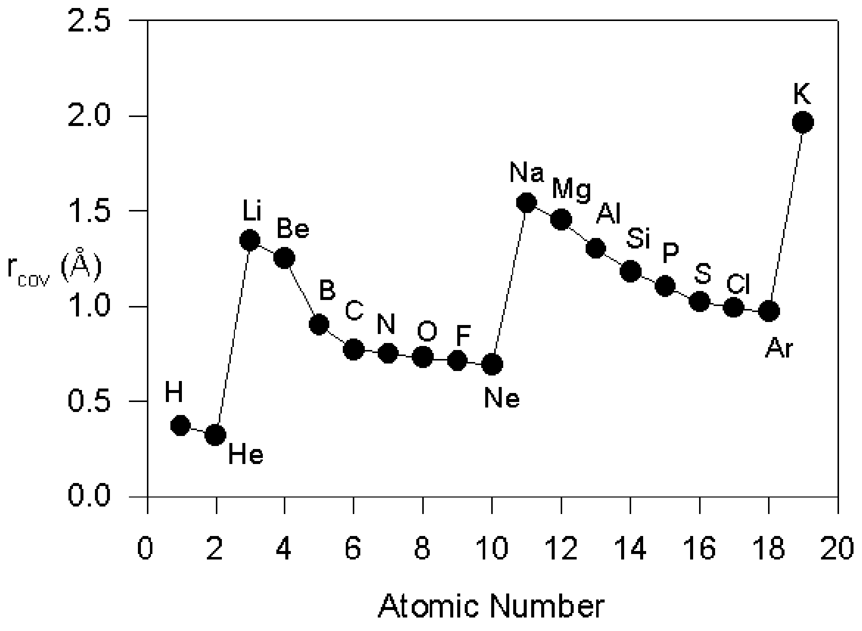
Electron Affinities



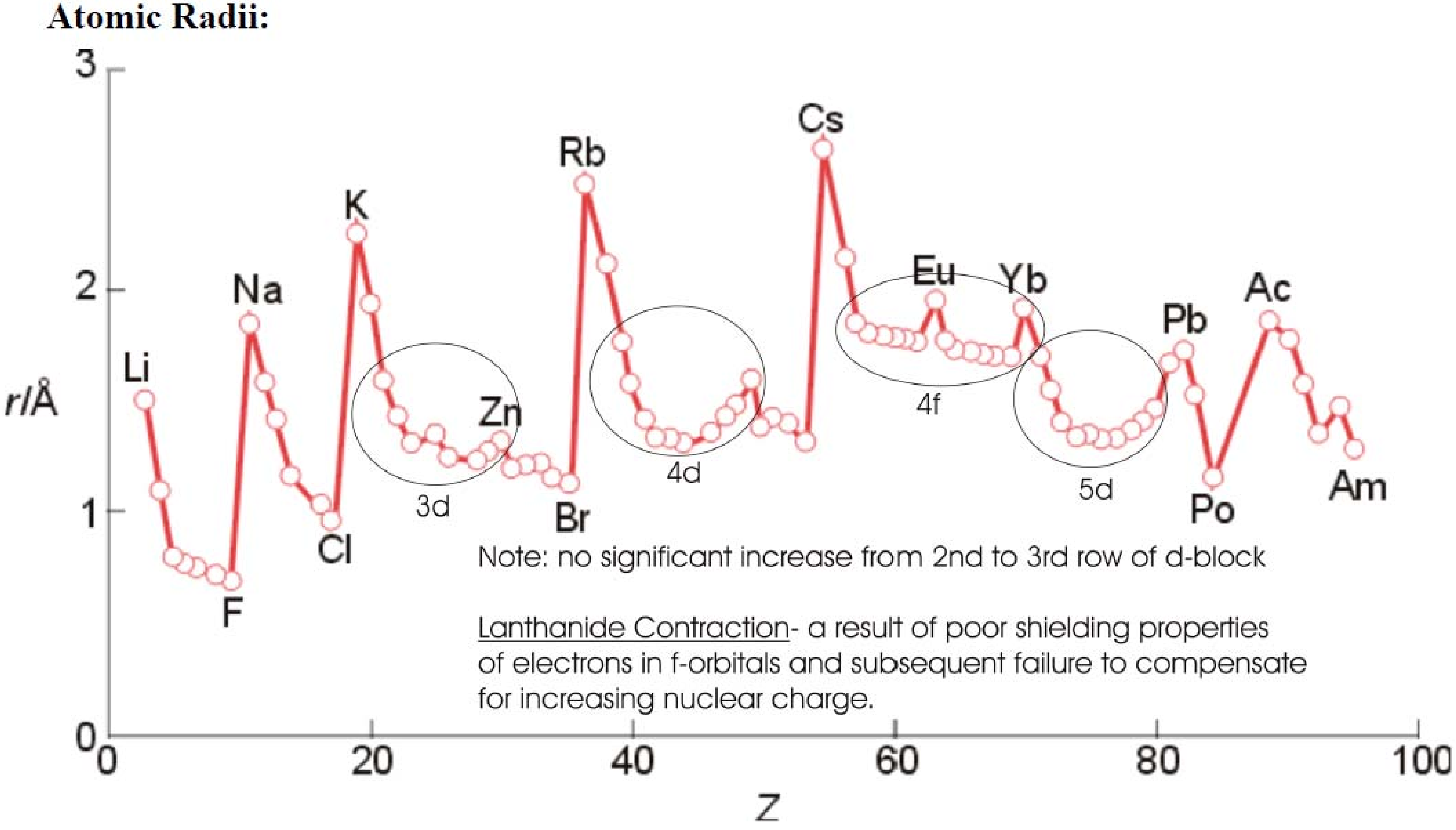


Atomic Radii





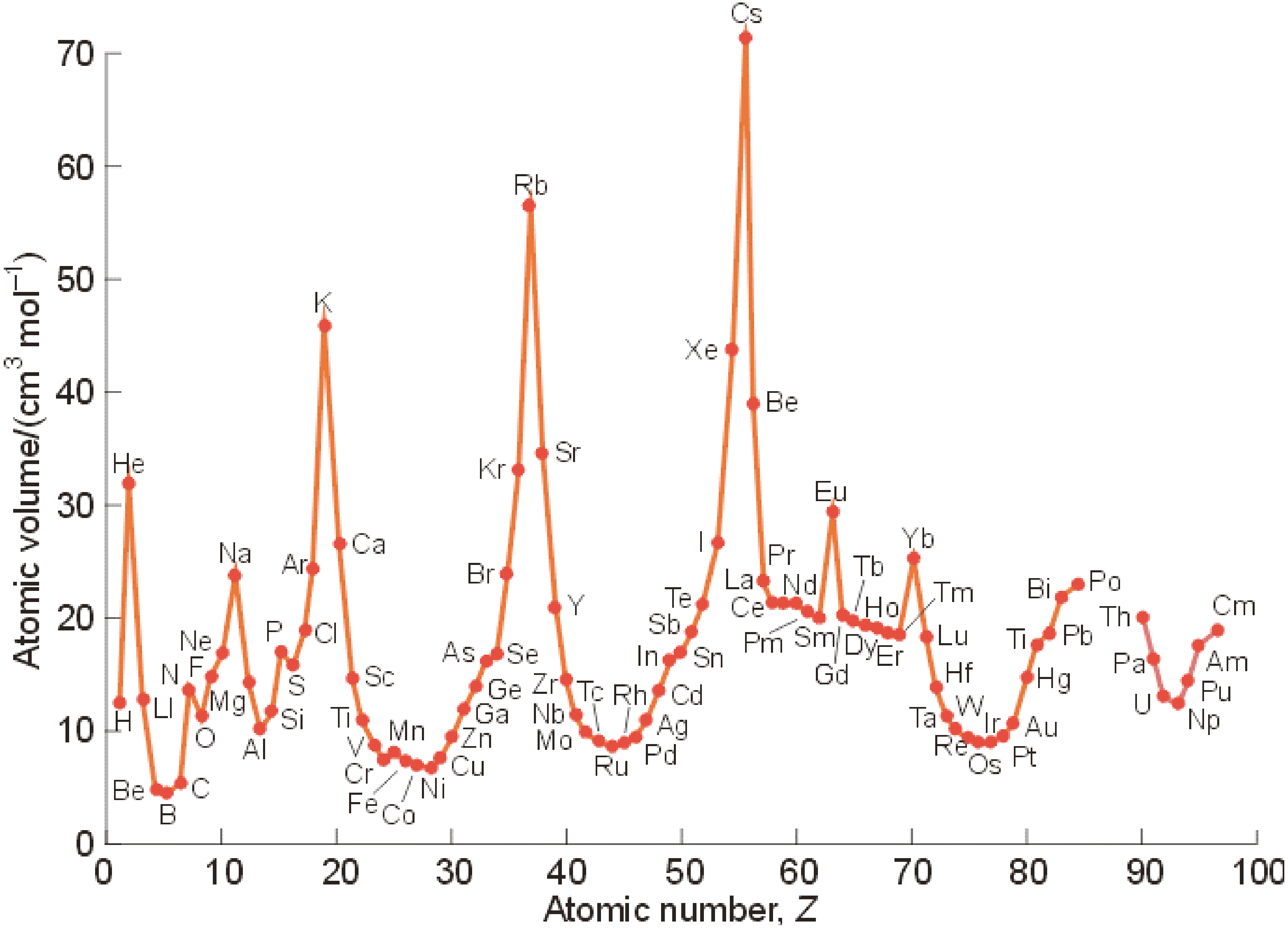
Atomic Radii



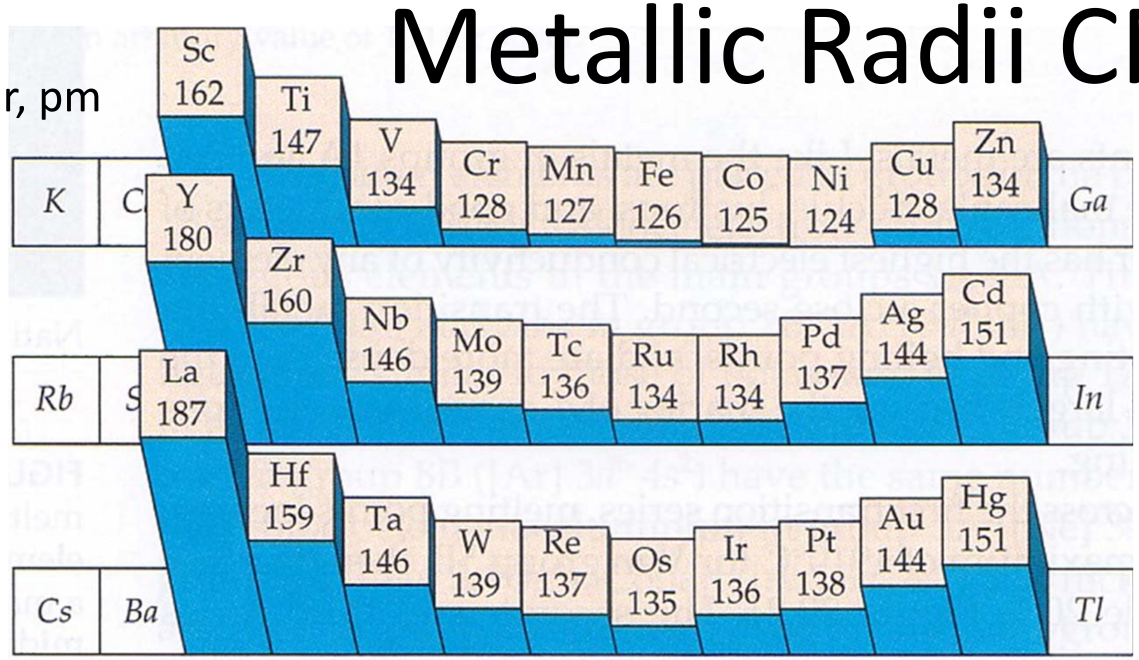
Note: no significant increase from 2nd to 3rd row of d-block

Lanthanide Contraction- a result of poor shielding properties of electrons in f-orbitals and subsequent failure to compensate for increasing nuclear charge.

Atomic Volumes

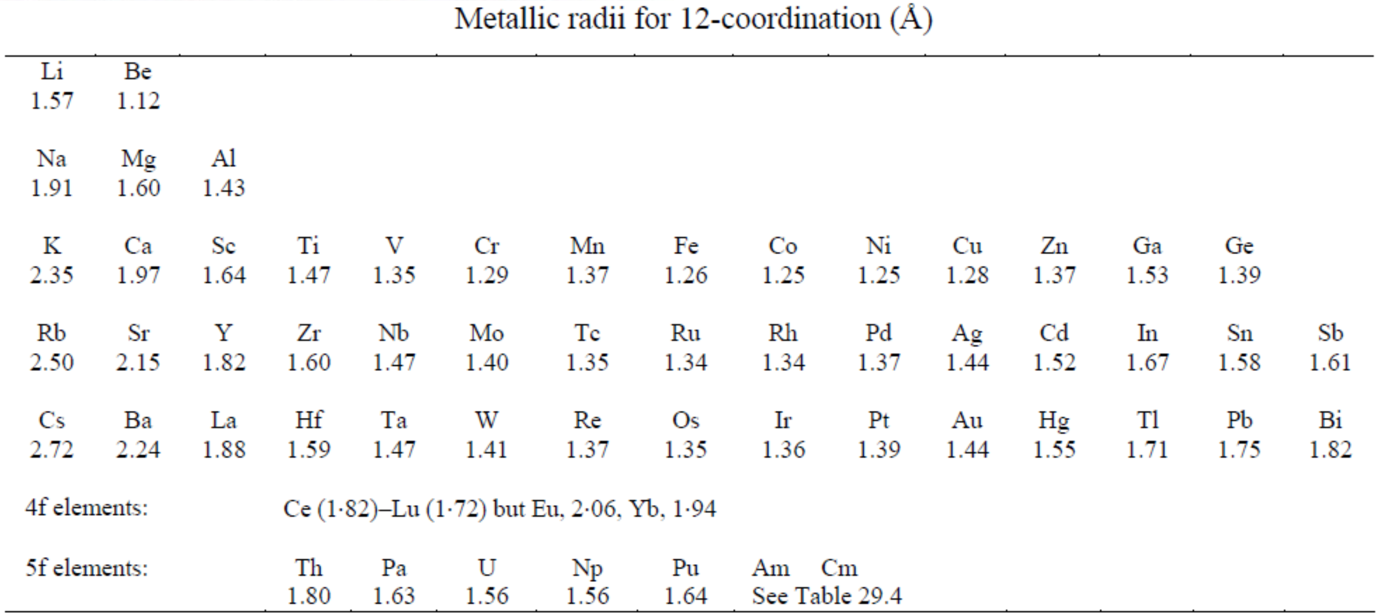


Metallic Radii CN = 12



Radius vs. CN:
CN = 12 Rel. R = 1.00
CN = 8 Rel. R = 0.97
CN = 6 Rel. R = 0.96
CN = 4 Rel. R = 0.88

solid solutions: a linear relationship = Vegard

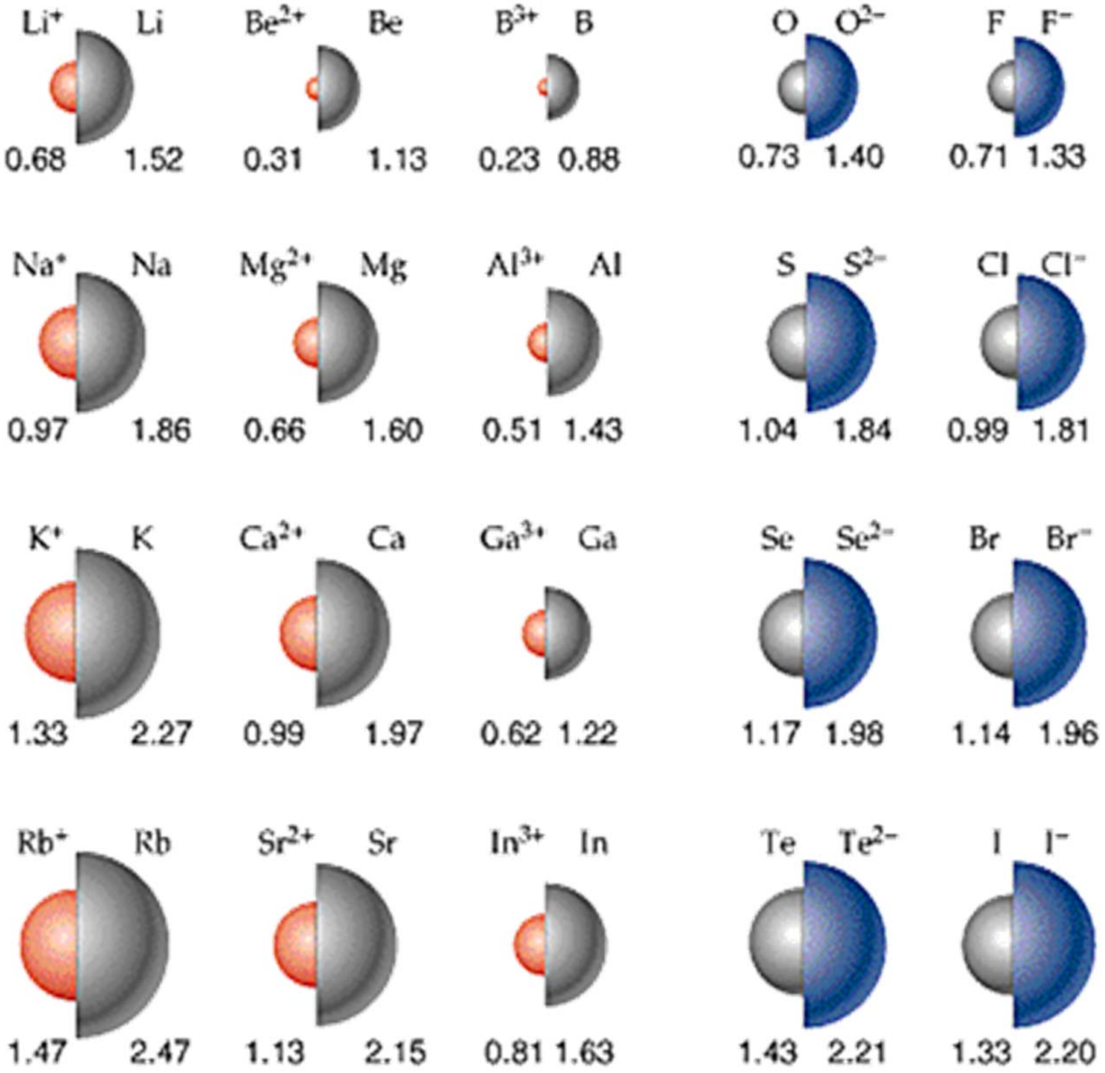


Metallic radii for 12-coordination (Å)

Li 1.57	Be 1.12													
Na 1.91	Mg 1.60	Al 1.43												
K 2.35	Ca 1.97	Sc 1.64	Ti 1.47	V 1.35	Cr 1.29	Mn 1.37	Fe 1.26	Co 1.25	Ni 1.25	Cu 1.28	Zn 1.37	Ga 1.53	Ge 1.39	
Rb 2.50	Sr 2.15	Y 1.82	Zr 1.60	Nb 1.47	Mo 1.40	Tc 1.35	Ru 1.34	Rh 1.34	Pd 1.37	Ag 1.44	Cd 1.52	In 1.67	Sn 1.58	Sb 1.61
Cs 2.72	Ba 2.24	La 1.88	Hf 1.59	Ta 1.47	W 1.41	Re 1.37	Os 1.35	Ir 1.36	Pt 1.39	Au 1.44	Hg 1.55	Tl 1.71	Pb 1.75	Bi 1.82
4f elements:			Ce (1·82)–Lu (1·72) but Eu, 2·06, Yb, 1·94											
5f elements:			Th 1.80	Pa 1.63	U 1.56	Np 1.56	Pu 1.64	Am Cm See Table 29.4						

Ionic Radii

r, Å



Oxidation State

1835 Wöhler Unorganische Chemie – oxydationsstufe

IUPAC “Gold Book” **Compendium of Chemical Terminology**

The oxidation state is the atom’s charge after ionic approximation of its bonds.

1. Atoms in an element have oxidation state 0.

2. The sum of the oxidation states for atoms in a compound is 0, in ions the algebraic sum of the oxidation states of the constituent atoms must be equal to the charge on the ion.

3. Fluorine in compounds has the oxidation state –1.

4. Alkaline metals in compounds have the oxidation state +1, alkaline-earth metals +2.

5. Hydrogen in compounds has the oxidation state +1 (except hydrides –1).

6. Oxygen in compounds has the oxidation state –2 (except peroxides –1).

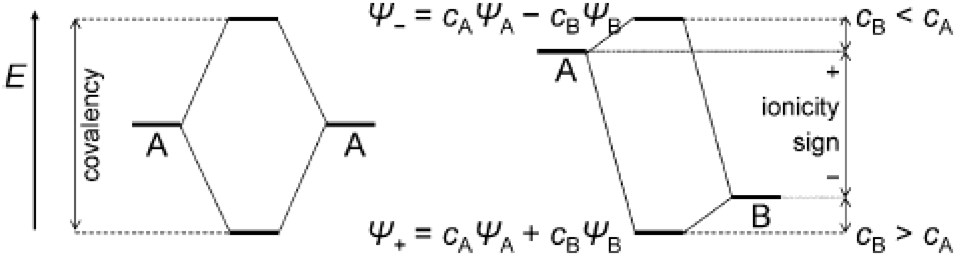
Oxidation State

The oxidation state of an atom in a compound is given by the hypothetical charge of the corresponding atomic ion that is obtained by **heterolytically** cleaving its bonds such that the atom with the higher electronegativity in a bond is allocated all electrons in this bond. Bonds between like atoms (having the same formal charge) are cleaved **homolytically**.

Criteria for the ionic approximation:

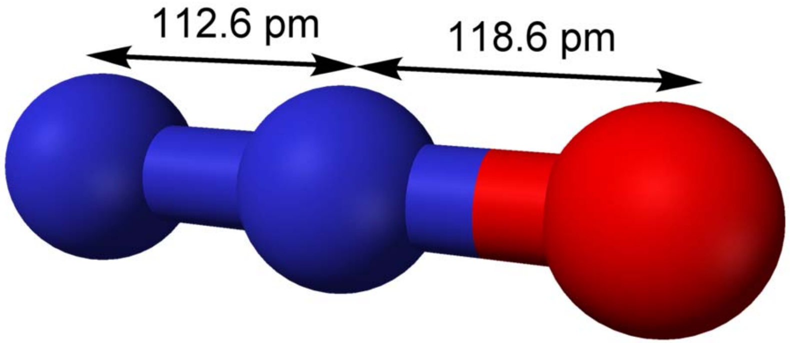
1) Extrapolation of the bond’s polarity
    - a) from the electronegativity difference
    - b) from the dipole moment
    - c) from quantum-chemical calculations of charges

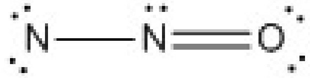
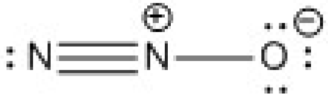
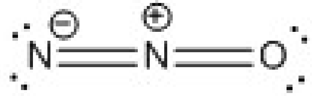
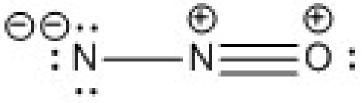
2) Assignment of electrons according to the atom’s contribution to the molecular orbital (MO)



Oxidation State

N_2O



NBO/DF-BP86/def2-SVP		Lewis Character
1		90.6 %
2		88.9 %*
3		96.4 %
4		94.0 %
5		91.7 %

* if treated as excited state.

Electronegativity - the 3rd Dimension of the Periodic Table

Pauling 1932
electronegativity χ_P based on bond energies, ability of an atom in a molecule to attract electrons for itself

Mulliken 1934
orbital, “absolute” electronegativity χ_M is an average of ionization energy and electron affinity

Allred + Rochow 1958
χ_A electronegativity is “a force” needed to remove an electron from the atom’s ground state (similarity to Coulomb’s Law).

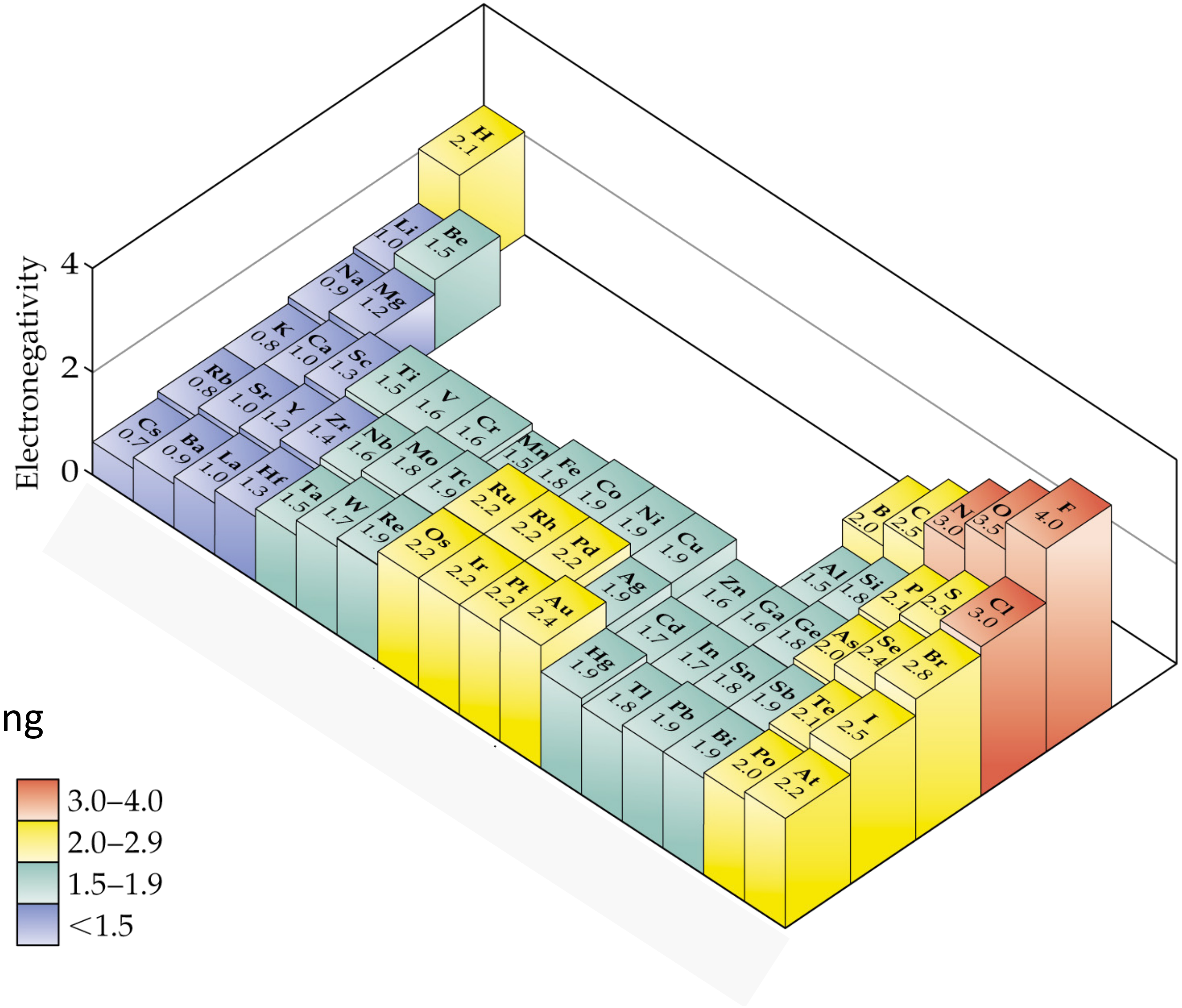
Electronegativity - the 3rd Dimension of the Periodic Table

Allen 1992
average valence-electron energy of the free atom, χ_{spec}

Sanderson
ratio of average electron density to that of corresponding rare gas atom, tendency of an atomic orbital to attract electrons from another atomic orbital with which it has combined to form a bond, chemical potential

Mulliken-Jaffe
electronegativity is the slope of the energy-vs-charge curve as it passes through the origin

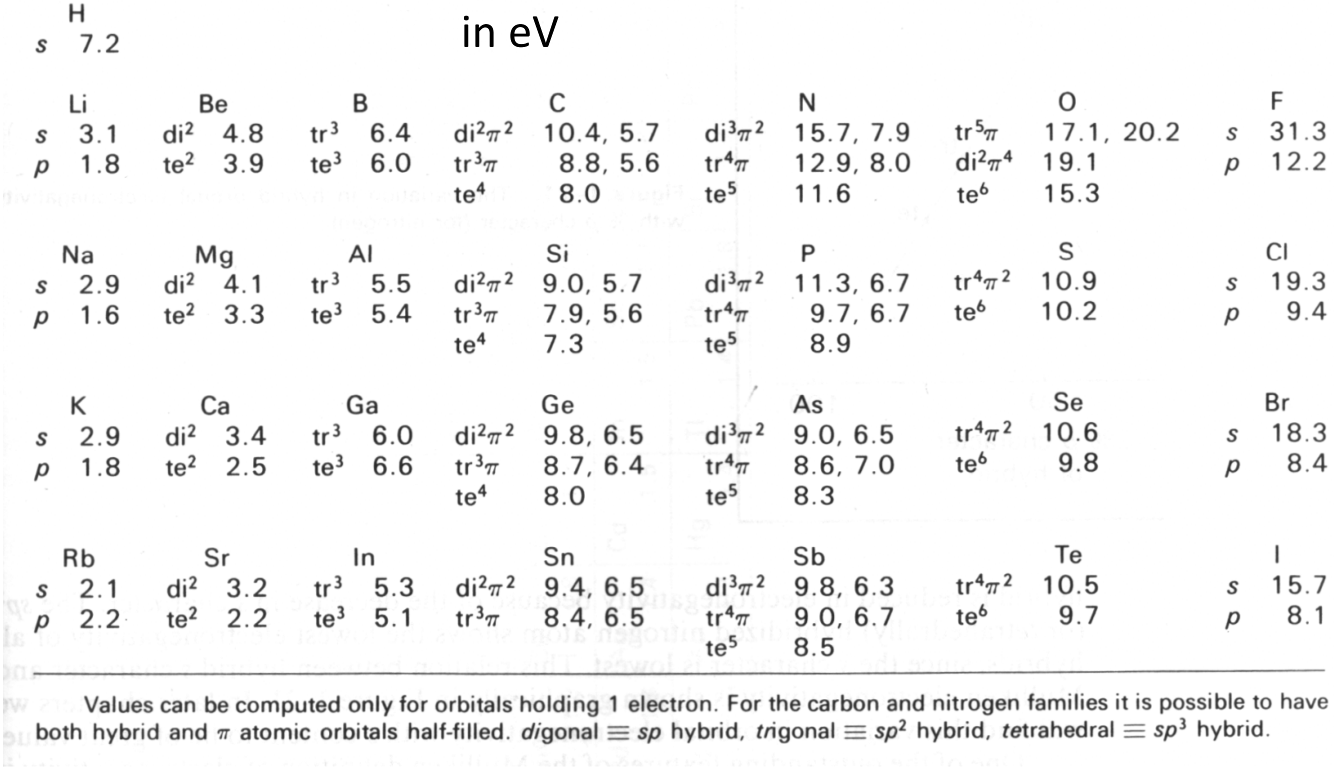
Electronegativity - the 3rd Dimension of the Periodic Table



Pauling

Mulliken Electronegativity

in eV



	H														
s	7.2														
	Li		**Be**		**B**		**C**		**N**		**O**		**F**
s	3.1	di^2	4.8	tr^3	6.4	$di^2\pi^2$	10.4, 5.7	$di^3\pi^2$	15.7, 7.9	$tr^5\pi$	17.1, 20.2	*s*	31.3
p	1.8	te^2	3.9	te^3	6.0	$tr^3\pi$	8.8, 5.6	$tr^4\pi$	12.9, 8.0	$di^2\pi^4$	19.1	*p*	12.2
						te^4	8.0	te^5	11.6	te^6	15.3		
	Na		**Mg**		**Al**		**Si**		**P**		**S**		**Cl**
s	2.9	di^2	4.1	tr^3	5.5	$di^2\pi^2$	9.0, 5.7	$di^3\pi^2$	11.3, 6.7	$tr^4\pi^2$	10.9	*s*	19.3
p	1.6	te^2	3.3	te^3	5.4	$tr^3\pi$	7.9, 5.6	$tr^4\pi$	9.7, 6.7	te^6	10.2	*p*	9.4
						te^4	7.3	te^5	8.9				
	K		**Ca**		**Ga**		**Ge**		**As**		**Se**		**Br**
s	2.9	di^2	3.4	tr^3	6.0	$di^2\pi^2$	9.8, 6.5	$di^3\pi^2$	9.0, 6.5	$tr^4\pi^2$	10.6	*s*	18.3
p	1.8	te^2	2.5	te^3	6.6	$tr^3\pi$	8.7, 6.4	$tr^4\pi$	8.6, 7.0	te^6	9.8	*p*	8.4
						te^4	8.0	te^5	8.3				
	Rb		**Sr**		**In**		**Sn**		**Sb**		**Te**		**I**
s	2.1	di^2	3.2	tr^3	5.3	$di^2\pi^2$	9.4, 6.5	$di^3\pi^2$	9.8, 6.3	$tr^4\pi^2$	10.5	*s*	15.7
p	2.2	te^2	2.2	te^3	5.1	$tr^3\pi$	8.4, 6.5	$tr^4\pi$	9.0, 6.7	te^6	9.7	*p*	8.1
								te^5	8.5				

Values can be computed only for orbitals holding 1 electron. For the carbon and nitrogen families it is possible to have both hybrid and π atomic orbitals half-filled. *di*gonal ≡ *sp* hybrid, *tri*gonal ≡ sp^2 hybrid, *te*trahedral ≡ sp^3 hybrid.

$$\chi_M = \frac{1}{2}(IE + EA) = -\mu$$

Chemical potential of the electrons

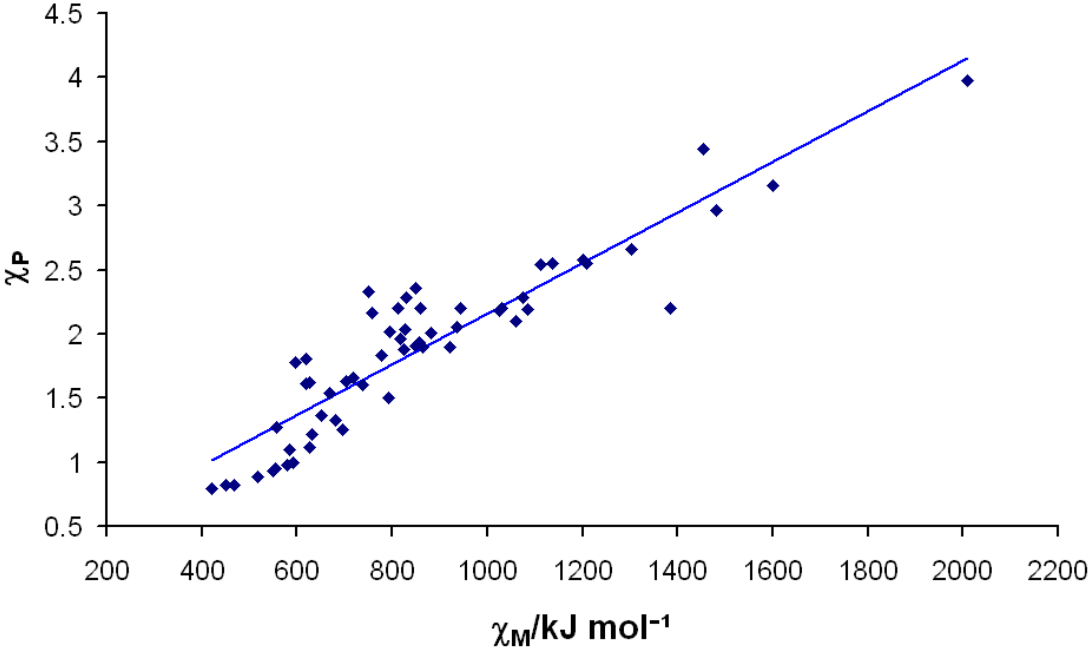
Mulliken Electronegativity

$$\chi_M = 0.178(IE + EA) + 0.17$$

Pauling scale, IE and EA in eV

$$\chi_M = 1.97 \times 10^{-3}(IE + EA) + 0.19$$

Pauling scale, IE and EA in kJ mol^{-1}



Allen Electronegativities

Electronegativity = the *average* one-electron energy of the valence-shell electrons in ground-state free atoms.
L.C. Allen, J. Am. Chem. Soc., 1989, **111**, 9003-9014

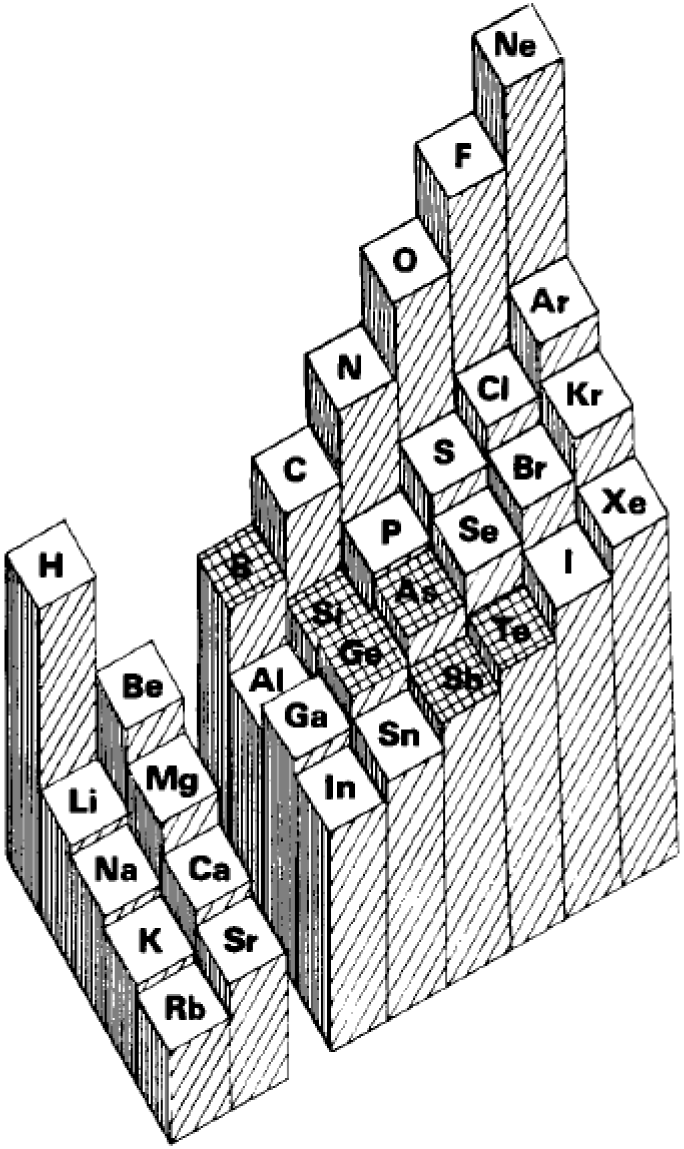
Only the Allen electronegativity is truly independent of the oxidation state, as it relates to the average valence-electron energy of the free atom.

Spectroscopic electronegativity:

m, n = number of p and s electrons, respectively
ε_s, ε_p = multiplet-averaged ionization potentials of s and p electrons (experimental data).

$$\chi_{spec} = \frac{m\varepsilon_p + n\varepsilon_s}{m+n}$$

Allen Electronegativities



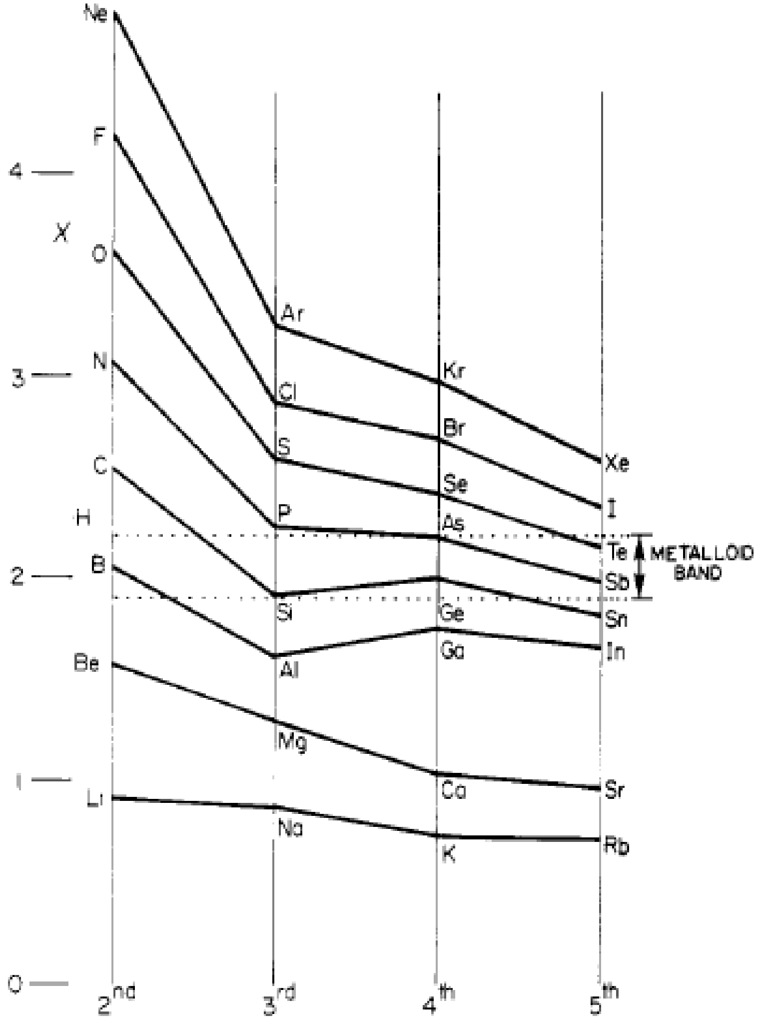


Table 1: Allen electronegativities[18–20] (in Pauling units).

H							He		
2.300							4.16		
Li	Be	B	C	N	O	F	Ne		
0.912	1.576	2.051	2.544	3.066	3.610	4.193	4.787		
Na	Mg	Al	Si	P	S	Cl	Ar		
0.912	1.293	1.613	1.916	2.253	2.589	2.869	3.242		
K	Ca	Ga	Ge	As	Se	Br	Kr		
0.734	1.034	1.756	1.994	2.211	2.424	2.685	2.966		
Rb	Sr	In	Sn	Sb	Te	I	Xe		
0.706	0.963	1.656	1.834	1.984	2.158	2.359	2.582		
Cs	Ba	Tl	Pb	Bi	Po	At	Rn		
0.659	0.881	1.789	1.854	2.01	2.19	2.39	2.60		
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
1.19	1.38	1.53	1.65	1.75	1.80	1.84	1.88	1.85	1.59
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
1.12	1.32	1.41	1.47	1.51	1.54	1.56	1.58	1.87	1.52
Lu[a]	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
1.09	1.16	1.34	1.47	1.60	1.65	1.68	1.72	1.92	1.76

[a] The variation across the lanthanoid series has not been evaluated.

Sanderson Electronegativities

The ability of an atom or ion to attract electrons to itself is dependent upon the effective nuclear charge felt by the outermost valence electrons.

As the effective nuclear charge increases the size of the atom decreases.

The Sanderson electronegativity ***S*** is proportional to the compactness of an atom:

$$S \approx \frac{Z}{\frac{4}{3}\pi r^3} \approx \frac{D}{D_0}$$

D is the electron density of an atom (its atomic number divided by its atomic volume (covalent radius cubed)) and D_0 is the expected electron density of an atom, calculated from extrapolation between the noble gas elements.

$$\sqrt{\chi_P} = a \times S + b$$

Electronegativity Equalization

When two or more atoms initially different in electronegativity combine chemically, they adjust to have the same intermediate electronegativity within the compound.

This intermediate electronegativity is given by **the geometric mean** of the individual electronegativities of the component atoms.

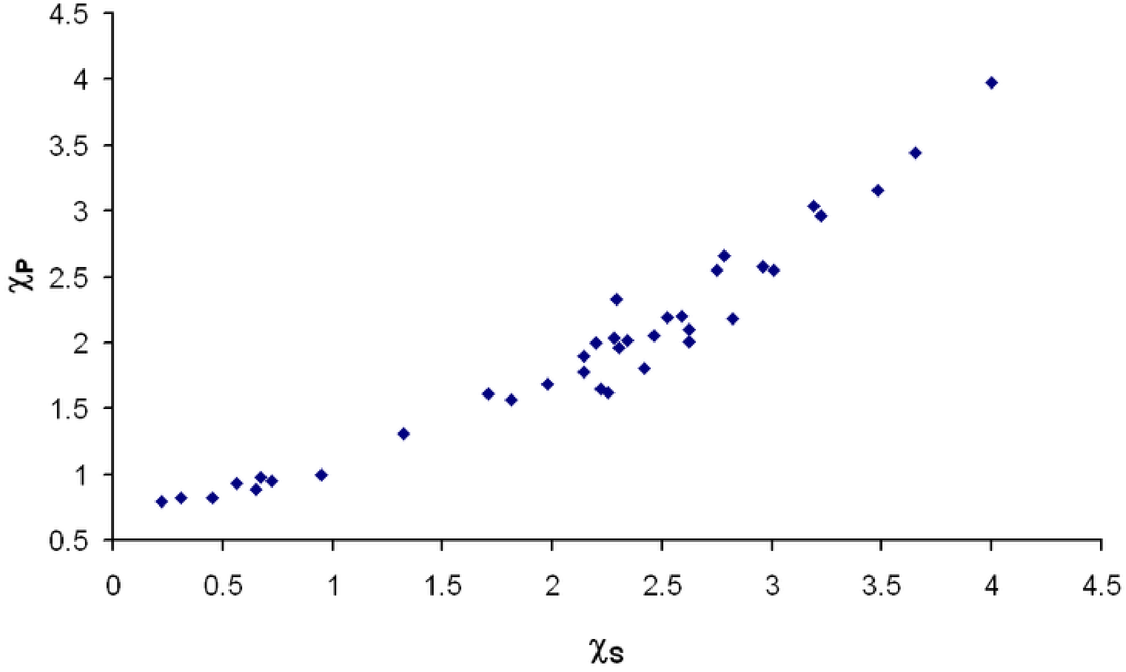
The electron density will flow from the more electropositive atom to the more electronegative atom, creating a partial positive charge on the former and a partial negative charge on the latter. As the positive charge on the electropositive atom increases, its effective nuclear charge increases, hence its electronegativity increases. The same trend happens in the opposite direction for the more electronegative atom, until the two have the same electronegativity – electronegativities are equalized and charge transfer stops.

The partial ionic charge and ionic radius of an ion are not constants, but vary depending upon the electronegativity of the surrounding atoms. Furthermore, the partial charge on an atom never exceeds +1 or –1.
The oxidation states do not reflect the true charge of an ion.

Electronegativity Equalization

$S(SnO_2) = (S_{Sn} \text{ x } S_O{}^2)^{1/3} = (4.28 \text{ x } 4.90^2)^{1/3} = 4.68$

$S(SrTiO_3) = (S_{Sr} \text{ x } S_{Ti} \text{ x } S_O{}^3)^{1/5} = (1.28 \text{ x } 2.09 \text{ x}4.90^3)^{1/5} = 3.16$



Electronegativity Equalization

$$\chi_A = a_A + b_A \delta_A \qquad \chi_B = a_B + b_B \delta_B$$

$$\chi_A = \chi_B \qquad \delta_A = -\delta_B$$

$$\delta_A = \frac{a_B - a_A}{b_A + b_B}$$

Sanderson Electronegativities

A–B

$$dG = dU + TdS - pdV + \Sigma\mu_i dN_i$$

$$dS = 0, pdV = 0$$

$$dG = dU + \Sigma\mu_i dN_i$$

$$dN_A = -dN_B = dN$$

$$dG = dU + (\mu_A - \mu_B)dN$$

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{V,S,n_i}$$

Mullikan-Jaffe Electronegativity

When the ionization energies and electron affinities of atoms are plotted against the oxidation state a smooth curve results and the total energy can be described by a quadratic formula

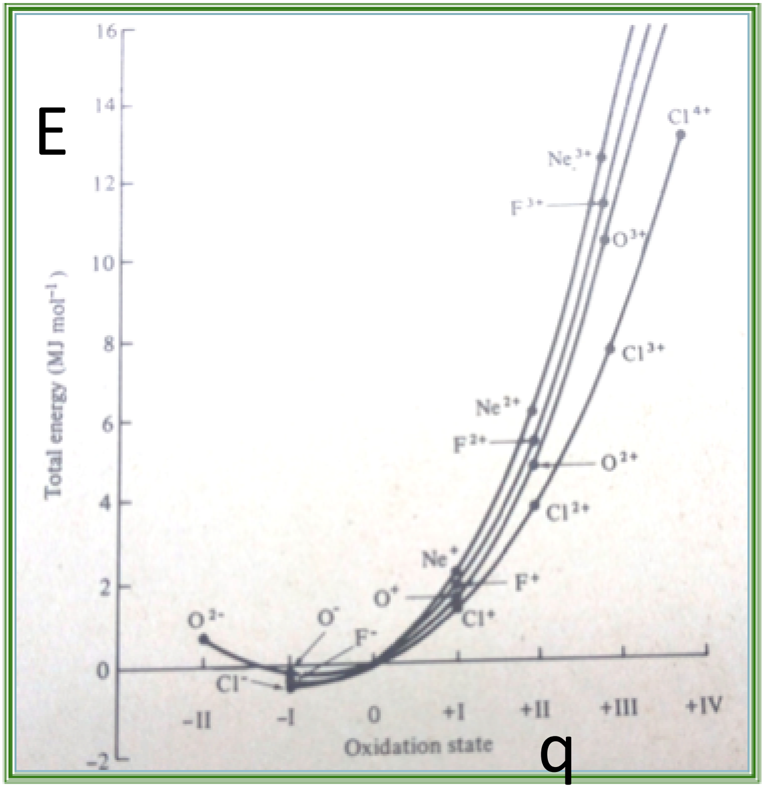
$$E = \alpha q + \beta q^2$$

Jaffe said that the Mullikan definition of electronegativity is the slope of this curve as it passes through the origin

E = total energy of an atom
q = ionic charge

q = 0 – neutral atom E = 0.

$$\chi_M = \left(\frac{\partial E}{\partial q}\right) = \alpha + 2\beta q$$



Mulliken-Jaffe Electronegativity

For q = +1 in the equation, the energy of the system corresponds to the first ionization energy IE

and

$$E = \alpha q + \beta q^2$$

for q= –1 the energy of the system corresponds to the **negative** of electron affinity EA.

$IE_V = \alpha + \beta$ (2) and $EA_V = -\alpha + \beta$ (3)

Therefore on adding equation (2) and (–3): $IE_V + EA_V = 2\alpha$

where **α** stands for **Mulliken electronegativity** χ_M

Mulliken-Jaffe Electronegativity

χ_M involves valence state ionization energy and electron affinities (calculated for atoms in the valence state as they exists in a molecule), takes into account the electronegativity of partially charged atoms emphasizing the effect the partial charge can have on the electronegativity of the atom.

$$E = \alpha q + \beta q^2 \qquad \chi_M = \left(\frac{\partial E}{\partial q}\right) = \alpha + 2\beta q = a + b\delta$$

δ = the partial ionic charge

a = inherent or neutral atom electronegativity

b = charge coefficient (rate of change of electronegativity with charge)

Large soft atoms – low b
Small hard nonpolarizable atoms – high b

1/b = charge capacity, ability to donate/absorb electrons

Hybridization and Electronegativity

Hybridization has a profound effect on electronegativity:

The s orbitals have lower energy hence greater electron attracting power
The greater the s character - the greater the electronegativity

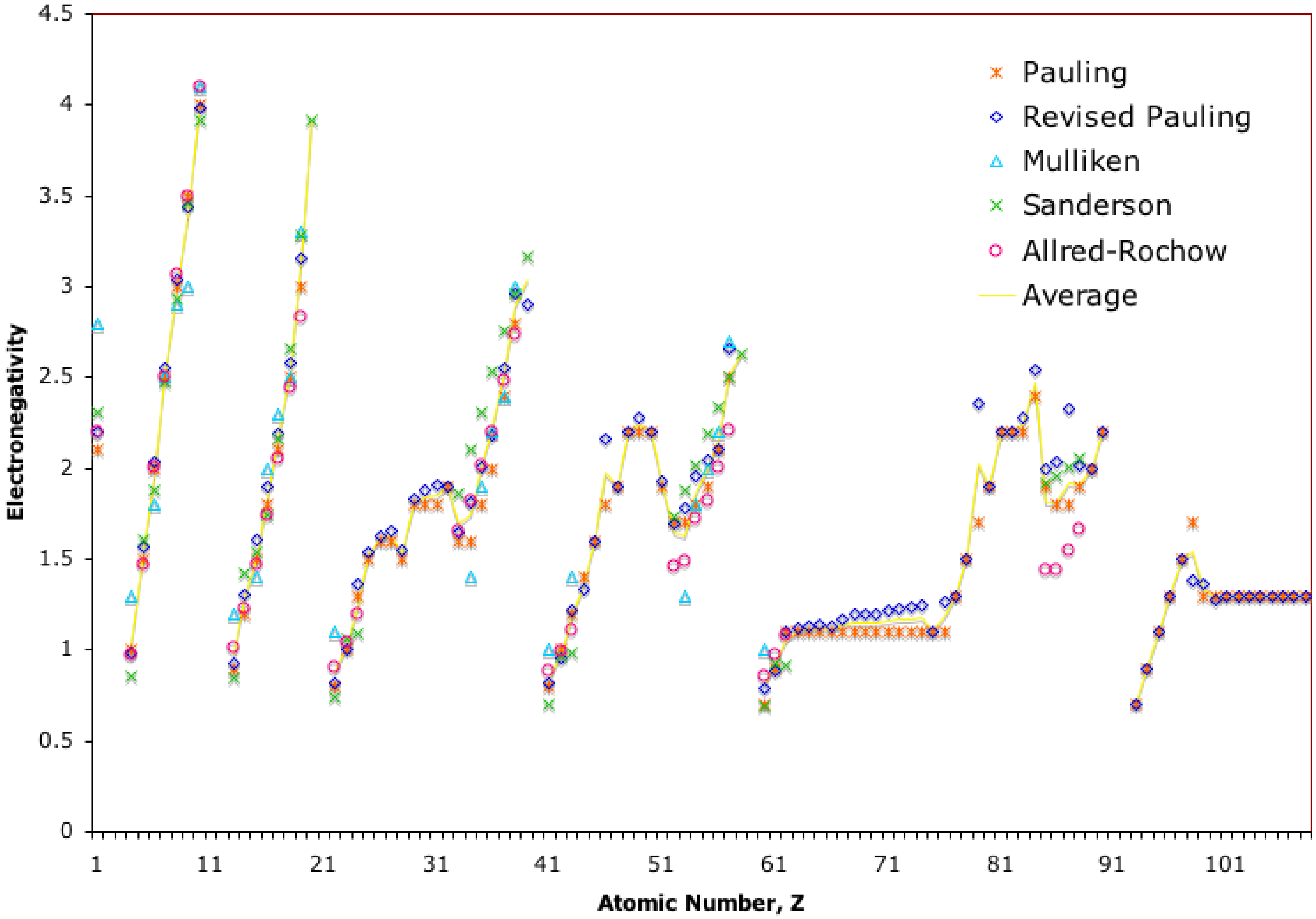
The factor affecting the acidity of hydrogen is the difference in electronegativity between hydrogen and the atom to which it is bonded
Acetylene has highly acidic hydrogen as the carbon atom is sp hybridized (50% s character) and has almost the same electronegativity as chlorine atom.
This is in contrast to methane in which the carbon atom is sp^3 hybridized (25% s character) and is not reactive

As the s character in hybridization of nitrogen increases the basicity of nitrogen will decrease. In ethane nitrile N is sp hybridized and hence very electronegative. The more electronegative the nitrogen atom less is the tendency to share the lone pair of electron. The basicity therefore decreases.

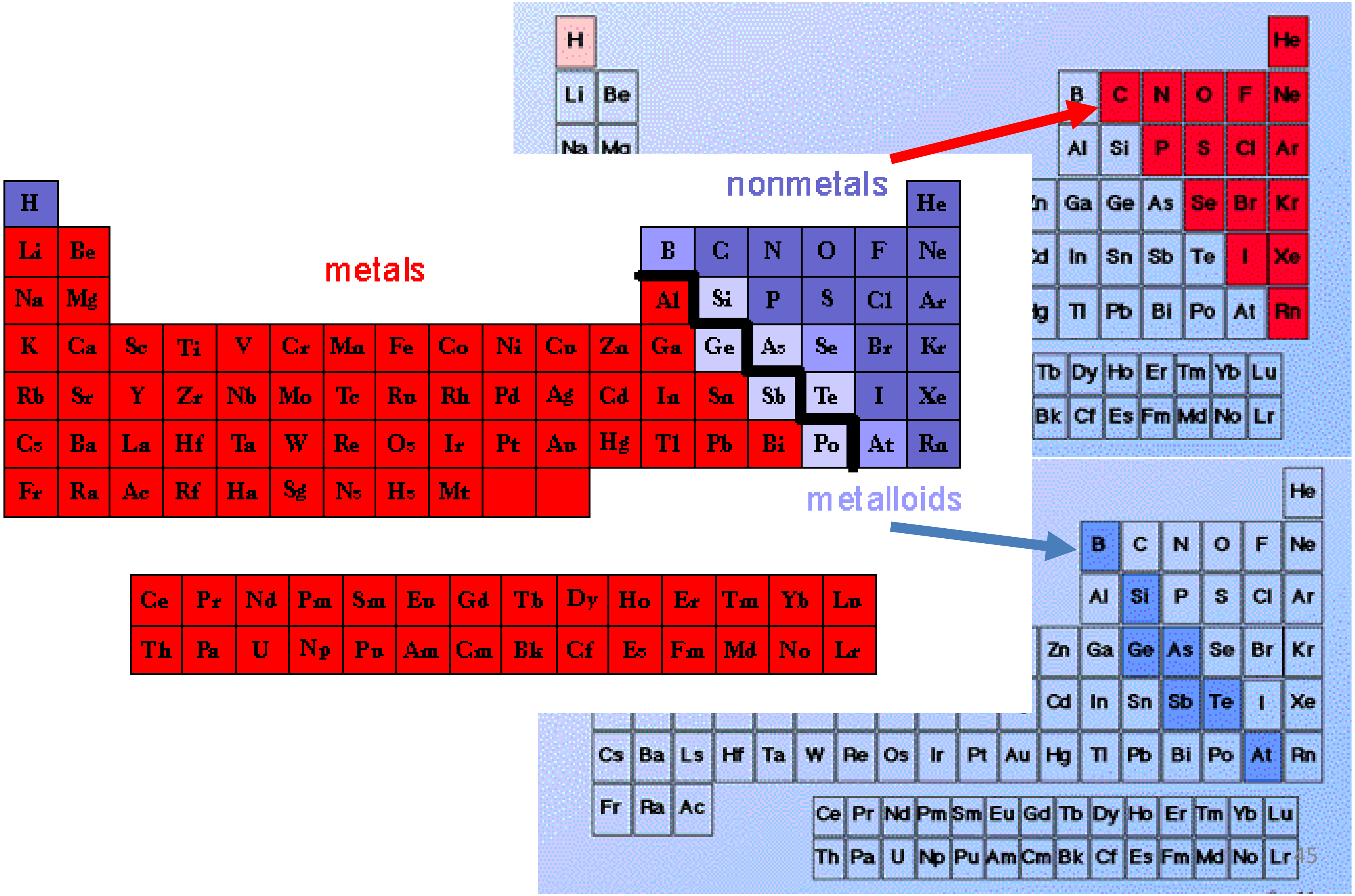
Hybridization and Electronegativity

Hybridization	sp^3	sp^2	sp
C	2.48	2.75	3.29
N	3.68	3.94	4.67

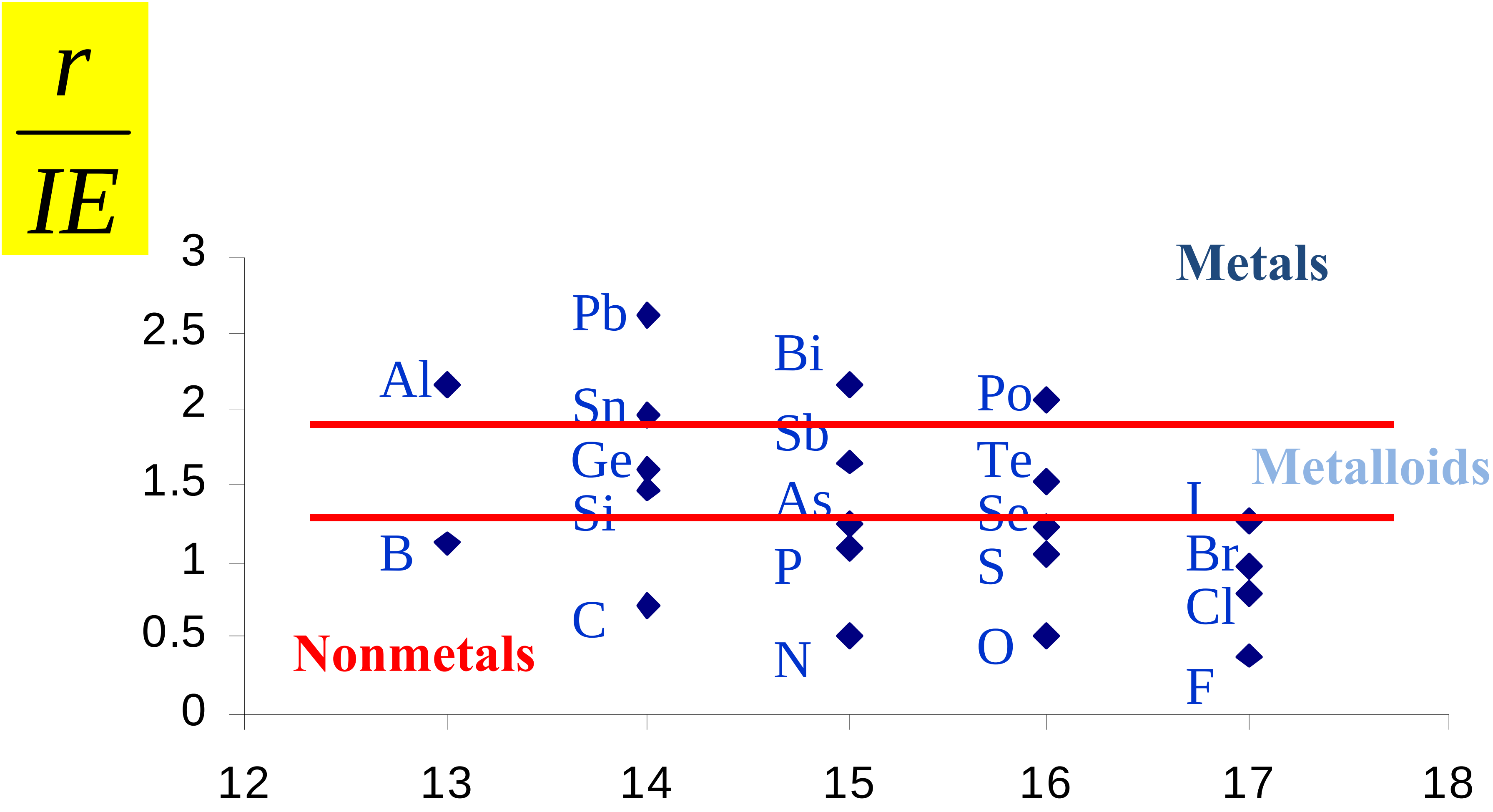
Electronegativity - the 3rd Dimension of the Periodic Table



Electronegativity and Chemical Properties



Chemical Properties



Chemical Properties